



## Oxidative decolorization of carmosine with acidic chloramine-T: Spectrophotometric, kinetic and mechanistic chemistry

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### ARTICLE INFORMATION

Received: 23 September 2011  
Received in revised form: 13 November 2011  
Accepted: 21 November 2011  
Online: 31 March 2012

### KEYWORDS

Azo dye  
Carmosine  
Acid medium  
Chloramine-T  
Decolorization  
Oxidation-kinetics

### ABSTRACT

Carmosine is mainly used as a colorant in food industries. The oxidative decolorization of this dye is of greater significance and understanding of its kinetic and mechanistic aspects in redox reactions is important. Chloramine-T bears diverse chemical properties and has been exploited as oxidant for a variety of substrates. It is commercially available, inexpensive, non toxic, water tolerant and easy to handle. A systematic kinetic study of the oxidation of carmosine with acidic chloramine-T (CAT: TsNCINa here Ts = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>) has been carried out in order to explore the mechanistic aspects of this redox system. UV-Visible spectrophotometry is used to monitor the reaction. Optimum conditions for the oxidative decolorization of carmosine with CAT were established. The kinetic results revealed that the reaction rate exhibits a first-order dependence each on [CAT]<sub>0</sub> and [carmosine]<sub>0</sub> and less than unit order dependence on [H<sup>+</sup>]. The reaction rate was examined for the effects of (a) *p*-toluenesulfonamide, (b) halide ions, (c) ionic strength, (d) dielectric permittivity and (e) solvent isotope. The reaction was studied at different temperatures and the activation parameters have been deduced. Oxidation products were characterized. Test for free radicals was found to be negative. The derived rate law based on the proposed mechanism is in complete agreement with the observed kinetic data.

### 1. Introduction

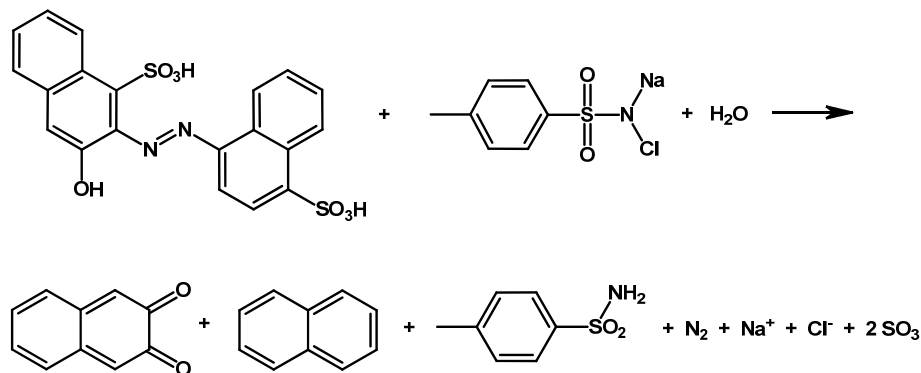
Effluents containing azo dyes discharged by dye, textile and food processing industries cause significant environmental problems. Minimization of toxicity caused by these dyes is a main issue in waste water treatment. Carmosine is one of the harmful dye effluents from food industries and removal of this dye by simple, cost effective and environmentally benign method is most required for healthy society. Azo dyes contain one or more azo groups (-N=N-) as the primary chromophore and they form the largest class of synthetic dyes. There are several monoazo dyes which are widely used as colorants in common foods and drugs [1]. The discharge of highly colored synthetic dye effluents can be very damaging to the receiving water bodies, since these dyes in water strongly absorb sunlight, which decreases the intensity of light absorbed by water plants and phytoplankton, reducing photosynthesis and the oxygenation of water reservoirs [2]. Also, public perception of water quality is greatly influenced by its color. The presence of unnatural colors is esthetically unpleasant and tends to be associated with contamination [3]. In addition, dyes used in the textile industry may be toxic to aquatic organisms and can be resistant to natural biological degradation [2,4,5]. Effluents containing azo dyes discharged by food and dye industries, cause significant environmental problems. Hence, removal of azo dye effluents generated by food and dye industries is a main issue in waste water treatment. These effluents are commonly treated using physico-chemical methods such as adsorption, photodegradation and coagulation. All of these processes are very expensive and not so simple. Therefore,

there is a need for inexpensive and simple methods to abolish harmful dyes in effluents. The oxidation of azo dyes has attracted much attention in recent years [6-9].

Carmosine is mainly used as a colorant in food industries. The oxidative decolorization of this dye is of greater significance and the understanding of its kinetic and mechanistic aspects in redox reactions is important. The literature review shows that there is no information on the oxidative decolorization of this dye from its kinetic and mechanistic view point. Consequently, this research program is designed through oxidative decolorization kinetic studies to determine the mechanism of this reaction.

The main aim of this work was to promote the decolorization of carmosine by environmentally friendly *N*-haloamine, which has a low energy cost and is inexpensive. The effectiveness of the proposed process was evaluated by its ability to decrease in color and total organic carbon content. The high efficiency observed with the dye model showed that this economic, easily operated and maintained treatment process could also be employed in the remediation of effluents.

The diverse nature of the chemistry of *N*-haloamines is consequence of their ability to act as sources of halonium cations, hypohalite species and *N*-anions which act both as electrophiles and nucleophiles [10-14]. They behave as mild oxidants and are suitable for the limited oxidation of several functional groups. Consequently, these reagents react with a wide variety of functional groups affecting an array of molecular transformations. Generally, these haloamines undergo a two-electron change while dihaloamines are four-electron oxidants [10].



Scheme 1

The reduction products are the respective sulfonamide and NaCl or HCl. The prominent member of this class of compounds, sodium *N*-chloro-4-methylbenzenesulfonamide, commonly known as chloramine-T (CAT;  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa}\cdot 3\text{H}_2\text{O}$ ) is a by-product of saccharin manufacture. The redox potential of chloramine-T/*p*-toluenesulfonamide is pH dependent [11] and decreases with increase in pH of the medium (1.139 V at pH = 0.65, 1.778 V at pH = 7.0 and 0.614 V at pH = 9.7). The nature of active oxidizing species of CAT depends on the pH of the medium and the reaction condition. Chloramine-T is a source of positive halogen and this reagent has been exploited as oxidant for a variety of substrates in both acidic and alkaline media [10,11,14-20]. Although a large numbers of various substrates have been oxidized by CAT, very few oxidation kinetic investigations of dyes have been carried out with CAT. Preliminary experimental results revealed that the oxidation of carmosine by CAT in alkaline medium is too slow to be measured but the reaction is facile in the presence of an acid. Hence, the present kinetic investigations have been carried out in acid medium.

In the light of available information and in continuation of our research interest in the kinetic and mechanistic investigations of oxidation of various substrates in general and dyes in particular by CAT, the title reaction was undertaken. Consequently, in this communication we report on the detailed kinetics of carmosine oxidation by CAT in  $\text{HClO}_4$  medium at 297 K in order to (i) elucidate a plausible mechanism, (ii) design appropriate kinetic model, (iii) ascertain the reactive species, (iv) characterize the oxidation products and (v) develop an optimum condition for the facile oxidation of the substrate.

## 2. Experimental

### 2.1. Materials

CAT (Merck) was purified by the method of Morris *et al.* [21]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored stoppered bottles until further use. The concentrations of stock solutions were periodically determined. Carmosine (S.D. Fine-Chem Ltd.) was of acceptable grade of purity and was used as received. An aqueous solution of carmosine was freshly prepared whenever required. Solvent isotope studies were made in  $\text{D}_2\text{O}$  (99.24% purity) medium supplied by Bhabha Atomic Research Centre, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout.

### 2.2. Kinetic measurements

The kinetic runs were performed under pseudo first-order conditions with a known excess of the  $[\text{CAT}]_0$  over  $[\text{carmosine}]_0$ .

at 303 K using a UV-visible spectrophotometer (Digital Spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were carried out between 288 and 313 K. For this purpose, a Raaga Ultra Cold Chamber with digital temperature control (India) was used. A constant temperature was maintained with an accuracy of  $\pm 0.1$  °C. Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of dye and  $\text{HClO}_4$  solutions and water (to keep the total volume constant for all runs) taken in separate tubes were thermostatted for 30 min at 297 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at  $\lambda_{\text{max}}$  of carmosine 518 nm for nearly three half lives. The absorbance readings at  $t = 0$  and  $t = t$  are  $D_0$  and  $D_t$ . Plots  $\log D_0/D_t$  versus time were made to evaluate the pseudo-first-order rate constants ( $k'$ ) which found reproducible within  $\pm 4\text{-}5\%$ . Regression analysis of the experimental data was carried out on an *fx-100W* scientific calculator to evaluate the regression coefficient,  $r$ .

### 2.3. Reaction stoichiometry

Reaction mixtures containing different ratios of CAT to carmosine were equilibrated at 297 K in  $1.00 \times 10^{-4}$  mol/dm<sup>3</sup>  $\text{HClO}_4$  for 48 h. Iodometric titrations of unreacted CAT showed that one mole of carmosine consumed one mole of CAT confirming the stoichiometry given in Scheme 1.

### 2.4. Product analysis

The reaction mixture in 1:1 ratio under stirred condition was allowed to progress for 48 h at 297 K. After the reaction, solution was neutralized with NaOH and the products were extracted with ether. The organic products were subjected to spot tests and chromatographic analysis (Thin layer chromatography (TLC) technique), which revealed the formation of oxidation products, namely naphthalene and 1,2-naphthoquinone. These oxidation products were separated by column chromatography and identified from their melting points: 80 °C (Lit. melting point (M.p.): 78-80 °C [8]) and 125 °C (Lit. M.p.: 124-126 °C [8]) for naphthalene and 1,2-naphthoquinone, respectively. These two products were further confirmed by GC-MS data obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectrum was obtained using the electron impact ionization technique. The mass spectra showed parent molecular ion peaks at 128 and 158 amu, confirming naphthalene and 1,2-naphthoquinone, respectively (Figure 1

and 2). Further, it was noticed that there was no further reaction between naphthalene and 1,2-naphthoquinone with CAT under the present set of experimental conditions.

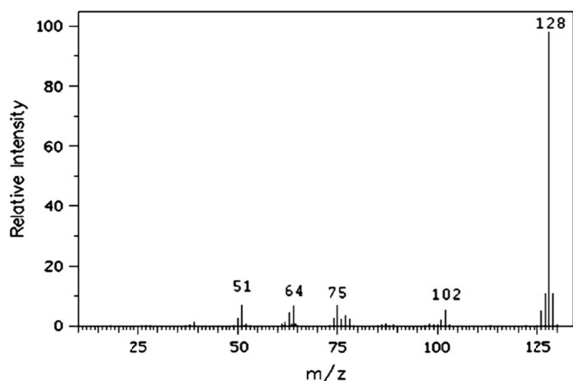


Figure 1. GC-Mass spectrum of naphthalene with its molecular ion peak at 128 amu.

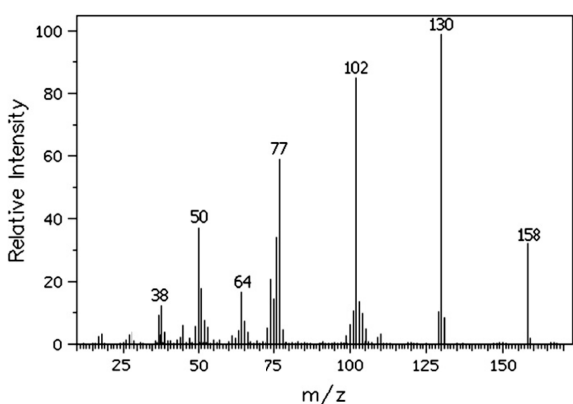


Figure 2. GC-Mass spectrum of naphthaquinone with its molecular ion peak at 158 amu.

*p*-Toluenesulfonamide was extracted with ethyl acetate and detected by paper chromatography [18]. Benzyl alcohol saturated with water was used as the solvent with 0.5 % vanillin in 1% HCl solution in ethanol as spray reagent ( $R_f = 0.905$ ). Further the parent molecular ion peak of 171 amu (Figure 3) confirms *p*-toluenesulfonamide. All other peaks observed in GC-Mass spectra can be interpreted in accordance with the observed structure.

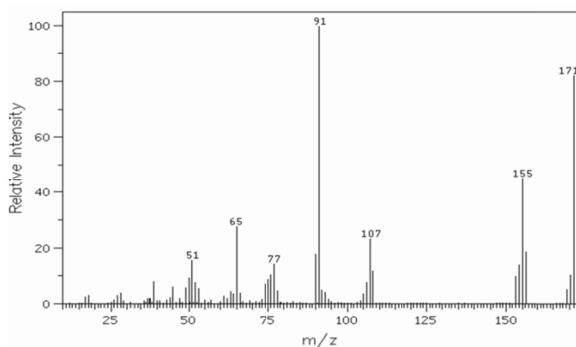


Figure 3. GC-Mass spectrum of *p*-toluenesulfonamide with its parent molecular ion peak at 171 amu.

### 3. Results and discussion

#### 3.1. Effect of reactant concentration on the rate

The oxidation of carmosine by CAT was kinetically investigated at different initial concentrations of the reactants in  $\text{HClO}_4$  medium at 297 K. Under pseudo first-order conditions of  $[\text{carmosine}]_0 \ll [\text{CAT}]_0$  at constant  $[\text{carmosine}]_0$ ,  $[\text{HClO}_4]$  and temperature, plots of  $\log(\text{absorbance})$  versus time were linear ( $r > 0.9901$ ), indicating a first-order dependence of rate on  $[\text{carmosine}]_0$ . The pseudo first-order rate constants ( $k'$ ) are listed in Table 1. Further, the values of  $k'$  remain unaltered with variation in  $[\text{carmosine}]_0$ , confirming the first-order dependence of the rate on  $[\text{carmosine}]_0$ .

Under the same experimental conditions, an increase in  $[\text{CAT}]_0$  increased the rate (Table 1). A plot of  $\log k'$  versus  $[\text{CAT}]_0$  was linear ( $r = 0.9976$ ) having a slope equal to unity, indicating a first-order dependence of the reaction rate on  $[\text{CAT}]_0$ . Further, a plot of  $k'$  versus  $[\text{CAT}]_0$  was linear ( $r = 0.9983$ ) passing through the origin, confirming the first-order dependence on  $[\text{CAT}]_0$ . At constant  $[\text{CAT}]_0$ ,  $[\text{carmosine}]_0$ , and temperature, the rate of the reaction increased with increase in  $[\text{HClO}_4]$  (Table 1). A plot of  $\log k'$  versus  $\log [\text{HClO}_4]$  was linear with a slope of 0.60, indicating a fractional-order dependence on  $[\text{HClO}_4]$ .

Table 1. Effect of variation of CAT, carmosine and  $\text{HClO}_4$  concentrations on the reaction rate at 297 K.

$10^4 [\text{CAT}]_0$ (mol dm <sup>-3</sup> )	$10^4 [\text{carmosine}]_0$ (mol dm <sup>-3</sup> )	$10^3 [\text{HClO}_4]$ (mol dm <sup>-3</sup> )	$10^4 k' \times (\text{s}^{-1})$
0.40	0.80	0.40	1.74
0.80	0.80	0.40	4.81
1.60	0.80	0.40	9.30
2.00	0.80	0.40	11.5
3.20	0.80	0.40	18.6
0.80	0.40	0.40	4.78
0.80	0.80	0.40	4.85
0.80	1.60	0.40	4.89
0.80	2.00	0.40	4.73
0.80	3.20	0.40	4.88
0.80	0.80	0.20	2.88
0.80	0.80	0.40	4.81
0.80	0.80	0.80	7.17
0.80	0.80	1.60	10.2
0.80	0.80	3.20	18.3

#### 3.2. Effects of halide and benzenesulfonamide concentration on the rate

Addition of *p*-toluenesulfonamide (PTS or  $\text{TsNH}_2$ ), reduction product of CAT ( $1.0 \times 10^{-3} - 8.0 \times 10^{-3}$  mol/dm<sup>3</sup>), to the reaction mixture did not affect the rate significantly. It indicates that PTS is not involved in any step prior to the rate-limiting step in Scheme 2 proposed.



Scheme 2

#### 3.3. Effect of ionic strength of the medium on the rate

Addition of halide ions,  $\text{Cl}^-$  or  $\text{Br}^-$ , in the form of their sodium salts ( $1.0 \times 10^{-3} - 8.0 \times 10^{-3}$  mol/dm<sup>3</sup>) showed no pronounced effect on the rate. This indicates that the halide ions play no role in the reaction. The ionic strength of the reaction medium was varied from 0.1 to 0.3 mol dm<sup>-3</sup> with  $\text{NaClO}_4$  solution keeping other experimental conditions constant. It was found that addition of  $\text{NaClO}_4$  showed negligible effect on the reaction rate, indicating the involvement of nonionic species in the rate-limiting step. Hence

no attempts were made to keep the ionic strength of the medium constant for kinetic runs.

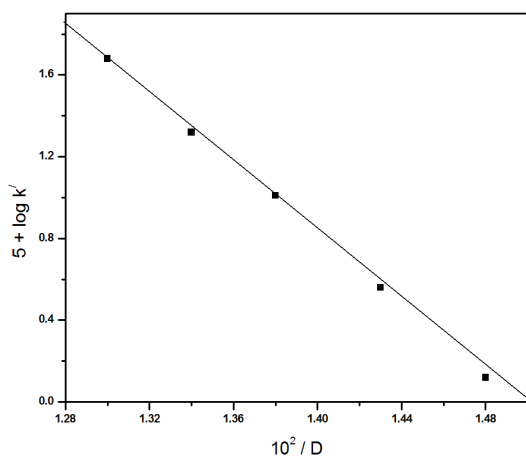
### 3.4. Effect of dielectric constant of the medium on the rate

The dielectric constant (D) of the medium was varied by adding MeOH (0-30 %; v/v) to the reaction mixture with all other experimental conditions being held constant. The rate decreased with increase in MeOH content (Table 2, Figure 4). A plot of  $\log k'$  versus  $1/D$  was linear ( $r = 0.9978$ ) with a negative slope. It was further noticed that no reaction of the dielectric with the oxidant under the experimental conditions employed. The values of the dielectric constant of  $\text{CH}_3\text{OH} - \text{H}_2\text{O}$  mixtures reported in the literature [22] were employed.

**Table 2.** Effect of varying dielectric constant (D) of medium on the rate of reaction at 297 K\*.

% MeOH (v/v)	D	$k' \times 10^4 \text{ (s}^{-1}\text{)}$
0	76.7	4.81
5	74.5	2.15
10	72.3	1.04
15	69.7	0.36
20	67.5	0.13

\*  $[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{carnosine}]_0 = 8.00 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$ .



**Figure 4.** A plot of  $\log k'$  versus  $1/D$ .

### 3.5. Effect of solvent isotope on the rate

As the oxidation of carnosine by CAT was accelerated by  $[\text{H}^+]$ , the solvent isotope effect was studied in  $\text{D}_2\text{O}$  as the solvent medium, with carnosine as a probe. Values of  $k'$  ( $\text{H}_2\text{O}$ ) and  $k'$  ( $\text{D}_2\text{O}$ ) were  $4.81 \times 10^{-4} \text{ s}^{-1}$  and  $4.96 \times 10^{-4} \text{ s}^{-1}$ , giving a solvent isotope effect  $k'(\text{H}_2\text{O}) / k'(\text{D}_2\text{O}) = 0.96$ .

### 3.6. Effect of temperature on the rate

The effect of temperature on the reaction rate was studied by performing the kinetic runs in the range of 288-313 K, keeping other experimental conditions constant. From the linear Arrhenius plot of  $\log k'$  versus  $1/T$  ( $r = 0.9930$ , Figure 5), values of activation parameters ( $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  and  $\log A$ ) for the overall reaction were evaluated. These data are presented in Table 3.

### 3.7. Test for free radicals

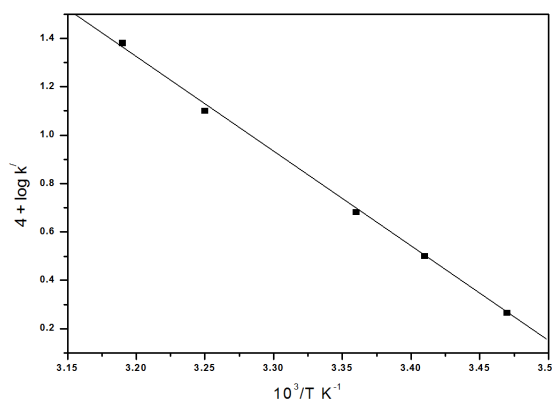
Addition of the reaction mixture to the acrylamide monomer did not initiate polymerization, indicating the absence of free radicals in the reaction mixture. Control experiments performed with solutions containing all the components of the reaction mixture except the oxidant and

with the individual oxidant solutions were found to be negative.

**Table 3.** Temperature dependence on the reaction rate and activation parameters for the oxidation of carnosine by CAT acid medium.

Temperature (K)	$k' \times 10^4 \text{ (s}^{-1}\text{)}$
288	1.84
293	3.16
297	4.81
307	12.6
313	23.4
$E_a$ (kJ mol <sup>-1</sup> )	71.7
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	69.2
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	91.8
$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	-75.4

$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{carnosine}]_0 = 8.00 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[\text{HClO}_4] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$ .

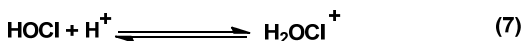
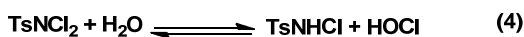


**Figure 5.** Arrhenius plot of  $\log k'$  versus  $1/T$ .

### 3.8. Reactive species of Chloramine-T

Chloramine-T ( $\text{TsNClNa}$ ) behaves as a strong electrolyte [21] in aqueous solutions, and depending upon the pH of the medium, it furnishes the following types of reactive species in solutions (Equilibrium 1-7).

Chloramine-T dissociates according to Equilibrium 1 in aqueous solution. The anion picks up a proton in acid (Equilibrium 2) to give the free acid  $\text{TsNHCl}$ . It undergoes disproportionation [23-25] via Equilibrium 3 giving rise to dichloramine-T and the parent amide. The free acid and dichloramine-T undergo hydrolysis (Equilibrium 4 and 5). Finally the hypochlorous acid undergoes ionization according to Equilibrium 6. Possibly the hypochlorous acid with a proton gives  $\text{H}_2\text{OCl}^+$  species (Equilibrium 7 and 8). Consequently, the possible oxidizing species in acidified CAT solutions are  $\text{TsNHCl}$ ,  $\text{TsNCl}_2$ ,  $\text{HOCl}$  and perhaps  $\text{H}_2\text{OCl}^+$ .

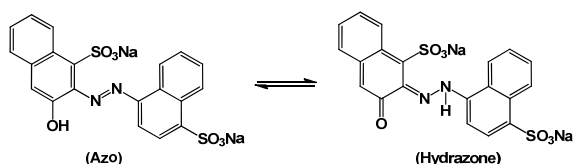


Absence of a retardation effect by the *p*-toluenesulfonamide rules out the involvement of HOCl in the reaction sequence. Bishop and Jennings [23] have shown in aqueous solutions of CAT, at pH > 3, the concentration of anion TsNCl<sup>-</sup> is greater than that of the free acid. Hence the protonation **Equilibrium 2** involving the anion can be assumed in aqueous acidic solution.

### 3.9. Reaction scheme

In the present investigations, the conjugate free acid TsNHCl is assumed to be most active oxidizing species. Based on the preceding discussion and experimental facts, **Scheme 2** is proposed to explain the reaction mechanism for the oxidation of carmosine by CAT in HClO<sub>4</sub> medium.

Dyes such as carmosine containing hydroxyl groups conjugated to azo group exhibit azo-hydrazone tautomerism as shown in **Scheme 3**.



Scheme 3

In the present case, the azo form of the dye reacts with the conjugate acid of the oxidant to form a substrate-CAT complex (X) with the elimination of TsNH<sub>2</sub>. The complex in acid medium undergoes protodesulfonation followed by hydrolysis and cleavage of azo bond to yield the ultimate products naphthalene and 1,2-naphthaquinone as shown in **Scheme 4**.

### 3.10. Kinetic rate law

A detailed mode of oxidation of carmosine by CAT in acid medium is depicted in **Scheme 4**, where the structure of the intermediate complex X is shown. In a fast initial equilibrium (step (i) of **Scheme 2**), the anion TsNCl<sup>-</sup>, in acid accelerating step generates the active oxidizing species TsNHCl.

In a slow / rate limiting step (step (ii)), the lone pair of electrons on oxygen of carmosine attacks the positive chlorine of TsNHCl forming an intermediate species X. This intermediate complex X (step (iii)) undergoes hydrolysis followed by several fast steps leading to the formation of naphthaquinone and naphthalene as end products.

If [CAT]<sub>t</sub> represents the total concentration of the oxidant, then from steps (i) and (ii) of **Scheme 2**,

$$[\text{CAT}]_t = [\text{TsN}^-\text{Cl}] + [\text{TsNHCl}] \quad (8)$$

By substituting [TsN<sup>-</sup>Cl] from step (i) of **Scheme 2**, into **Equation 8** and solving for [TsNHCl], one gets,

$$[\text{TsNHCl}] = \frac{K_1[\text{CAT}]_t[\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (9)$$

From the slow and rate determining step (step (ii) of **Scheme 2**),

$$\text{Rate} = k_2 [\text{TsNHCl}] [\text{carmosine}] \quad (10)$$

By substituting for [TsNHCl] from **Equation 9** into **Equation 10**, the following rate law is obtained:

$$\text{Rate} = \frac{K_1 k_2 [\text{CAT}]_t [\text{Carmosine}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (11)$$

The derived rate law (**Equation 11**) is in good agreement with the experimental results, wherein a first order dependence of rate on each [CAT]<sub>0</sub> and [carmosine]<sub>0</sub> and a fractional order dependence on [H<sup>+</sup>].

Since rate = [CAT]<sub>0</sub>, **Equation 11** can be transformed into **Equation 12**.

$$\frac{1}{k'} = \frac{1}{K_1 k_2 [\text{Carmosine}] [\text{H}^+]} + \frac{1}{k_2 [\text{Carmosine}]} \quad (12)$$

A plot of 1/k' versus 1/[carmosine] passes through the origin confirming observed kinetics. Further from the slope and intercept of the linear plot of 1/k' versus 1/[H<sup>+</sup>], values of protonation constant (K<sub>1</sub>) and dissociation constant (k<sub>2</sub>) were found to be 2.612 × 10<sup>5</sup> dm<sup>3</sup>/mol and 208.3 dm<sup>3</sup>/mol.s, respectively.

### 3.11. Effect of dielectric constant

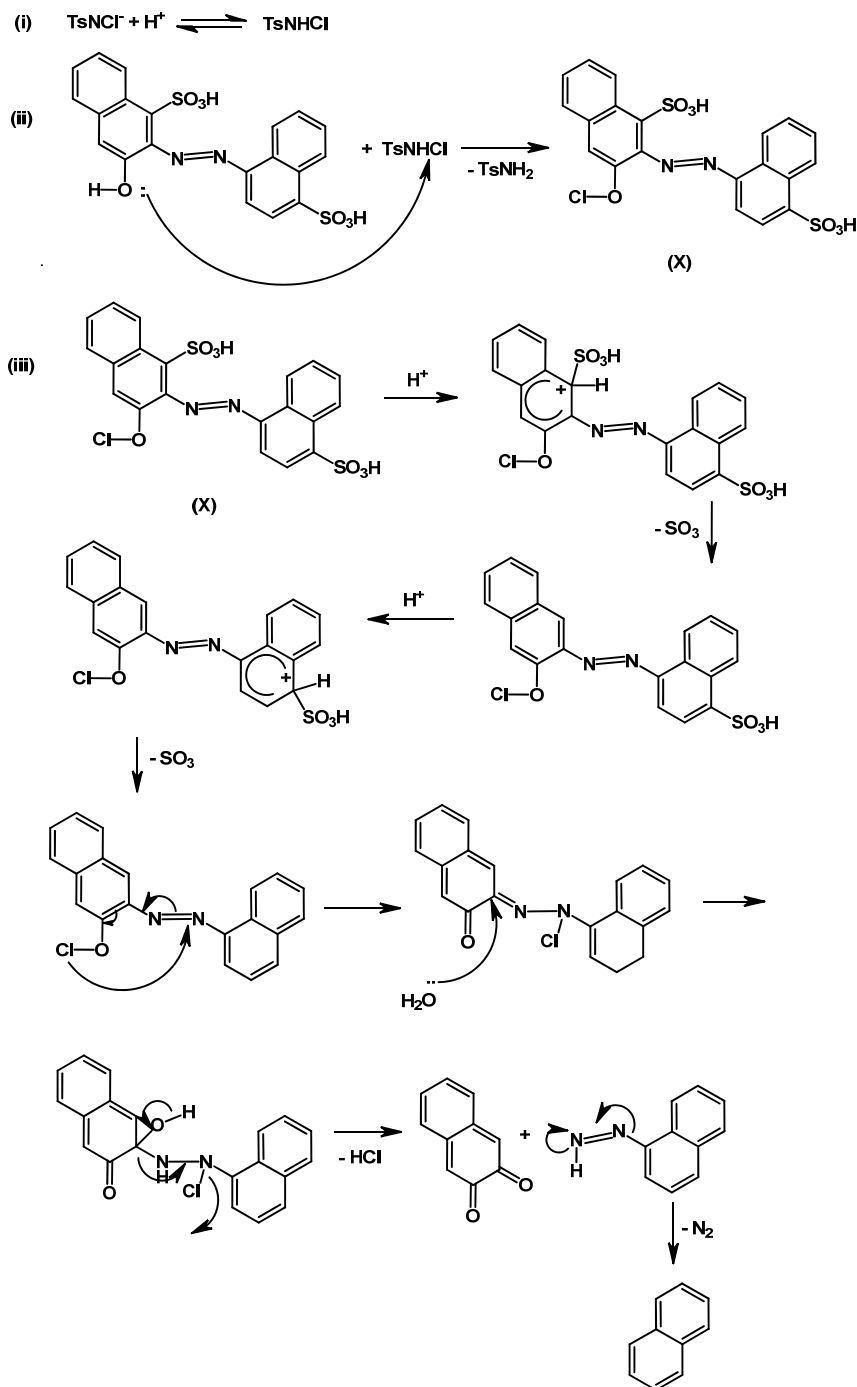
Several approaches have been put forward to explain quantitatively the effect of the dielectric constant of the medium on the rates of reactions in solutions. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [26] has shown that a plot of log k' against 1/D gives a straight line with a negative slope (**Figure 4**; r > 0.9943) for the reaction between a negative ion and a dipole or between two dipoles, while a positive slope indicates a reaction between a positive ion and a dipole. The negative dielectric effect in the present studies is in agreement with dipole-dipole nature of the rate-limiting step in the proposed **Scheme 4** and the reaction pathways are suggested to explain the kinetic results.

### 3.12. Solvent isotope studies

Reactions in aqueous medium that are susceptible to acid-base catalysis have been studied in heavy water (D<sub>2</sub>O) after equilibrium. Since most oxidation reactions of organic compounds involve the cleavage of C-H bond, deuterium isotope effect on such reactions gives information regarding the nature of the rate limiting step. In the present investigations, solvent isotope studies have shown that the rate of reaction is higher in D<sub>2</sub>O medium. For a reaction involving a fast equilibrium with H<sup>+</sup> or OH<sup>-</sup> ion transfer, the rate increases in D<sub>2</sub>O medium since D<sub>3</sub>O<sup>+</sup> and OD<sup>-</sup> are a stronger acid and a stronger base respectively, than H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions [27-28]. The observed solvent isotope effect of k' (H<sub>2</sub>O) / k' (D<sub>2</sub>O) < 1 is due to the greater acidity of D<sub>3</sub>O<sup>+</sup> compared to H<sub>3</sub>O<sup>+</sup>. However, the magnitude of increase in rate in D<sub>2</sub>O is small as compared to the expected value which is 2-3 times greater. This may be due to the fractional order dependence of the rate on [H<sup>+</sup>]. Hence, this observation supports the proposed mechanism.

The negligible influence of variation of ionic strength and addition of *p*-toluenesulfonamide and halide ions are in agreement with the proposed mechanism. The proposed mechanism is also supported by the moderate value of energy of activation and other thermodynamic parameters (**Table 3**). The fairly high positive values of ΔG<sup>‡</sup> and ΔH<sup>‡</sup> indicate that the transition state is highly solvated while the negative entropy of activation reflects the formation of a compact and ordered transition state. Further, the experimental observation shows that there is no effect of *p*-toluenesulfonamide, halide ions and ionic strength on the reaction rate which also substantiates the proposed mechanism.

In the present redox system the optimum conditions for the controlled oxidation of carmosine by CAT to naphthalene and 1,2-naphthaquinone were established in acid medium. These products are largely used in the syntheses of naphthalene analogues such as naphthols and naphthalene sulfonic acid, which are widely used in dyestuff industries. Consequently, this redox system can be scaled up to industrial operation.



Scheme 4

#### 4. Conclusions

Furthermore, carmosine is one of the chief components in the effluents of various industries and is environmentally hazardous and also carcinogenic compound. Hence, the present simple method developed can be adopted for treating the carmosine dye present in industrial effluents to reduce toxicity caused by this dye. Also, this method offers several advantages including short reaction time, ease of isolation of products, cost effective and relatively non-toxic reagents which make the reaction process simple, elegant and environmentally benign.

The kinetics of oxidation of carmosine by chloramine-T in acid medium obeys the rate law  $-\frac{d[\text{CAT}]}{dt} = k [\text{CAT}]_0 [\text{Carmosine}]_0 [\text{acid}]^{0.60}$ . Oxidation products were identified by GC-MS analysis. The present method developed for the oxidative decolorization of carmosine with CAT offers several advantages including cost effective and relatively non-toxic reagents, which make the reaction process simple, smooth and environmentally benign. Furthermore, the simple and elegant method developed in the present research can be adopted for

treating the carmosine dye present in industrial effluents to minimize the toxicity caused by this dye.

### Acknowledgements

One of the authors (Jayachamarajapura Pranesh Shubha) thanks the Principal and the Management, Don Bosco Institute of Technology for the facilities and encouragement.

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