

# Kinetics of Oxidation of Pantothenic Acid by Chloramine-T in Perchloric Acid and in Alkaline Medium Catalyzed by OsO<sub>4</sub>: A Mechanistic Approach

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**ABSTRACT:** Kinetics of oxidation of pantothenic acid (PA) by sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) in the presence of HClO<sub>4</sub> and NaOH (catalyzed by OsO<sub>4</sub>) has been investigated at 313 K. The stoichiometry and oxidation products are same in both media; however, their kinetic patterns were found to be different. In acid medium, the rate shows first-order dependence on [CAT]<sub>0</sub>, fractional-order dependence on [PA]<sub>0</sub>, and inverse fractional-order on [H<sup>+</sup>]. In alkaline medium, the rate shows first-order dependence each on [CAT]<sub>0</sub> and [PA]<sub>0</sub> and fractional-order dependence on each of [OH<sup>-</sup>] and [OsO<sub>4</sub>]. Effects of added *p*-toluenesulfonamide and halide ions, varying ionic strength, and dielectric constant of medium as well as solvent isotope on the rate of reaction have been investigated. Activation parameters were evaluated, and the reaction constants involved in the mechanisms have been computed. The proposed mechanisms and the derived rate laws are consistent with the observed kinetics. © 2005 Wiley Periodicals, Inc. *Int J Chem Kinet* 37: 201–210, 2005

## INTRODUCTION

Pantothenic acid (PA; vitamin B<sub>5</sub>) occurs in all living tissues, and its wide distribution in animal and plant tissues is indicative of its fundamental role in metabolism. Pantothenic acid is a precursor of coenzyme-A, which

plays an important role in carbon metabolism particularly in energy transformations [1,2]. Lack of PA results in malnutrition in humans as well as in animals [3]. Kinetics of oxidation of PA by Ce(IV) and KMnO<sub>4</sub> in acid and alkaline media has been reported [4,5]. But there seems to be no work reported in the literature on the oxidation kinetics of PA using *N*-haloamines.

The chemistry of *N*-haloamines has evoked considerable interest because of their versatile properties. The prominent member of this group, chloramine-T

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(*p*-Me-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NCINa · 3H<sub>2</sub>O or CAT), is a well-known analytical reagent, and the mechanistic aspects involved in many of its reactions have been documented [6–13]. However, very little information is available in the literature on CAT reactions with vitamins. In view of these facts, the title reaction was undertaken. Oxidation of PA by CAT in acid medium is facile but in alkaline medium the reaction is sluggish. However, the use of OsO<sub>4</sub> as catalyst in alkaline medium brings about rapid oxidation. The main object of the present study is to explain the plausible reaction mechanisms and also to put forward the appropriate rate laws based on the kinetic results.

## EXPERIMENTAL

Chloramine-T (E. Merck) was purified by the method of Morris et al. [14]. An aqueous solution of CAT was prepared, standardized periodically by the iodometric titration, and stored in brown bottles to prevent its photochemical deterioration. Stock solution of pantothenic acid (S.D. Fine Chem.) was prepared by dissolving the appropriate amount of sample in doubly distilled water. The dielectric constant or permittivity (*D*) of the reaction medium was altered by the addition of methanol in varying proportions (% v/v). All other chemicals used were of analytical grade. Solvent isotope studies were performed using D<sub>2</sub>O (99.2%) supplied by the Bhabha Atomic Research Centre, Mumbai, India. Preliminary experiments showed that the reaction was not affected by the changes in ionic strength of the medium (0.1–0.5 mol dm<sup>-3</sup>) using NaClO<sub>4</sub> solution and hence no attempt was made to keep it constant.

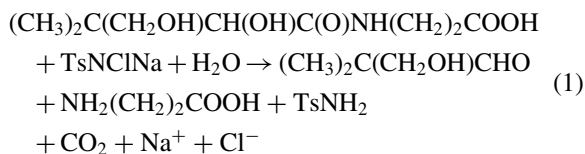
### Kinetic Measurements

The kinetic experiments were carried out under pseudo-first-order conditions by maintaining the excess of [PA]<sub>0</sub> over [CAT]<sub>0</sub>, and procedure followed is similar to those reported earlier [9]. The course of the reaction was studied for at least two half-lives. The pseudo-first-order rate constants (*k'*) calculated from the linear plots of log [CAT] vs. time were reproducible within ±5%.

### Stoichiometry

Reaction mixtures containing varying ratios of CAT to PA in the presence of acid or alkali (OsO<sub>4</sub> in alkaline medium) were equilibrated at 313 K for 48 h. Estimation of the unreacted CAT showed that 1 mole of PA consumed 1 mole of CAT in both the media. The observed stoichiometry can be represented by

Eq. (1):



where Ts = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>.

The reaction products were eluted with ether solvent, and organic products were subjected to spot tests [15] and chromatographic analysis [16,17], which revealed the presence of 2,2-dimethyl-3-hydroxypropanaldehyde. The presence of aldehyde was further confirmed by its IR spectrum that showed a band at 3416 and 1730 cm<sup>-1</sup> for OH stretching and C=O stretching respectively, where as the band observed at 2857 cm<sup>-1</sup> is due to aldehydic stretching. The presence of aldehyde was also confirmed [18] by its 2,4-DNP derivative, and the amount of aldehyde was calculated from the weight of hydrazone formed and the yield of the aldehyde was found to be 55%. Another product β-alanine was identified by known test [19]. It was further confirmed by its IR spectrum. IR spectral bands were observed at 3364 and 3260 cm<sup>-1</sup> corresponding to NH<sub>2</sub> and 1745 cm<sup>-1</sup> for COOH. The reduction product of CAT, *p*-toluensulfonamide (TsNH<sub>2</sub>), was detected [20] by paper chromatography (*R<sub>f</sub>* = 0.905). The liberated CO<sub>2</sub> was identified by the conventional limewater test.

## RESULTS AND DISCUSSION

The kinetics of oxidation of PA by CAT was investigated at several initial concentrations of the reactants in acid and alkaline media. In alkaline medium, the reaction was found to be very sluggish and alternatively it was found that OsO<sub>4</sub> is an excellent catalyst for the oxidation of PA. Since, the present kinetic investigations have been carried out in both acid and alkaline media, for the sake of convenience the salient features obtained in these two media are discussed separately in the following.

### Kinetics of Oxidation in Acid Medium

With the substrate in excess, at constant [HClO<sub>4</sub>], [PA]<sub>0</sub>, and temperature, plots of log [CAT] vs. time were linear (*r* > 0.9936) indicating a first-order dependence of rate on [CAT]<sub>0</sub>. The values of pseudo-first-order rate constants (*k'*) are given in Table I. Further, the values of *k'* are unaffected with variation of [CAT]<sub>0</sub>, confirming first-order dependence on [CAT]<sub>0</sub>. The rate increases with increase in [PA]<sub>0</sub> (Table I), and a plot

**Table I** Effect of Varying CAT, PA, and HClO<sub>4</sub> Concentrations on the Reaction Rate<sup>a</sup>

10 <sup>3</sup> [CAT] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>2</sup> [PA] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>4</sup> [HClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	10 <sup>4</sup> <i>k'</i> (s <sup>-1</sup> )
0.5	2.0	2.0	3.80
1.0	2.0	2.0	3.84
2.0	2.0	2.0	3.79
3.0	2.0	2.0	3.72
4.0	2.0	2.0	3.82
1.0	1.0	2.0	2.19
1.0	2.0	2.0	3.84
1.0	3.0	2.0	4.68
1.0	4.0	2.0	5.54
1.0	6.0	2.0	7.50
1.0	2.0	1.5	4.10
1.0	2.0	2.0	3.84
1.0	2.0	4.0	3.14
1.0	2.0	6.0	2.70
1.0	2.0	8.0	2.50
1.0	2.0	10.0	2.25

<sup>a</sup> Temp. = 313 K.

of log *k'* vs. log [PA] was linear ( $r = 0.9989$ ) with a slope of 0.69 indicating a fractional-order dependence of rate on [PA]<sub>0</sub>. Furthermore, a plot of *k'* vs. [PA] was linear ( $r = 0.9926$ ) with an intercept, confirming the fractional-order dependence on [PA]<sub>0</sub>. Values of *k'* decrease with increase in [HClO<sub>4</sub>] (Table I), and a plot of log *k'* vs. log [HClO<sub>4</sub>] was linear ( $r = 0.9976$ ) with a negative slope of 0.33 indicating an inverse fractional-order dependence of rate on [HClO<sub>4</sub>]. Addition of *p*-toluenesulfonamide (PTS or TsNH<sub>2</sub>) and halide ions, Cl<sup>-</sup> or Br<sup>-</sup> ions, in the form of NaCl or NaBr ( $1.5 \times 10^{-4}$ – $10 \times 10^{-4}$  mol dm<sup>-3</sup>) or variation of the ionic strength (*I*) of medium using NaClO<sub>4</sub> solution (0.1–0.5 mol dm<sup>-3</sup>) showed no significant effect on the rate. The dielectric constant of the solvent medium was varied by adding methanol (0–30% v/v), which did not had any influence on the rate. Solvent isotope effect was studied using D<sub>2</sub>O, and the reaction was further retarded with  $k' = 3.34 \times 10^{-4}$  s<sup>-1</sup> in D<sub>2</sub>O and  $3.84 \times 10^{-4}$  s<sup>-1</sup> in H<sub>2</sub>O leading to a solvent isotope effect  $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O}) = 1.15$ .

The reaction was carried out in a range of temperature 303–323 K, keeping other experimental conditions constant. From the linear Arrhenius plot of log *k'* vs. 1/*T* ( $r = 0.9991$ ), values of composite activation parameters  $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ , and  $\Delta S^\ddagger$  were computed. These results are summarized in Table II. Addition of reaction mixture to acrylamide in an inert atmosphere did not initiate polymerization of the latter showing the absence of any free radical in the reacting system.

**Table II** Temperature Dependence and Activation Parameters for the Oxidation of PA by CAT in Acid Medium<sup>a</sup>

Temperature (K)	10 <sup>4</sup> <i>k'</i> (s <sup>-1</sup> )	10 <sup>4</sup> <i>k</i> <sub>3</sub> (s <sup>-1</sup> )
303	1.66	5.90
308	2.64	7.60
313	3.84	12.5
318	5.63	18.12
323	8.00	24.5
$E_a$ (kJ mol <sup>-1</sup> )	62.0	(51.1)
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	59.4	(48.5)
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	97.1	(94.3)
$\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )	-121	(-147)

Values in the parentheses are activation parameters for the rate-determining step.

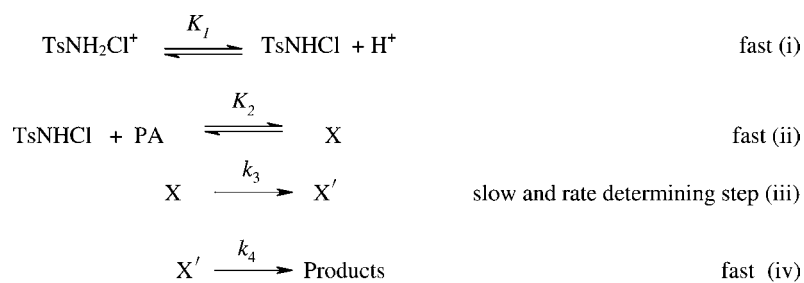
<sup>a</sup> [CAT]<sub>0</sub> =  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [PA]<sub>0</sub> =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [HClO<sub>4</sub>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>.

## Mechanism of Oxidation in Acid Medium

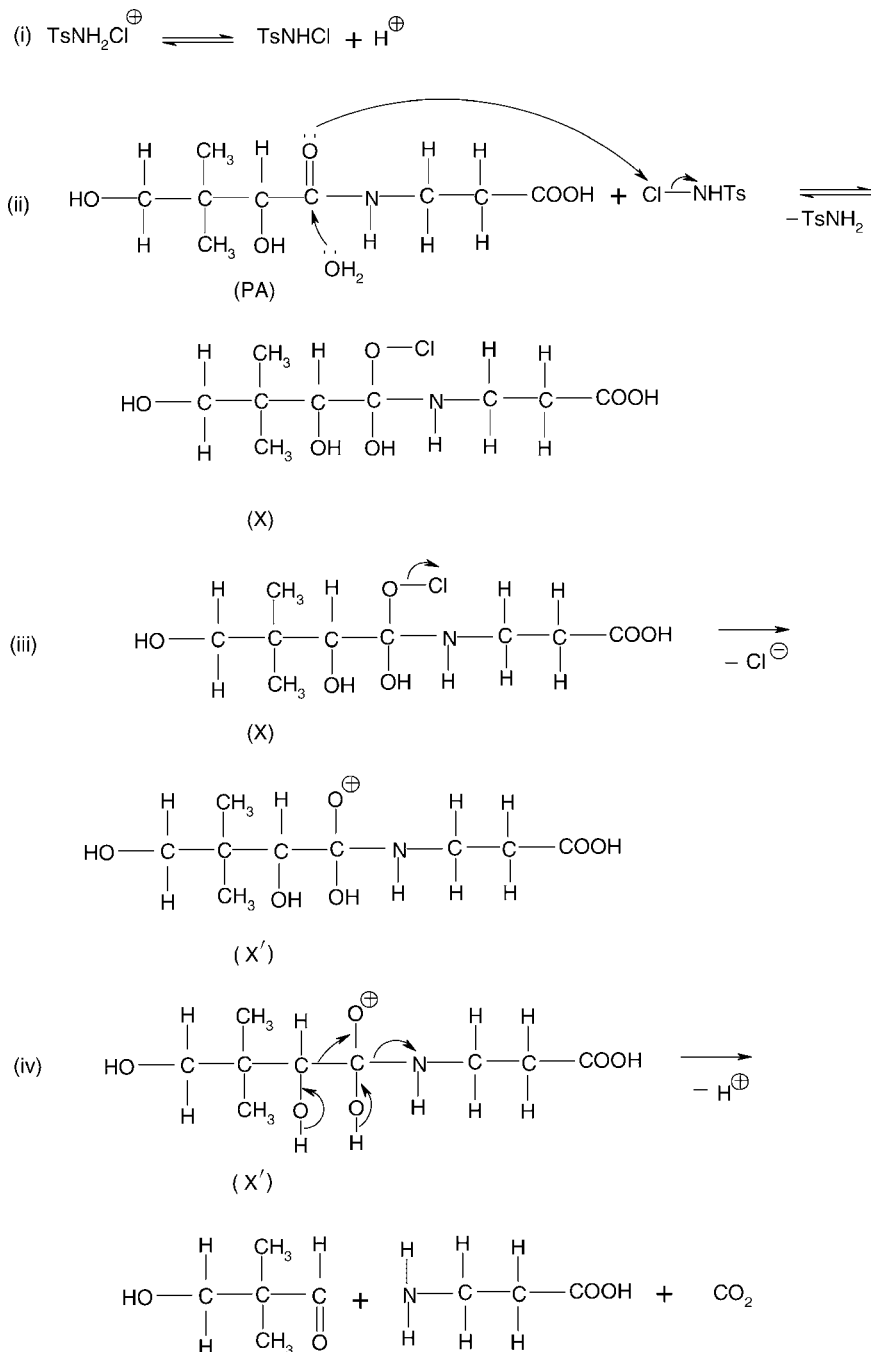
Chloramine-T acts as an oxidizing agent in both acidic and alkaline media [21–24]. Generally, CAT undergoes a two-electron change in its reactions forming PTS and NaCl as reduction products. The oxidation potential of the CAT–PTS couple varies with the pH of the medium (1.139 V at pH 0.65, 0.778 V at pH 7.0, and 0.614 V at pH 9.7). The possible oxidizing species in acidified CAT solution [23] are TsNHCl, TsNCl<sub>2</sub>, HOCl, and probably H<sub>2</sub>OCl<sup>+</sup> and in alkaline solution are TsNHCl, HOCl, TsNCl<sup>-</sup>, and OCl<sup>-</sup>. If TsNCl<sub>2</sub> and HOCl were to behave as oxidants, then the rate law would have followed a second-order dependence on [CAT]<sub>0</sub> and a first-order retardation by the added [TsNH<sub>2</sub>]. However, experimental observations are contrary to these expectations. Similarly, if H<sub>2</sub>OCl<sup>+</sup> were to be the reactive species, there would have been a positive effect of [H<sup>+</sup>] on the rate, which did not occur. Hence TsNHCl is the probable reactive species for the oxidation of PA in acid medium. Narayanan and Rao [25] and Subhashini et al. [26] have reported that monochloramine-T (CAT) can get further protonated as TsNH<sub>2</sub>Cl<sup>+</sup> with a value of  $1.0 \times 10^2$  dm<sup>3</sup> mol<sup>-1</sup> at 25°C for the second protonation constant.

In the present work, an inverse dependence of rate on [H<sup>+</sup>] suggests that the deprotonation of TsNH<sub>2</sub>Cl<sup>+</sup> results in the formation of TsNHCl, which is a likely oxidizing species involved in the oxidation of PA in acid medium. In view of preceding facts, Scheme 1 can be proposed to account for the observed kinetics for PA–CAT reaction in acid medium.

A detailed mechanistic investigation of PA–CAT reaction in acid medium is presented in Scheme 2, in which the complex intermediate species X and X'



Scheme 1



Scheme 2

structures are shown. Based on the above scheme, the total CAT concentration is given by

$$[\text{CAT}]_t = [\text{TsNH}_2\text{Cl}^+] + [\text{TsNHCl}] + [\text{X}] \quad (2)$$

This equation leads to the rate law given below,

$$\text{Rate} = \frac{K_1 K_2 k_3 [\text{CAT}]_t [\text{PA}]}{[\text{H}^+] + K_1 \{1 + K_2 [\text{PA}]\}} \quad (3)$$

Rate law (3) is in accordance with the experimental results, wherein a first-order dependence of rate on [CAT], a fractional-order in [PA], and an inverse fractional-order in  $[\text{H}^+]$  have been noted.

Since  $\text{rate} = k' [\text{CAT}]_t$ , Eq. (3) can be transformed into Eqs. (4) and (5):

$$k' = \frac{K_1 K_2 k_3 [\text{PA}]}{[\text{H}^+] + K_1 \{1 + K_2 [\text{PA}]\}} \quad (4)$$

$$\frac{1}{k'} = \frac{1}{K_2 k_3 [\text{PA}]} \left\{ \frac{[\text{H}^+]}{K_1} + 1 \right\} + \frac{1}{k_3} \quad (5)$$

Based on Eq. (5), plots of  $1/k'$  vs.  $1/[\text{PA}]$  ( $r = 0.9987$ ) and  $1/k'$  vs.  $[\text{H}^+]$  ( $r = 0.9941$ ) were found to be linear. From the slopes and intercepts of these plots, values of formation constants  $K_1$  and  $K_2$  and decomposition constant  $k_3$  were calculated and found to be  $K_1 = 4.64 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $K_2 = 30.8 \text{ dm}^3 \text{ mol}^{-1}$ , and  $k_3 = 1.25 \times 10^{-3} \text{ s}^{-1}$  respectively. Since, the rate was fractional order in  $[\text{PA}]_0$ , the Michaelis–Menten kinetics [27] was adopted to study the effect of  $[\text{PA}]_0$  on the rate at different temperatures. From plots of  $1/k'$  vs.  $1/[\text{PA}]$ , values of  $k_3$  were calculated. Activation parameters for the rate-determining step were computed from the plot of  $\log k_3$  vs.  $1/T$  ( $r = 0.9949$ ). These results are presented in Table II.

The effect of varying solvent composition on the rate of reaction has been described in detail earlier in various monographs [28–31]. For the limiting case of zero angle of approach between two dipoles or an ion–dipole system, Amis [31] has shown that a plot of  $\log k'$  vs.  $1/D$  gives a straight line having a negative slope for the reaction involving a negative ion and dipole or between two dipoles, while a positive slope was obtained for a positive ion–dipole interaction. The total absence of the effect of varying dielectric constant on the rate observed in the present work cannot be explained by Amis theory [31]. Applying the Born equation [30], Laidler and co-workers [29] derived the following equation for a dipole–dipole reaction:

$$\ln k' = \ln k_0 + 3/8kT(2/D - 1) \times \left[ \mu_A^2/r_A^3 + \mu_B^2/r_B^3 - \mu_{\ddagger}^2/r_{\ddagger}^3 \right] \quad (6)$$

where  $k_0$  is the rate constant in a medium of infinite dielectric constant,  $\mu$  is the dipole moment, and  $r$  refers to the radii of the reactants and activated complex. It is seen that the rate should be greater in a medium of lower dielectric constant, when  $r_{\ddagger}^3 > r_A^3 + r_B^3$ . On the other hand,  $r_{\ddagger}^3 \approx r_A^3 + r_B^3$  implies the absence of dielectric constant effect on the rate, as observed in the present investigation, signifies that the transition state is not very different from the reactants.

Solvent isotope studies in  $\text{D}_2\text{O}$  medium shows a retardation of the rate in the present case. It is well known that,  $\text{D}_3\text{O}^+$  is a stronger acid than the hydronium ion [32]. Hence for a pre-equilibrium proton transfer, generally the solvent isotope effect is about two to three times greater, but the value of 1.15 obtained in the present investigation depicts the fractional-order dependence of rate on  $[\text{H}^+]$ . The reduction product ( $\text{TsNH}_2$ ) had no effect on the rate indicating that it was involved in pre-equilibrium with the oxidant. The ineffectiveness of changing ionic strength of the medium on the rate indicates the involvement of nonionic species in the rate-determining step. The negligible effect of halide ions on the rate indicates that neither interhalogen nor free chlorine was formed prior to the rate-determining step. All these observations are in conformity with the proposed mechanism. The mechanism is further supported by the low enthalpy of activation and high  $\Delta G^\ddagger$  which indicate that the transition state is slightly solvated. The high negative entropy of activation shows the formation of a more ordered transition state with less degrees of freedom.

### Kinetics of Oxidation in Alkaline Medium Catalyzed by $\text{OsO}_4$

Under the condition  $[\text{PA}]_0 \gg [\text{CAT}]_0$ , plots of  $\log [\text{CAT}]$  vs. time are linear ( $r > 0.9946$ ) indicating a first-order dependence of rate on  $[\text{CAT}]_0$ . The pseudo-first-order rate constants ( $k'$ ) were unaffected (Table III) by the variation in  $[\text{CAT}]_0$ , confirming the first-order dependence on  $[\text{CAT}]_0$ . The increase in rate with increase of  $[\text{PA}]_0$  yields a linear plot of  $\log k'$  vs.  $\log [\text{PA}]$  ( $r = 0.9986$ ), having a slope equal to unity, indicating a first-order dependence of the reaction rate on  $[\text{PA}]_0$  (Table III). Further, plot of  $k'$  vs.  $[\text{PA}]$  was linear ( $r = 0.9982$ ) passing through the origin, confirming the first-order dependence of the rate on  $[\text{PA}]_0$ . The rate of the reaction increased with increase in  $[\text{NaOH}]$  (Table III), and a plot of  $\log k'$  vs.  $\log [\text{NaOH}]$  was linear ( $r = 0.9986$ ) with fractional slope (0.45) showing a fractional-order dependence of the rate on  $[\text{NaOH}]$ . Further, the rate of the reaction increases with increasing  $[\text{OsO}_4]$  (Table III), and a plot of  $\log k'$  vs.  $\log [\text{OsO}_4]$  was linear ( $r = 0.9957$ ) with a slope less than unity

**Table III** Effect of Varying CAT, PA, NaOH, and OsO<sub>4</sub> Concentrations on the Reaction Rate<sup>a</sup>

10 <sup>3</sup> [CAT] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>2</sup> [PA] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>2</sup> [NaOH] (mol dm <sup>-3</sup> )	10 <sup>6</sup> [OsO <sub>4</sub> ] (mol dm <sup>-3</sup> )	10 <sup>4</sup> k' (s <sup>-1</sup> )
0.5	2.0	5.0	5.0	4.29
1.0	2.0	5.0	5.0	4.26
2.0	2.0	5.0	5.0	4.30
3.0	2.0	5.0	5.0	4.37
4.0	2.0	5.0	5.0	4.20
1.0	1.0	5.0	5.0	1.95
1.0	1.5	5.0	5.0	3.00
1.0	2.0	5.0	5.0	4.26
1.0	3.0	5.0	5.0	5.97
1.0	4.0	5.0	5.0	8.35
1.0	2.0	2.0	5.0	2.75
1.0	2.0	4.0	5.0	3.75
1.0	2.0	5.0	5.0	4.26
1.0	2.0	8.0	5.0	5.15
1.0	2.0	10.0	5.0	5.75
1.0	2.0	5.0	2.0	1.91
1.0	2.0	5.0	4.0	3.25
1.0	2.0	5.0	5.0	4.26
1.0	2.0	5.0	8.0	5.50
1.0	2.0	5.0	10.0	6.45

<sup>a</sup> Temp. = 313 K.

(0.74) indicating a fractional-order dependence of rate on [OsO<sub>4</sub>].

Addition of *p*-toluensulfonamide (1.0 × 10<sup>-3</sup>–5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>) and halide ions, Cl<sup>-</sup> or Br<sup>-</sup> ions in the form of NaCl or NaBr (1.0 × 10<sup>-3</sup>–5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>), or variation of ionic strength (I) of the medium (0.1–0.5 mol dm<sup>-3</sup>) had no pronounced effect on the reaction rate. The effect of dielectric constant of the solvent mixture was studied by varying the MeOH content (0–20% v/v), which showed no significant effect on the rate. The solvent isotope effect was studied using D<sub>2</sub>O and the reaction rate was further increased with k' = 4.90 × 10<sup>-4</sup> s<sup>-1</sup> in D<sub>2</sub>O medium and 4.26 × 10<sup>-4</sup> s<sup>-1</sup> in H<sub>2</sub>O leading to solvent isotope effect k' (H<sub>2</sub>O)/k' (D<sub>2</sub>O) = 0.86.

The reaction was carried out at different temperatures (303–323 K) and the activation parameters were evaluated (Table IV) from a linear plot of log k' vs. 1/T (r = 0.9995). The reaction mixture failed to initiate polymerization reaction in aqueous acrylamide solution indicating the absence of free radicals.

### Mechanism of Oxidation in Alkaline Medium Catalyzed by OsO<sub>4</sub>

In alkaline solution of CAT, TsNCl<sub>2</sub> does not exist; and hence the expected reactive species are TsNHCl, HOCl,

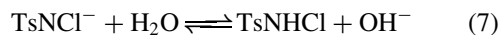
**Table IV** Temperature Dependence and Activation Parameters for the Oxidation PA by CAT in Alkaline Medium.<sup>a</sup> Also Values of Catalytic Constant (K<sub>C</sub>) at Different Temperature and Activation Parameters Calculated from K<sub>C</sub> Values

Temperature (K)	10 <sup>4</sup> k' (s <sup>-1</sup> )	10 <sup>5</sup> k' (s <sup>-1</sup> )	K <sub>C</sub>
303	2.00	(2.05)	1.92
308	3.05	(4.50)	2.17
313	4.26	(6.00)	3.05
318	6.20	(9.10)	4.42
323	9.02	(16.0)	6.21
E <sub>a</sub> (kJ mol <sup>-1</sup> )	59.9	(92.8)	36.3
ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	57.3	(90.2)	33.7
ΔG <sup>‡</sup> (kJ mol <sup>-1</sup> )	97.0	(102)	73.9
ΔS <sup>‡</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	-127	(-38.3)	-128

Values in parentheses refer to uncatalyzed oxidation of PA by CAT.

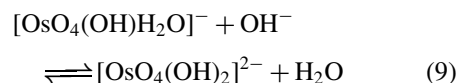
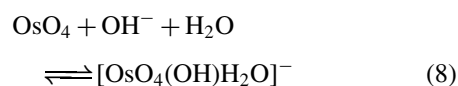
<sup>a</sup> [CAT]<sub>0</sub> = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [PA]<sub>0</sub> = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [NaOH] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [OsO<sub>4</sub>] = 5.0 × 10<sup>-6</sup> mol dm<sup>-3</sup>.

and TsNCl<sup>-</sup>. Hardy and Johnston [24] have reported the following equilibrium in alkaline solutions of CAT:

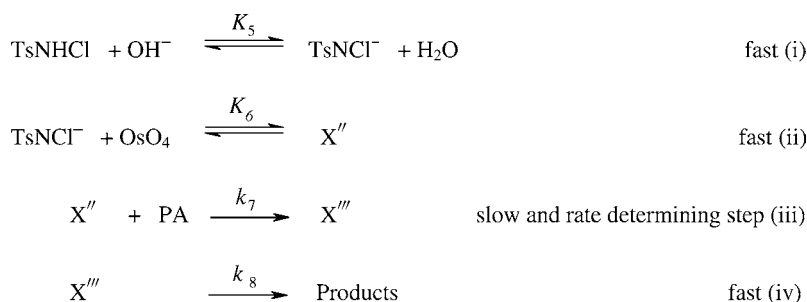


Based on the kinetic results, the TsNCl<sup>-</sup> anion is the most likely oxidizing species in alkaline medium.

It has been shown that osmium has a stable +8 oxidation state [33–35] and exists in the following equilibria in alkaline solutions:



The complexes [OsO<sub>4</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup> and [OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>, which can be reduced to [OsO<sub>2</sub>(OH)<sub>4</sub>]<sup>2-</sup>, with octahedral geometries are less likely to form species of higher coordination with the oxidant. It is more realistic to postulate that OsO<sub>4</sub>, which has tetrahedral geometry, as the active catalyst species can effectively form a complex with the oxidant species. Furthermore, the first-order dependence of the rate on [CAT]<sub>0</sub> and [PA]<sub>0</sub>, a fractional-order dependence each on [OsO<sub>4</sub>] and [OH<sup>-</sup>], indicates that the intermediate complex formed from OsO<sub>4</sub> and CAT serves as an oxidant and the possible oxidizing species here would be TsNCl<sup>-</sup>. In view of these findings, it is likely that Scheme 3 is more probable for explaining the oxidation of PA by CAT in alkaline medium in the presence of OsO<sub>4</sub>.



Scheme 3

A detailed mechanistic interaction of  $\text{OsO}_4$  catalyzed PA–CAT reaction in NaOH medium is presented in Scheme 4, in which the structures of complex intermediate species  $\text{X}''$  and  $\text{X}'''$  are given.

The total effective concentration of CAT is

$$[\text{CAT}]_t = [\text{TsNHCl}] + [\text{TsNCl}^-] + [\text{X}''] \quad (10)$$

which leads to the following rate law:

$$\begin{aligned}
 \text{Rate} &= \frac{-d[\text{CAT}]_t}{dt} \\
 &= \frac{K_5 K_6 k_7 [\text{CAT}]_t [\text{PA}] [\text{OH}^-] [\text{OsO}_4]}{[\text{H}_2\text{O}] + K_5 [\text{OH}^-] + K_5 K_6 [\text{OH}^-] [\text{OsO}_4]}
 \end{aligned} \quad (11)$$

Rate law (11) is in agreement with the experimental data.

Since  $\text{rate} = k' [\text{CAT}]_t$ , rate law (11) can be transformed into following Eqs. (12)–(15):

$$k' = \frac{K_5 K_6 k_7 [\text{PA}] [\text{OH}^-] [\text{OsO}_4]}{[\text{H}_2\text{O}] + K_5 [\text{OH}^-] + K_5 K_6 [\text{OH}^-] [\text{OsO}_4]} \quad (12)$$

$$\begin{aligned}
 \frac{1}{k'} &= \frac{[\text{H}_2\text{O}]}{K_5 K_6 k_7 [\text{PA}] [\text{OH}^-] [\text{OsO}_4]} \\
 &+ \frac{1}{K_6 k_7 [\text{PA}] [\text{OsO}_4]} + \frac{1}{k_7 [\text{PA}]}
 \end{aligned} \quad (13)$$

$$\begin{aligned}
 \frac{1}{k'} &= \frac{1}{[\text{OH}^-]} \left\{ \frac{[\text{H}_2\text{O}]}{K_5 K_6 k_7 [\text{PA}] [\text{OsO}_4]} \right\} \\
 &+ \left\{ \frac{1}{K_6 k_7 [\text{PA}] [\text{OsO}_4]} + \frac{1}{k_7 [\text{PA}]} \right\}
 \end{aligned} \quad (14)$$

$$\begin{aligned}
 \frac{1}{k'} &= \frac{1}{[\text{OsO}_4]} \left\{ \frac{[\text{H}_2\text{O}]}{K_5 K_6 k_7 [\text{PA}] [\text{OH}^-]} + \frac{1}{K_6 k_7 [\text{PA}]} \right\} \\
 &+ \frac{1}{k_7 [\text{PA}]}
 \end{aligned} \quad (15)$$

A plot of  $1/k'$  vs.  $1/[\text{OH}^-]$  from Eq. (14) yields

$$\text{slope} = \frac{[\text{H}_2\text{O}]}{K_5 K_6 k_7 [\text{PA}] [\text{OsO}_4]}$$

and

$$\text{intercept} = \frac{1}{K_6 k_7 [\text{PA}] [\text{OsO}_4]} + \frac{1}{k_7 [\text{PA}]}$$

Similarly, a plot of  $1/k'$  vs.  $1/[\text{OsO}_4]$  from Eq. (15) yields

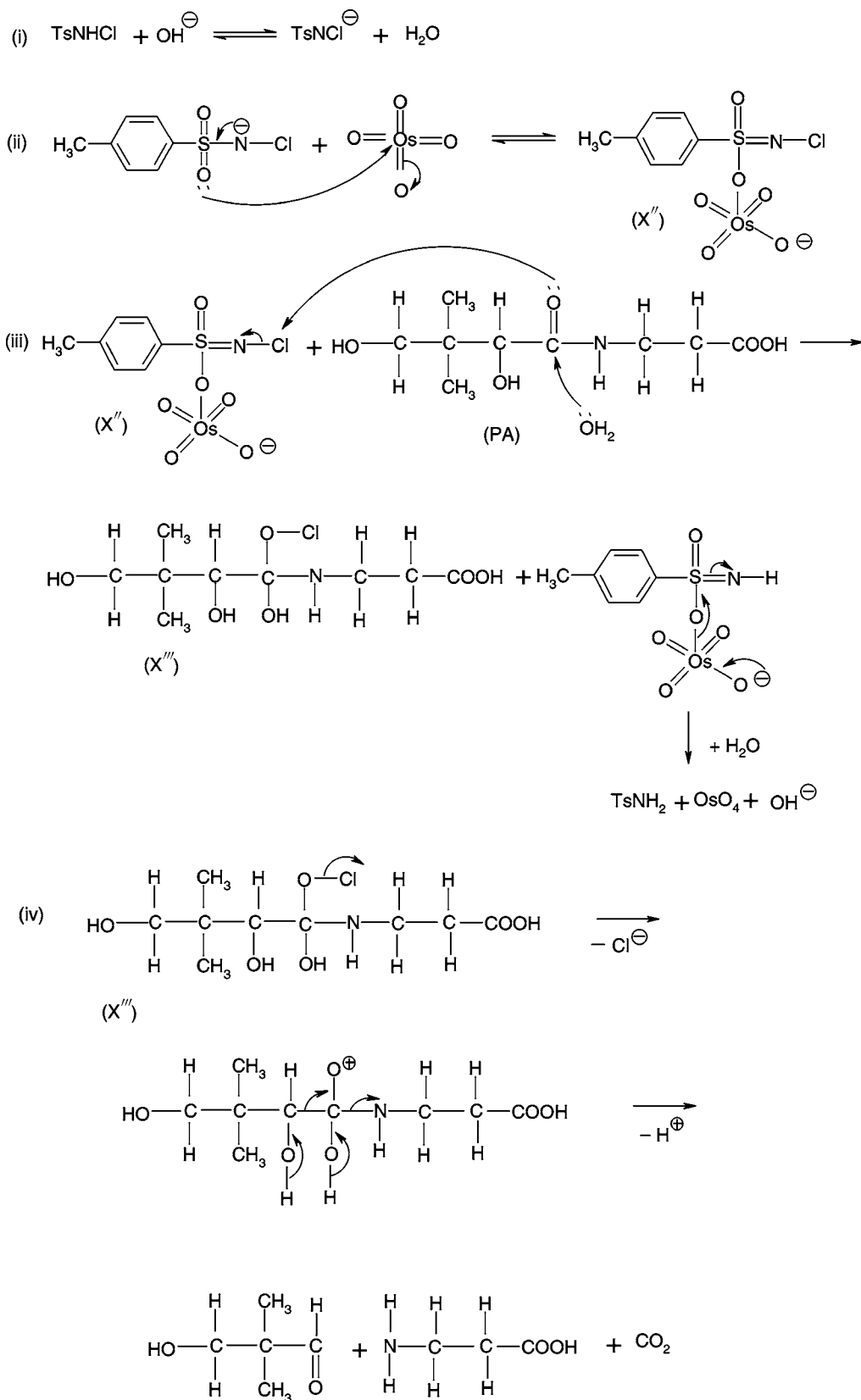
$$\text{slope} = \frac{[\text{H}_2\text{O}]}{K_5 K_6 k_7 [\text{PA}] [\text{OH}^-]} + \frac{1}{K_6 k_7 [\text{PA}]}$$

and

$$\text{intercept} = \frac{1}{k_7 [\text{PA}]}$$

Therefore from the slopes and intercepts of Eqs. (14) and (15), the values of  $K_5$ ,  $K_6$ , and  $k_7$  are calculated for the standard run with  $[\text{CAT}]_0 = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{PA}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaOH}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , and  $[\text{OsO}_4] = 5.0 \times 10^{-6} \text{ mol dm}^{-3}$  at 313 K. The values obtained are  $k_7 = 7.14 \times 10^{-2} \text{ s}^{-1}$ ,  $K_6 = 2.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ , and  $K_5 = 5.55 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ .

The solvent isotope effect  $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O}) = 0.86$  is noticed in alkaline medium. This is generally correlated with the greater basicity of  $\text{OD}^-$  compared to  $\text{OH}^-$  ions [32] which supports the initial equilibrium and the rate-determining step in Scheme 3. However, there is small magnitude of increase of rate in  $\text{D}_2\text{O}$  medium which may be due to the fractional-order dependence on  $[\text{OH}^-]$ . The experimental observation shows that there is no effect of *p*-toluenesulfonamide, halide ions, ionic strength, and dielectric constant of the medium on the rate which substantiates the mechanism proposed. This mechanism is also supported by the moderate values of energy of activation and other



Scheme 4



activation parameters. The fairly high positive values of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  indicate that the transition state is highly solvated, while large negative value of  $\Delta S^\ddagger$  suggests formation of the compact activated complex with a fewer degrees of freedom.

It was thought worthwhile to compare the reactivity of PA by CAT in the absence of osmium tetroxide catalyst under the identical experimental conditions. The reaction was carried out at different temperatures (303–323 K) and from the Arrhenius plot of  $\log k'$  vs.  $1/T$  ( $r = 0.9885$ ), values of the activation parameters for the uncatalyzed reaction were calculated. These data are presented in Table IV. Further, it has been pointed out by Moelwyn-Hughes [28] that in presence of the catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously.

$$k_1 = k_0 + K_C[\text{catalyst}]^x \quad (16)$$

Here  $k_1$  is the observed pseudo-first-order rate constant in the presence of  $\text{OsO}_4$  catalyst,  $k_0$  is the pseudo-first-order rate constant for the uncatalyzed reaction (in the absence of  $\text{OsO}_4$  catalyst),  $K_C$  is the catalytic constant, and  $x$  is the order of the reaction with respect to  $\text{OsO}_4$  and is found to be 0.74 in the present study. The values of  $K_C$  were calculated at different temperatures using the equation

$$K_C = (k_1 - k_0)/[\text{OsO}_4]^{0.74} \quad (17)$$

These values were found to vary for different temperatures. Further, the plots of  $\log K_C$  vs.  $1/T$  were found to be linear ( $r = 0.9858$ ) and values of activation parameters were computed. All these results are summarized in Table IV. It was found that  $\text{OsO}_4$  catalyzed reaction is about sevenfold faster than the uncatalyzed reaction. This is confirmed by the observed activation parameters. Hence, the observed rate of oxidation obtained in presence of  $\text{OsO}_4$  catalyst justifies the facile oxidation of PA by CAT in alkaline medium.

In conclusion, the stoichiometry and products of oxidation of PA by CAT in acid and alkaline media is same, but their kinetic patterns are different. It was also found that  $\text{OsO}_4$  was an efficient catalyst for the oxidation of PA by CAT in alkaline medium.

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