Kinetic and mechanistic studies on the oxidative decolourisation of Orange-II dye with alkaline chloramine-T

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The mono-azo dye, Orange-II (acid orange 7), is mainly used to dye materials like textiles, paper, leather and cosmetics. It is important to understand the kinetic and mechanistic aspects of the oxidative decolourisation of Orange-II dye. A simple, efficient and cost-effective oxidation method is developed for the reaction. A detailed kinetic study of the oxidative decolourisation of orange-II dye with chloramine-T (CAT) in alkaline medium at 308 K has been carried out spectrophotometrically at 486 nm. The reaction shows a first-order dependence of rate both on $[CAT]_o$ and $[Orange\text{-}II]_o$ and an inverse-fractional- order on $[OH^-]$. The reaction was studied at different temperatures and the thermodynamic parameters have been evaluated. The reaction was subjected to change in (i) ionic strength, (ii) *p*-toluenesulfonamide and (iii) chloride ions, and the effects of these on the reaction rate were determined. Oxidation products of Orange-II were characterised as 1,2-naphthaquinone and benzenesulfonic acid by GC-MS analysis. The observed kinetic results have been explained by a general mechanism to understand the elementary pathways of this redox system. The relevant kinetic modelling has been worked out.

Keywords: Orange-II, chloramine-T, oxidative-decolourisation, kinetics, mechanism

Azo dyes constitute a large group of colourants and were used to dye various materials. Orange-II (C.I. Acid orange 7) is a synthetic mono-azo dye and it is chemically known as sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene)hydrazinyl]benzenesulfonate. It is commonly used as a colourant in the textile, paper, leather, cosmetics and food industries.[1] Wastewater released from dyeing industries in which Orange-II used is highly coloured and hence leads to environmental and health problems.[2] Oxidative decolourisation is considered a simple and economic method for the removal of dyestuffs from wastewater. The literature shows that the oxidative decolourisation methods available for Orange-II dye are quite limited.[3-7] from their kinetic and mechanistic aspects. The mechanism of oxidative decolourisation of Orange-II by CAT in $HClO_4$ medium has been investigated kinetically and reported by our research group.[8] But, to date, similar investigations in alkaline medium are not available in the literature. This aroused our interest to carry out a detailed kinetic and mechanistic study of the oxidative decolourisation of Orange-II with CAT in NaOH medium. It was also intended to compare the present results with those obtained in acid medium.[8] Hence, in the present research we have developed a simple, efficient and economic oxidative technique for decolourisation of Orange-II dye with CAT in alkaline medium. The main target of the present research was to explore the kinetic and mechanistic chemistry of the oxidative decolourisation reaction of Orange-II-CAT redox system in alkaline medium. We report here that the present redox reaction in alkaline medium differs from the same redox reaction studied in acid medium[8] in some kinetic and mechanistic aspects.

The diverse nature of the chemistry of *N*-haloamines is a consequence of their ability to act as source of species, such as halonium cations, hypohalites and *N*-anions which act as bases, nucleophiles and nitrinoids.[1-9] They behave as mild oxidants and are suitable for the limited oxidation of several groups. Consequently, these reagents react with a wide variety of functional groups effecting an array of molecular transformations.[9-13] Generally, monohaloamines undergo a two-electron change while dihaloamines are four-electron oxidants.[14] The reduction products are the respective sulfonamide and NaCl or NaBr. The prominent member of this class, sodium *N*-chloro-4-methyl benzenesulfonamide, commonly known as chloramine-T (CAT), is a by-product of saccharin manufacture. The *N*-Cl bond in CAT is highly polar and hence it is a fairly strong electrophile. The redox potential of chloramine-T is pH dependent and decreases with increase in the pH of the medium.[14] The nature of the active oxidising species of CAT depends on the pH of the medium and the reaction conditions. Chloramine-T is a source of positive halogen and this reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline media. [10-13, 15-21]. In addition to the above facts, CAT is commercially available, inexpensive, water-tolerant, non-toxic and easy to handle.[12]

The main focus of the present research work is two-fold: (i) to establish the optimum conditions for the facile decolourisation of Orange-II dye by the oxidation process and (ii) to study the kinetics and mechanism of the oxidative decolourisation of Orange-II with chloramine-T in alkaline medium. It was also of interest to compare the present results with those obtained in acid medium.[8] This type of research could shed some light on the chemical oxidation behaviour of Orange-II for the chemists who are working in the field of environmental chemistry.

Experimental

Chloramine-T (Merck) was purified by the method of Morris *et al.*[22]. An aqueous solution of CAT was prepared fresh whenever required, standardised iodometrically and stored in brown bottles until further use to prevent photochemical deterioration. The concentration of the stock solution of CAT was determined periodically iodometrically. Orange-II (Sigma) was used as received and an aqueous solution of the desired strength of the dye was prepared afresh each time. All other chemicals used were of analytical grade. Double-distilled water was used throughout.

Kinetic procedure

Detailed kinetic runs were performed under pseudo-first-order conditions of $[CAT]_o >> [Orange\text{-}II]_o$ at 308 K in the presence of NaOH. Kinetic measurements were carried out using a UV-Vis spectrophotometer. A thermostatic water bath was used to maintain the desired temperature with an accuracy of ±0.1°C. Reactions were carried out in glass stoppered pyrex boiling tubes whose outer surface was coated black to eliminate any photochemical effects. Chloramine-T, as well as the requisite amounts of Orange-II, NaOH solutions and water (to keep the total volume constant for all the kinetic runs) were taken in separate boiling tubes and were thermostatted for about 30 min at 308 K. The reaction was initiated by the rapid addition

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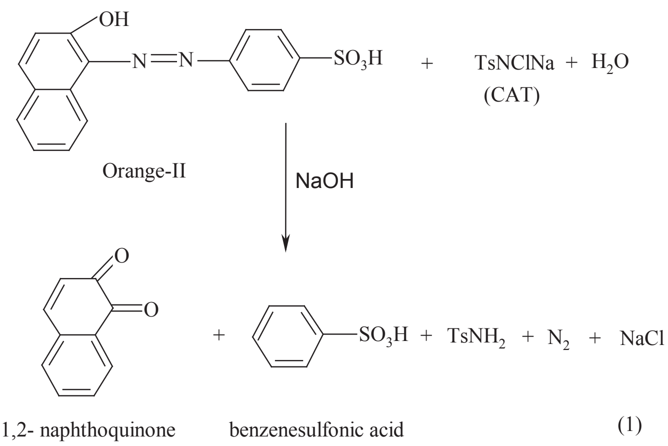
of a measured amount of oxidant to the stirred reaction mixture. Immediately, a 4 mL aliquot of the reaction mixture was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at 486 nm (λ_{max} of the dye) for nearly three half-lives. The absorbance readings at t = 0 and t = t are D_0 and D_t. Plots of log D_o/D_t *versus* time were made to evaluate the pseudo-first-order rate constants (k' s^{-1}) which were found reproducible within ± 5%. Regression coefficients (R^2) for all the linear plots were carried out on an fx-100 W Scientific Calculator.

Reaction stoichiometry

Reaction mixtures containing varying ratios of CAT to Orange-II in the presence of 1.0 x 10^{-3} M NaOH were equilibrated at 308 K for 24 h. Determination of unreacted CAT by iodometry showed that one mole of Orange-II consumed 1 mole of CAT. The observed stoichiometry can be represented by Eqn (1):



(1)

(Here Ts = $CH_3C_6H_4SO_2^-$)

Product analysis

The reaction mixture in the stoichiometric ratio under stirred condition was allowed to progress for 24 h at 308 K. After completion of the reaction (monitored by TLC), the reaction products were neutralised with acid and the products were extracted twice with diethyl ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique), which revealed the formation of oxidation products, namely 1,2-naphthoquinone and benzenesulfonic acid. These were separated by column chromatography and confirmed by GC–MS analysis. The mass spectra showed a molecular ion peak at 158 amu and 158 amu, clearly confirming 1,2-naphthoquinone and benzenesulfonic acid, respectively. Furthermore, it was noted that there was no reaction between 1, 2-naphthoquinone or benzenesulfonic acid with CAT 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.[17] 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). Nitrogen was identified by the conventional test.

Results

Decolourisation of Orange-II was performed efficiently by the oxidation process using CAT as an oxidant. This redox system is most efficient in alkaline medium. In the course of this research, the optimum conditions for the facile oxidative decolourisation of Orange-II were established. The kinetics of oxidation of Orange-II with CAT was investigated at several initial concentrations of the reactants in alkaline medium.

Under pseudo-first-order conditions in which $[CAT]_o >> [Orange\text{-}II]_o$, and at constant [NaOH] and temperature (308 K), plots of log [absorbance] *versus* time were linear ($R^2 > 0.9990$), indicating a first-order dependence of rate on [Orange-II]. The pseudo-first-order rate constants (k' s^{-1}) obtained by these plots were constant for the different initial concentrations of Orange-II employed (Table 1), thus confirming the first-order dependence of rate on [Orange-II]. Values of k' increases with increase in $[CAT]_o$ (Table 1). A plot of log k' *versus* log[CAT] was linear (R^2 = 0.9210) with a slope of unity, showing a first-order dependence of rate on $[CAT]_o$. Also, the second-order rate constants $k'' = k'/$[CAT] were fairly constant (Table 1), establishing a first-order dependence of rate on $[CAT]_o$. Furthermore, a plot of k' *versus* [CAT] was linear (R^2 = 0.9875) passing through the origin endorsing the first-order dependence of rate on $[CAT]_o$ and also the intermediates formed are transient.

There was a decrease of rate with increase in [NaOH] (Table 1) and a plot of log k' *versus* log [NaOH] was linear ($R^2 = 0.9930$) with a negative slope of –0.33, indicating an inverse- fractional-order dependence of rate on hydroxyl ion concentration. A graph showing the decolourisation rate as a function of pH using the present data (Table 1) and earlier data in acid medium.[8] This is illustrated in Fig. 1. Addition of the reduction product of CAT, *p*-toluenesulfonamide (PTS: 5.0 × 10^{-4} M) did not affect the rate,

Table 1 Effect of varying concentrations of CAT, Orange-II and NaOH on the rate of reaction at 308 K

10^3 $[CAT]_o$ M	10^4 $[Orange\text{-}II]_o$ M	10^3 [NaOH] M	10^4 k'/s^{-1}
0.5	1.0	1.0	1.29 (2.58)
1.0	1.0	1.0	2.50 (2.50)
2.0	1.0	1.0	4.82 (2.41)
4.0	1.0	1.0	9.42 (2.36)
8.0	1.0	1.0	18.9 (2.36)
2.0	0.5	1.0	5.05
2.0	1.0	1.0	4.82
2.0	2.0	1.0	4.95
2.0	4.0	1.0	4.84
2.0	8.0	1.0	4.80
2.0	1.0	0.1	11.1
2.0	1.0	0.5	6.32
2.0	1.0	1.0	4.82
2.0	1.0	2.0	3.75
2.0	1.0	6.0	2.88

The values in parentheses refer to second-order rate constants. (k'' dm^3 mol^{-1} s^{-1}).

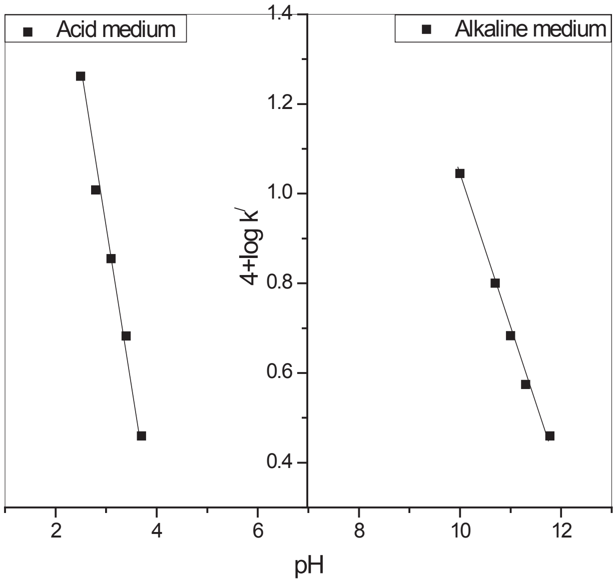


Fig. 1 Plot of log *k' versus* pH. Experimental conditions are as in Table 1 and ref. 8.

Table 2 Effect of varying temperature on the rate of reaction and activation parameters for the oxidation of Orange-II by CAT in alkaline medium

Temperature/K	$10^4\ k'/\text{s}^{-1}$
298	1.97
303	3.49
308	4.82
313	8.92
318	13.42
E_a/kJ mol^{-1}	74.90
$\Delta H^{\neq}$/kJ mol^{-1}	72.30
$\Delta G^{\neq}$/kJ mol^{-1}	75.70
$\Delta S^{\neq}$/J K^{-1} mol^{-1}	−93.90
Log A	9.20

$[\text{CAT}]_o = 2.0 \times 10^{-3}$ M; $[\text{Orange-II}]_o = 1.0 \times 10^{-4}$ M; $[\text{NaOH}] = 1.0 \times 10^{-3}$ M.

which inferred that PTS is not involved in a pre-equilibrium step with the oxidant. Similarly, addition of NaCl (5.0×10^{-4} M) had no significant effect on the rate, indicating that neither inter-halogen nor free chlorine was formed during the reaction sequence.

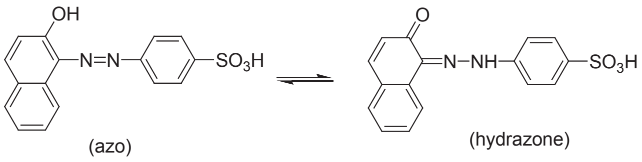
The ionic strength of the medium was varied by adding 0.2 M $NaClO_4$ solution to the reaction system. There was no effect of it on the rate of reaction and hence no attempt was made to keep the ionic strength constant for the kinetic runs. The effect of temperature on the rate was studied by conducting the kinetic runs at different temperatures (298–318K). From the linear Arrhenius plot of log *k'* *versus* 1/T ($R^2 = 0.9926$), values of the activation parameters were computed. All these results are summarised in Table 2. Addition of an aqueous solution of acrylamide to the reaction mixture did not initiate any polymerisation. This confirms the absence of free radical species in the reaction mixture.

Discussion

There is a special interest for studying chloramine-T reaction mechanisms, as it behaves both as oxidising and chlorinating agent for a variety of a substances in both acidic and alkaline medium.[15-21] An aqueous solution of CAT behaves as a strong electrolyte and depending on the pH of the medium, it furnishes different types of reactive species. Morris *et al.*[22], Bishop and Jennings,[23] Hardy and Johnston[24], and Pryde and Soper[25] have shown the existence of several equilibria in acid and alkaline solutions of CAT. The possible oxidising species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl and possibly H_2O^+Cl, and in alkaline solutions TsNHCl, HOCl, $TsNCl^-$ and OCl^-. From these four possible oxidising species of CAT in alkaline medium, the most reactive species in the present study will be decided from the observed kinetic results.

Hardy and Johnston[24] have reported that there could be a considerable concentration of TsNHCl even in alkaline CAT solutions. If HOCl is primarily involved, a first-order retardation of rate by the added PTS is expected, but no such effect was noticed. Several researchers have observed the retarding influence of OH^- ions on the rate of CAT reactions with a number of substrates[26-29] and suggested that the reaction in weakly alkaline solution of CAT is due to the formation of the conjugate acid TsNHCl from $TsNCl^-$ in a OH^--retarding step. In the present study, an inverse-fractional-order dependence of rate on $[OH^-]$, and the lack of effect on the ratio of added PTS clearly indicate that TsNHCl is the most effective reactive species.

Azo dyes containing hydroxyl group conjugated to azo group exhibit azo-hydrazone tautomerism as shown below.



For dyes where the hydroxyl group is *ortho* to the azo link, the aqueous solution favours the hydrazone form. In the present case, the hydrazone form of Orange-II is involved in the reaction.

In view of the above facts, Scheme 1 can be formulated for the oxidative decolourisation of Orange-II with CAT in alkaline medium to account the experimental results. In Scheme 1, an initial equilibrium step (step(i)) involves hydrolysis of the anionic form of CAT, $TsNCl^-$, forming the conjugate acid TsNHCl in a OH^--retarding step. In the next slow and rate-determining step, a lone pair of electrons present on the nitrogen atom of the imine group of Orange-II attacks the chlorine of the conjugate acid, forming an intermediate complex (X) with the elimination of *p*-toluenesulfonamide ($TsNH_2$). This intermediate complex by several fast steps (step(iii)), in the presence of a molecule of H_2O, yields the ultimate products, 1,2-naphthoquinone and benzenesulfonic acid with the elimination of HCl and N_2.

The rate law for Scheme 1 can be deduced as follows:

If $[\text{CAT}]_t$ represents the total effective concentration of CAT, then

$$[\text{CAT}]_t = [\text{TsNCl}^-] + [\text{TsNHCl}] \tag{2}$$

By substituting for $[\text{TsNCl}^-]$ from equilibrium (i) of Scheme 1 in Eqn (2) and solving for [TsNHCl], one obtains

$$[\text{TsNHCl}] = \frac{K_1 [\text{CAT}]_t [\text{H}_2\text{O}]}{[\text{OH}^-] + K_1 [\text{H}_2\text{O}]} \tag{3}$$

From the slow/rate-determining step of Scheme 1,

$$\text{Rate} = k_2[\text{TsNHCl}]\,[\text{Orange-II}] \tag{4}$$

Substituting for [TsNHCl] from Eqn (3) into Eqn (4), yields the following rate law:

$$\text{Rate} = \frac{K_1 k_2 [\text{CAT}]_t [\text{Orange-II}] [\text{H}_2\text{O}]}{[\text{OH}^-] + K_1 [\text{H}_2\text{O}]} \tag{5}$$

Rate law (5) is in good agreement with the observed experimental results.

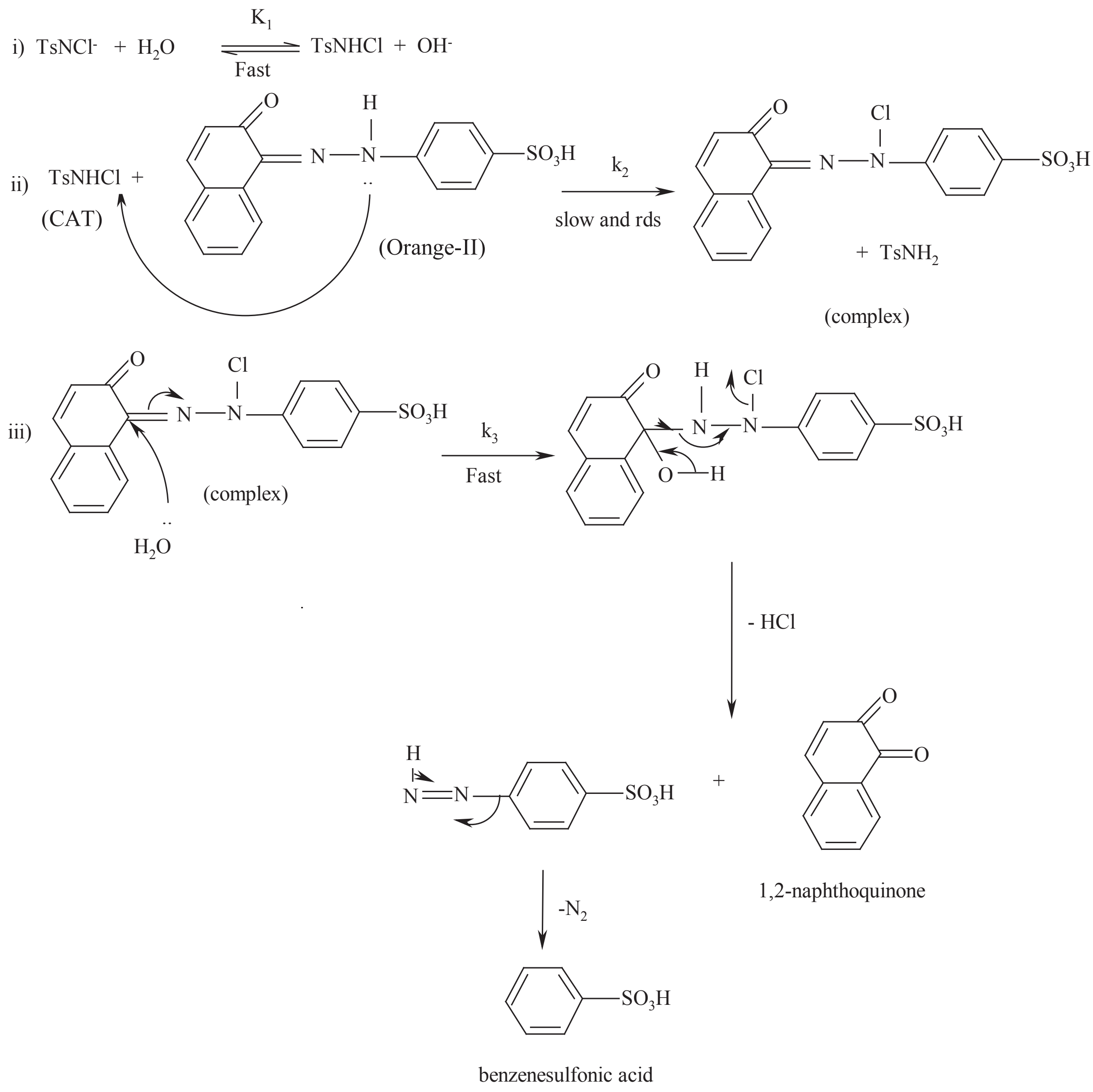
Since rate = *k'* $[\text{CAT}]_t$, rate law (5) can be transformed as,

$$k' = \frac{K_1 k_2 \ [\text{Orange-II}][\text{H}_2\text{O}]}{[\text{OH}^-] \ + \ K_1 \ [\text{H}_2\text{O}]} \tag{6}$$

$$\frac{1}{k'} = \frac{[\text{OH}^-]}{K_1 k_2 [\text{Orange-II}][\text{H}_2\text{O}]} + \frac{1}{k_2 \ [\text{Orange-II}]} \tag{7}$$

The validity of this rate law was verified by plotting 1 / *k' versus* $[OH^-]$ which was found to be linear ($R^2 = 0.9890$).

The influence of a charged species on the rate of reaction is known as the salt effect [30]. The primary salt effect is the influence of electrolyte concentration on the rate of reaction, whereas the secondary salt effect is the actual change in the



Scheme 1 A detailed mechanistic interpretation for the oxidative decolourisation of Orange-II dye with CAT in alkaline medium.

concentration of the reaction ions resulting from the addition of the electrolytes. For primary salt effect, Bronsted has given a relation between the reaction rate *(k)* and the ionic strength (I) in a reaction involving ions of charges Z_A and Z_B and later on it was modified by Bjerrum as,

$$\log k = \log k_0 + 1.018\, Z_A Z_B \sqrt{I} \tag{8}$$

Here k and k_0 are the rate constants at ionic strength I (of an inert salt) and at infinitely dilute concentration (I=0), respectively. Acccording to this equation, a plot of log k *versus* $\sqrt{I}$ is a straight line with a slope equal to 1.018 $Z_A Z_B$. In the present investigation, variation of ionic strength of the medium by adding $NaClO_4$ (0.2 M) solution did not alter the rate, indicating that one of the reactant species is non-electrolytic as shown in step (ii) of Scheme 1. Hence, the observed ionic strength effect is consistent with the Bronsted–Bjerrum concept[30] and the proposed Scheme 1.

The proposed mechanism is also supported by the moderate values of energy of activation and other thermodynamic parameters. The fairly high positive values of Gibbs free energy of activation and enthalpy of activation indicate that the transition state is highly solvated. The large negative entropy of activation accounts for the formation of the compact activated complex with fewer degrees of freedom. The experimental observation shows that there is no effect of *p*-toluensulfonamide, chloride ions and ionic strength on the reaction rate which also substantiates the proposed mechanism and the derived rate law.

Oxidative decolourisation of Orange-II with CAT in acid medium[8] differs from that in alkaline medium from the following aspects: (i) It is interesting to note that although the decolourisation kinetic orders are the same (first-order) with respect to each [CAT] and [Orange-II] in both acid and alkaline media, but the order on [OH^-] (inverse-fractional-order) is somewhat different from that on [H^+] (fractional-order), (ii) The energy of activation reveals that the rate of decolourisation of Orange-II with CAT is faster in acid medium (*E*a = 71.7 kJ mol^{-1}) compared to alkaline medium (*E*a = 74.9 kJ mol^{-1}). (iii) The oxidation products of Orange-II-CAT redox reaction in acid medium are benzene and 1,2-napthoquinone, whereas in alkaline medium they are 1,2-naphthoquinone and benzenesulfonic acid. (iv) In acid medium, the azo form of

Orange-II has been considered as the reactive substrate species whereas in alkaline medium hydrogen form was considered, and (v) The rate law in acid medium is, rate = K_1k_2 [CAT] [Orange-II] [H^+] / 1+ K_1[H^+] whereas it takes the form rate = K_1k_2[CAT] [Orange-II][H_2O] / [OH^-] + K_1 [H_2O] in alkaline medium. Due to its simplicity and cost-effectiveness, this method can be adopted to decolourise Orange-II dye.

Conclusions

For the oxidative decolourisation of Orange-II with chloramine-T in alkaline medium, the experimental rate law obtained is: $-d[CAT]/dt = k\,[CAT]_o\,[Orange\text{-}II]_o\,[NaOH]^{-0.33}$. 1,2-naphthaquinone and benzenesulfonic acid were identified as the oxidation products of Orange-II by GC-MS data. Activation parameters were evaluated. The observed results have been explained by a plausible mechanism and the related rate law has been deduced. The present redox system developed is simple, effective and inexpensive for the decolourisation of Orange-II dye.

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