Oxidative decolorisation of Eriochrome Black T with Chloramine-T: kinetic, mechanistic, and spectrophotometric approaches

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The kinetics and mechanism of oxidative decolorisation of Eriochrome Black T (EBT) with sodium *N*-chloro-*p*-toluenesulfonamide or Chloramine-T (CAT), catalysed by osmium tetroxide [Os(VIII)] in alkaline medium and uncatalysed in acid medium, have been spectrophotometrically investigated at 303 K. The reaction exhibited a first-order dependence of rate on $[CAT]_0$ and $[EBT]_0$ in both media, and also with respect to $[H^+]$. The order with respect to $[OH^-]$ and $[Os(VIII)]$ was fractional. Activation parameters were deduced. It was observed that the uncatalysed decolorisation reaction was *ca.* eightfold faster in acid medium in comparison with alkaline medium, while the Os(VIII)-catalysed reaction was *ca.* sevenfold faster than the uncatalysed reaction. Mechanisms and rate laws were determined. The chemical oxygen demand of Eriochrome Black T dye was also determined. Importantly, the developed oxidative decolorisation method is simple, efficient, inexpensive, requires less time, and is environmentally benign. Hence, it can be adapted for treating Eriochrome Black T present in industrial and laboratory wastewater.

Introduction

Azo dyes and pigments form the largest class of synthetic dyes. Their chromophore is an aromatic system attached to the azo group. Eriochrome Black T (EBT) {3-hydroxy-4-[(1-hydroxy-2-naphthyl)azo]-7-nitro-1-naphthalenesulfonic acid sodium salt; CI 14645} (CI Mordant Black 11) is a mono-azo dye that is widely used as a metal ion indicator for the determination of calcium, magnesium, zinc, nickel, etc. Moreover, it has been employed for dyeing wool and also possesses chelating properties [1]. Wastewater containing this dye, discharged by industries and laboratories, poses considerable health and environmental problems, as it is carcinogenic and toxic. Hence, the removal of EBT dye from wastewater is a prodigious task. To mitigate this problem, several oxidation, degradation, and adsorption methods have been developed for the decolorisation of EBT dye [2–4]. To the best of the authors' knowledge, no reports are available in the literature on the oxidative decolorisation of EBT with +1 oxidant with regards to its kinetic and mechanistic aspects. In addition, no investigations have been made of the impact of platinum metal ions as catalysts in the oxidative decolorisation of this dye.

N-metallo-*N*-haloarylsulfonamides, generally known as *N*-haloamines, contain halogen in the +1 oxidation state and exhibit diverse behaviour. Their versatile nature is attributed to their ability to act both as bases and nucleophiles [5]. They are capable of affecting an array of molecular transformations, including limited oxidation of specific groups [6–8]. Chloramine-T (CAT) (p-CH₃C₆H₄SO₂NCl-Na.3H₂O) is the most important member of this class of compounds and behaves as an oxidising/analytical agent in both acidic and alkaline media [6–11]. It is commercially available, inexpensive, water tolerant, relatively non-toxic, and easy to handle [7]. Although CAT has been exploited as an oxidising agent for a variety of substrates to clarify their kinetic and mechanistic picture, very limited information is available in the literature about the oxidative behaviour of CAT towards dyes [9–11]. It is for these reasons that CAT has been chosen as an oxidant in the present research.

The process of catalysis plays an important role in the production of chemicals and growth of chemical industries. Research into catalysis is a major field in applied, environmental, and medicinal science. The abundant use of platinum-metal-ion-catalysed reactions in many important industrial processes such as hydrogenation, carboxylation, oxidation, and reduction has created an interest among researchers owing to its significance in understanding the mechanistic chemistry of a particular redox system [12,13]. The mechanism of catalysis to some extent is complicated by the formation of different intermediate complexes, free radicals, and different oxidation states. In recent years, Os(VIII), Ru(III), Rh(III), Pd(II), Pt(IV), and Ir(III) have also been widely used as homogeneous catalysts because these elements demonstrate a strong catalytic influence in many reactions. Some of these systems have proved to be suitable for kinetic analysis [13]. During preliminary kinetic investigations, EBT–CAT redox reactions in alkaline medium were found to be sluggish, but became facile in the presence of a microquantity (10^{-5} mol dm^{-3}) of osmium tetroxide [Os(VIII)].

In view of the above, the present communication reports for the first time on the kinetic and mechanistic aspects of the oxidative decolorisation of EBT with CAT, catalysed by Os(VIII) in alkaline medium and uncatalysed in acid medium, under identical experimental conditions. The objectives of the present investigations were: (i) to establish the optimum conditions for the facile oxidative decolorisation of EBT with CAT; (ii) to compile all possible kinetic data; (iii) to elucidate plausible mechanisms; (iv) to derive relevant rate laws; (v) to ascertain reactive species; (vi) to identify oxidative decolorisation products; (vii) to correlate

the reaction rate in acid and alkaline media, and also Os(VIII)-catalysed and uncatalysed reactions.

Experimental

Materials and methods

CAT (Merck, USA) was purified by the method of Morris *et al.* [14]. An aqueous solution of CAT was prepared afresh whenever required, standardised by the iodometric method, and stored in brown bottles until further use to prevent its photochemical deterioration. The concentration of CAT stock solution was periodically determined iodometrically.

were reported. Regression coefficients (R^2) were evaluated using an fx-100 W scientific calculator (Casio, Japan).

Stoichiometry and characterisation of products

Reaction mixtures containing different ratios of CAT:EBT in the presence of 5.0×10^{-3} mol dm^{-3} of HClO$_4$/NaOH and 1.56×10^{-5} mol dm^{-3} of OsO$_4$ (in alkaline medium) were equilibrated at 303 K for 24 h. Determination of the unreacted CAT iodometrically showed that 1 mol of EBT consumed 1 mol of CAT in both media. Accordingly, the stoichiometric equation in Scheme 1 can be formulated.
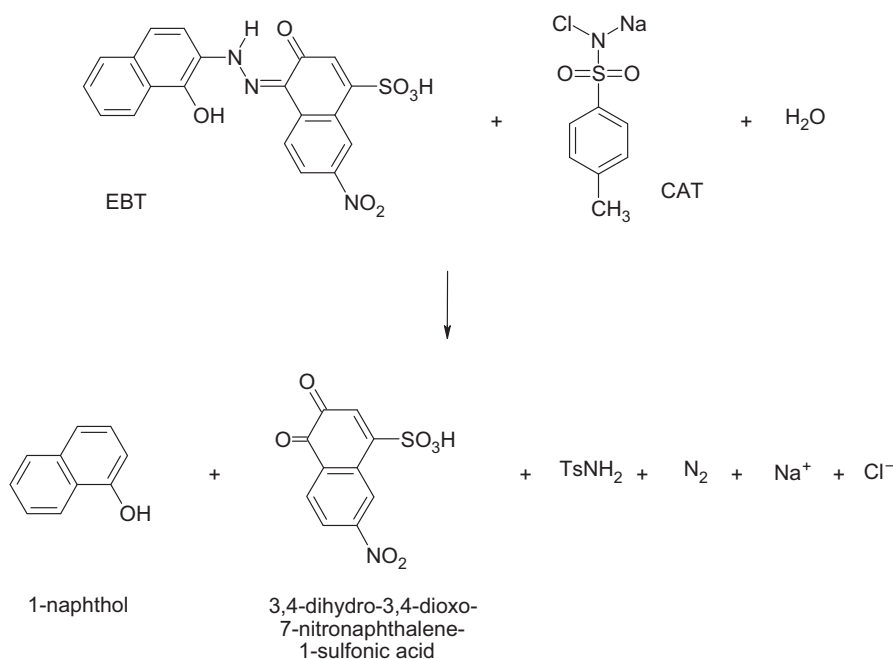
Scheme 1   Reaction Stoichiometry where $T_s = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$

EBT (Sd Fine Chemicals Ltd, India) was used as received, and an aqueous solution of the desired strength of the dye was prepared afresh each time. A solution of OsO$_4$ (Merck) in 0.01 mol dm^{-3} of sodium hydroxide (NaOH) was used as the catalyst. Allowance was made for the amount of NaOH present in the catalyst solution while preparing for kinetic runs. All other chemicals used were of analytical grade. Doubly distilled water was used throughout the experiment. A UV-3101 PC UV-vis–NIR scanning spectrophotometer (Shimadzu, Japan) was used for studying the formation of the intermediate complex.

The kinetic runs were performed under pseudo-first-order conditions by ensuring an excess of CAT over EBT in perchloric acid (HClO$_4$ and NaOH media at 303 K. UV-vis spectrophotometry (Digital Spectrophotometer 166; Systronics, India) was used as a basic analytical approach, and absorbance measurements were made at 520 nm (λ_{max} of EBT dye). The experimental procedure followed was identical to that reported earlier [9]. The oxidative decolorisation kinetics were followed for more than 80% completion of the reaction. The absorbance readings at $t = 0$ and $t = t$ are denoted by D_0 and D_t. Plots of log D_0/D_t *vs* time were made to evaluate the pseudo-first-order rate constants k' (s^{-1}). All kinetic runs were carried out twice to check reproducibility; reproducibility with $\pm 4\%$ error was found. The mean values of the rate constants

The reaction mixture in stoichiometric ratio under stirred conditions was allowed to progress in the presence of HClO$_4$/NaOH and Os(VIII) (in alkaline medium) for *ca.* 24 h at 303 K. After completion of the reaction (monitored by thin-layer chromatography), the reaction products were neutralised with dilute NaOH/HClO$_4$ and extracted with ethyl acetate. Separation of these products was achieved using silica gel (60–100 mesh) column chromatography and hexane/ethyl acetate (8:6 v/v) as mobile phase. The organic products were identified as naphthalene-2-ol and 7-nitro-3,4-dioxo-3,4-dihydro-naphthalene-1-sulfonic acid in both cases, which was confirmed by gas chromatography-mass spectrometry (GC-MS) analysis. GC-MS data were obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectra showed a molecular ion peak at 144 (Figure 1) and 284 amu (Figure 2), clearly confirming these products. It was also noted that there was no further reaction of these products under the present set of experimental conditions. Additionally, naphthalene-2-ol and 7-nitro-3,4-dioxo-3,4-dihydro-naphthalene-1-sulfonic acid are of diverse importance as intermediates for the agricultural, pharmaceutical, rubber, and textile industries. The reduction product of CAT, *p*-toluenesulfonamide (PTS or TsNH$_2$), was extracted with ethyl acetate and detected by paper chromatography [9] using
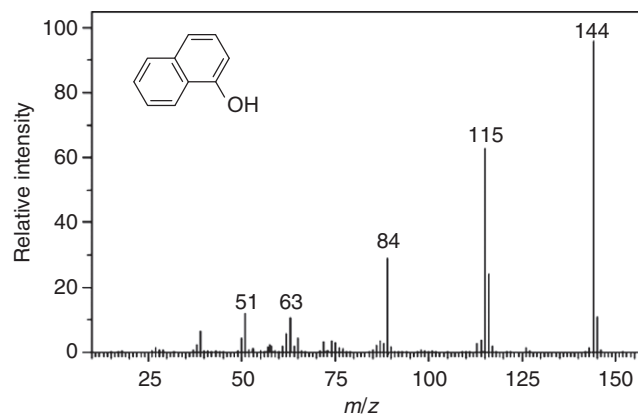
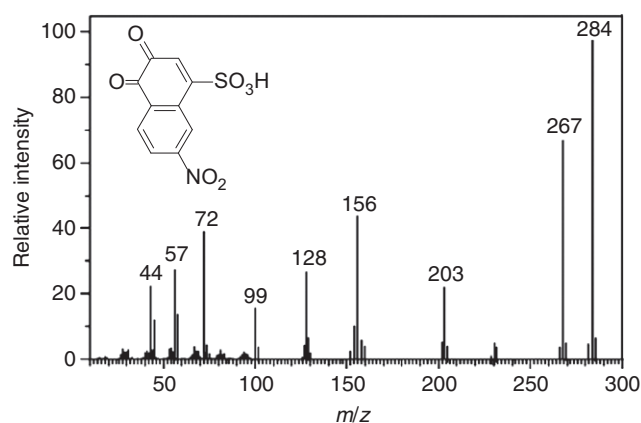**Figure 1** GC-MS of naphthalene-2-ol with its parent molecular ion peak at 144 amu

Figure 2 GC-MS of 7-nitro-3,4-dioxo-3,4-dihydro-naphthalene-1-sulfonic acid with its parent molecular ion peak at 284 amu

PhCH$_2$OH saturated with water as the solvent with 0.5% vanillin in 1% hydrochloric acid (HCl) solution in ethanol (EtOH) as the spray reagent (R_f = 0.905). Nitrogen was identified by the conventional test.

Results and Discussion

Under an identical set of experimental conditions, preliminary experimental results revealed that the EBT–CAT reactions in HClO$_4$ medium were facile, but the reactions became very sluggish in alkaline medium. However, a microquantity (10^{-5} mol dm^{-3}) of OsO$_4$ potentially catalysed the same reaction in alkaline medium. Consequently, the kinetics of oxidative decolorisation of EBT with CAT in acid medium and in alkaline medium catalysed by Os(VIII) was spectrophotometrically investigated with several initial concentrations of the reactants. The stoichiometry and oxidative decolorisation products were the same in both media, but the kinetic and mechanistic patterns were found to be different.

Under the experimental conditions [EBT]$_0$ ≪ [CAT]$_0$, at constant [CAT]$_0$, [HClO$_4$]/[NaOH], [Os(VIII)] (in alkaline medium), and temperature, plots of log [absorbance] *vs* time were linear (R^2 > 0.9833) (Table 1), indicating a first-order dependence of rate on [EBT]$_0$ in both media. The linearity of these plots, together with the constancy of the slopes obtained at different [EBT]$_0$, confirms the first-order dependence of rate on [EBT]$_0$. The calculated pseudo-first-order rate constants k' (s^{-1}) are listed in Tables 2 and 3. Under the

Table 1 EBT decolorisation with time at 303 K (representative run)[a]

Time, min	Absorbance		log D_0/D_t	
	Acid medium	Alkaline medium	Acid medium	Alkaline medium
0	0.610	0.861		
5	0.517	0.698	0.071	0.091
10	0.494	0.585	0.091	0.167
15	0.398	0.515	0.185	0.223
20	0.349	0.435	0.242	0.296
25	0.311	0.394	0.292	0.339
30	0.286	0.329	0.328	0.417
35	0.245	0.291	0.396	0.471
40	0.206	0.262	0.471	0.516
45	0.158	0.235	0.586	0.563
50	0.136	0.215	0.651	0.602
55	0.112	0.191	0.736	0.653
60	0.096	0.175	0.821	0.691

a [CAT]$_0$ = 5.0 × 10^{-3} mol dm^{-3}; [EBT]$_0$ = 4.0 × 10^{-4} mol dm^{-3}; [HClO$_4$] / [NaOH] = 5.0 × 10^{-3} mol dm^{-3}; [Os(VIII)] = 1.56 × 10^{-5} mol dm^{-3} (in alkaline medium).

Table 2 Effect of varying the CAT, EBT, and HClO$_4$ concentrations on the rate of the reaction at 303 K

10^3 [CAT]$_0$, mol dm^{-3}	10^4 [EBT]$_0$, mol dm^{-3}	10^3 [HClO$_4$], mol dm^{-3}	10^4 k', s^{-1}
1.0	4.0	5.0	1.70
3.0	4.0	5.0	3.68
5.0	4.0	5.0	5.11
7.0	4.0	5.0	7.67
10.0	4.0	5.0	11.50
5.0	1.0	5.0	4.99
5.0	2.0	5.0	4.93
5.0	4.0	5.0	5.11
5.0	8.0	5.0	5.29
5.0	10.0	5.0	5.18
5.0	4.0	1.0	1.05
5.0	4.0	3.0	2.98
5.0	4.0	5.0	5.11
5.0	4.0	7.0	7.00
5.0	4.0	10.0	10.00

same experimental conditions, the rate of the reaction increased in [CAT]$_0$ (Tables 2 and 3), and plots of log k' *vs* log [CAT]$_0$ were linear (R^2 > 0.9910) with a unit slope in both media. This confirmed that the kinetics of the reaction was first-order with respect to [CAT]$_0$ in acid and alkaline media. Further, plots of k' *vs* [CAT]$_0$ were linear (R^2 = 0.9963), passing through the origin, confirming the first-order dependence of rate on [CAT]$_0$ in both cases. The reaction rate increases with an increase in both [HClO$_4$] and [NaOH] (Tables 2 and 3), and a plot of log k' *vs* log [H$^+$] was linear (R^2 = 0.9978) with a unit slope, confirming a first-order dependence of rate on [H$^+$]. However, the order in alkaline medium was found to be less than unity (0.82), indicating a fractional-order dependence of rate on [OH$^-$] in alkaline medium (R^2 = 0.9949). The values of k' increased with an increase in [Os(VIII)] (Table 3), and a plot of log k' *vs* log [Os(VIII)] was linear (R^2 = 0.9932) with a slope of 0.66. This ensured that the order of the reaction with respect to [Os(VIII)] was fractional.

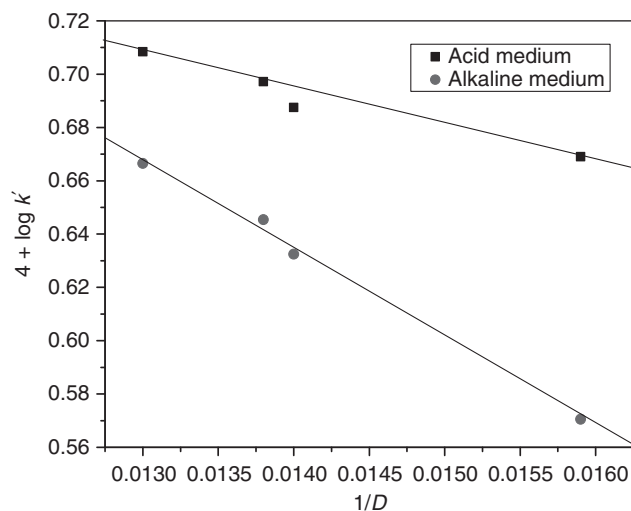**Table 3** Effect of varying CAT, EBT, NaOH, and Os(VIII) concentrations on the rate of reaction at 303 K

10^3 [CAT]$_0$, mol dm^{-3}	10^4 [EBT]$_0$, mol dm^{-3}	10^3 [NaOH], mol dm^{-3}	10^5 [Os(VIII)], mol dm^{-3}	10^4 k', s^{-1}
1.0	4.0	5.0	1.56	1.0
3.0	4.0	5.0	1.56	2.49
5.0	4.0	5.0	1.56	4.64
7.0	4.0	5.0	1.56	6.58
10.0	4.0	5.0	1.55	10.60
5.0	1.0	5.0	1.56	4.58
5.0	2.0	5.0	1.56	4.60
5.0	4.0	5.0	1.56	4.64
5.0	8.0	5.0	1.56	4.55
5.0	10.0	5.0	1.56	4.69
5.0	4.0	5.0	0.50	1.92
5.0	4.0	5.0	1.00	2.98
5.0	4.0	5.0	1.50	4.64
5.0	4.0	5.0	3.00	6.35
5.0	4.0	5.0	5.00	8.90
5.0	4.0	1.0	1.56	0.92
5.0	4.0	3.0	1.56	2.69
5.0	4.0	5.0	1.56	4.64
5.0	4.0	7.0	1.56	5.23
5.0	4.0	10.0	1.56	7.15

The addition of the reduction product of CAT, PTS (TsNH$_2$: 2.0×10^{-3} mol dm^{-3}), to the reaction mixture did not alter the rate significantly in either case, suggesting its non-involvement in pre-equilibrium with CAT. Also, the addition of 5.0×10^{-3} mol dm^{-3} of sodium chloride (NaCl) had no effect on the rate in either medium, signifying no role for the chloride ion in the reaction. The effect of the dielectric constant (D) of the solvent medium of the reaction mixture was studied by varying the percentage of methanol (MeOH) (0–30% v/v). Values of the dielectric constant of MeOH–water mixtures reported in the literature [15] were employed. The rate was found to decrease with an increase in MeOH content in both media. The rate constants k' (10^4 s^{-1}) determined at different D values of 76.73, 72.37, 67.48, and 62.71 were 5.11, 4.98, 4.87, and 4.67 in acid medium, whereas in alkaline medium they were 4.64, 4.42, 4.29, and 3.72

Figure 3 Plots of log k' *vs* 1/*D* in acid and alkaline media

respectively. Plots of log k' *vs* 1/*D* were found to be linear ($R^2 > 0.9942$) with negative slopes (Figure 3).

The effect of the ionic strength of the medium on the rate of the reaction was carried out in the presence of 0.2 mol dm^{-3} NaClO$_4$ solution, with other experimental conditions being kept constant. The ionic strength showed a negligible influence on the reaction rate in both media, indicating the involvement of non-ionic species in the rate-determining steps (RDSs). Subsequently, the ionic strength of the reaction system was not fixed constant for kinetic runs. The reaction was studied at different temperatures (293–313 K), and, from Arrehenius plots of log k' *vs* 1/*T* ($R^2 > 0.9932$), activation parameters for the composite reaction were computed in both cases. These results are summarised in Table 4. The addition of aqueous solutions of acrylamide to the reaction mixture did not cause polymerisation. This suggests the absence of free radical species involvement during the reaction sequence in acid and alkaline media.

Reactive species of Chloramine-T

CAT (TsNClNa) acts as an oxidising agent in both acidic and alkaline media [16]. In general, CAT undergoes a

Table 4 Effect of varying the temperature on the rate of the reaction and the activation parameters for the oxidative decolorisation of EBT with CAT in acid and alkaline media[a]

	10^4 k', s^{-1}			
		Alkaline medium		
	Acid medium	Uncatalysed	Os(VIII) catalysed	k_c
293 K	2.39	0.32	2.29	1.77
298 K	3.98	0.49	3.45	2.67
303 K	5.11	0.65	4.64	3.60
308 K	8.02	0.96	6.98	5.44
313 K	10.3	1.34	9.23	7.10
E_a, kJ mol^{-1}	46.7	51.5	42.3	38.0
$\Delta H^{\neq}$, kJ mol^{-1}	44.2 ($\pm$0.01)	49.0 ($\pm$0.02)	37.3($\pm$0.05)	35.5($\pm$0.01)
$\Delta G^{\neq}$, kJ mol^{-1}	119 ($\pm$0.35)	123 ($\pm$0.21)	115 ($\pm$0.32)	106 ($\pm$0.11)
$\Delta S^{\neq}$, J K^{-1} mol^{-1}	−248 ($\pm$0.11)	−246 ($\pm$0.11)	−248 ($\pm$0.05)	−234 ($\pm$0.11)
log A	13.9	10.2	12.4	15.6

a [CAT]$_0$ = 5.0×10^{-3} mol dm^{-3}; [EBT]$_0$ = 4.0×10^{-4} mol dm^{-3}; [HClO$_4$] / [NaOH] = 5.0×10^{-3} mol dm^{-3}; [Os(VIII)] = 1.56×10^{-5} mol dm^{-3} (in alkaline medium).

two-electron change in its reactions, forming the reduction products PTS and NaCl. The redox potential of the CAT–PTS couple varies with the pH of the medium, having values of 1.139 V 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. CAT behaves like a strong electrolyte [16] and, depending on the pH of the medium, furnishes [14,16,17] different reactive species in solutions. Monochloramine-T (TsNHCl), dichloramine-T (TsNCl$_2$), hypochlorous acid (HOCl), and possibly H$_2$O$^+$Cl are the predominant oxidising species of CAT in acid medium. In alkaline solutions, TsNCl$_2$ does not exist, and the possible reactive species are TsNHCl, TsNCl$^-$, HOCl, and OCl$^-$. Out of the aforesaid four possible oxidising species of CAT in each acid and alkaline medium, the most reactive species in the present study will be determined from the observed kinetic results.

Tautomerism of Eriochrome Black T

Azo dyes, such as EBT, containing hydroxyl groups conjugated to an azo group, exhibit azo–hydrazone tautomerism as shown in Scheme 2.
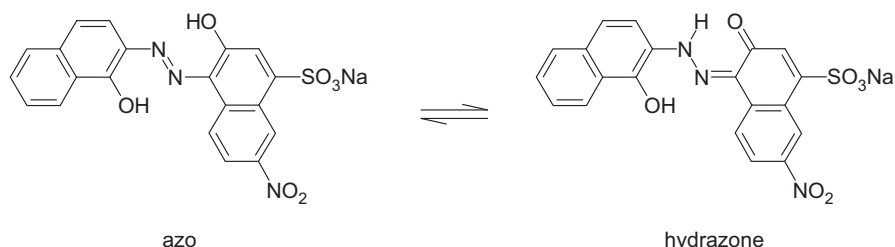
Scheme 2 Tautomerism of EBT dye

For dyes where the hydroxyl group is ortho to the azo link, the aqueous solution favours the hydrazone form [18]. In the present case, the hydrazone form of EBT is involved in the reaction.

Reaction scheme and rate law in acid medium

The possible oxidising species in acidified CAT solutions are TsNHCl, TsNCl$_2$, HOCl, and possibly H$_2$O$^+$Cl. If TsNCl$_2$ is taken as the reactive species, then the rate law predicts a second-order dependence on [CAT]$_0$. This is not true in the present case, as a first-order dependence of rate with respect to [CAT]$_0$ is observed. If HOCl acts as a reactive species, it will lead to a first-order retardation of rate upon the addition of PTS (TsNH$_2$), which is contrary to the observed zero effect of PTS on the rate. Hence, TsNCl$_2$ and HOCl were ruled out as reactive species. Further, based on knowledge of the equilibrium, disproportionation, and hydrolysis constants of reactions, Bishop and Jennings [16] as a first approximation calculated the concentrations of different species in 0.05 mol dm^{-3} CAT solutions at different pH values. The acid form of CAT (TsNHCl) is found to be the predominant species under acidic conditions. In the present investigations, the rate of the reaction is accelerated by [H$^+$], and hence TsNHCl can be postulated as the most reactive species in acid medium. Based on the preceding discussion and kinetic results, a suitable mechanism (Scheme 3) has been proposed for the oxidation of EBT with CAT in acid medium.

In Scheme 3, X is the complex intermediate species. An initial equilibrium involves protonation of TsNCl$^-$, forming the active oxidising species of CAT, TsNHCl [step (i)]. In the

next slow and rate-determining step [step (ii)], a lone pair of electrons present on the nitrogen atom of the imine group of EBT attack the positive chlorine of TsNHCl, forming an intermediate complex (**X**), with the loss of a proton and elimination of PTS (TsNH$_2$). The complex **X** in the presence of a molecule of water, through several fast steps [step (iii)], yields the ultimate products with the elimination of a molecule each of HCl and N$_2$.

Applying steady-state conditions for TsNHCl, and with the assumption that $k_1 \gg k_2$ [EBT], the rate law:

$$\text{Rate} = \frac{-\text{d[CAT]}}{\text{d}t} = \frac{k_1 k_3}{k_2}[\text{CAT}][\text{H}^+][\text{EBT}] \tag{1}$$
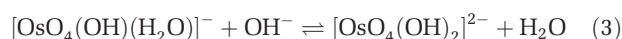
can be derived, which is in agreement with the experimental results.

## Reaction scheme and rate law in alkaline medium

In alkaline solutions of CAT, TsNCl$_2$ does not exist, and hence the expected reactive species are TsNHCl, TsNCl$^-$, HOCl, and OCl$^-$. Further, Hardy and Johnston [17] have reported different equilibria in alkaline solutions of bromamine-B (BAB). According to the different equilibria of BAB, if PhSO$_2$NHBr, HOBr, and OBr$^-$ were to be the reactive oxidising species, then retardation of the rate by added benzenesulfonamide (PhSO$_2$NH$_2$) and OH$^-$ would be expected. Given that *N*-haloamines have similar properties, the above argument can be extended to CAT also. In the present case, that of PTS on the rate of the reaction is negligible, and that of OH$^-$ on the rate of the reaction is positive. Hence, these three reactive species can easily be ruled out. It is therefore reasonable to assume that TsNCl$^-$ is the reactive oxidising species in the alkali accelerating step, as is observed in the present study. The same anion was postulated as the reactive oxidising species for the alkali acceleration reaction in early studies by the present authors [19–21].

Osmium tetroxide is known to be an efficient catalyst in the oxidation of several organic compounds by various oxidants in aqueous alkaline medium [12,13,22–26]. It has been shown that osmium is stable in its +8 oxidation state [27,28], and in alkaline solutions the following equilibria exist:

$$\text{OsO}_4 + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons [\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^- \tag{2}$$

$$[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^- + \text{OH}^- \rightleftharpoons [\text{OsO}_4(\text{OH})_2]^{2-} + \text{H}_2\text{O} \tag{3}$$

The complexes [OsO$_4$(OH)(H$_2$O)]$^-$ and [OsO$_4$(OH)$_2$]$^{2-}$, which can be reduced to [OsO$_2$(OH)$_4$]$^{2-}$, with octahedral geometries, are less likely to form higher coordination species with the oxidant/substrate. It is more realistic to
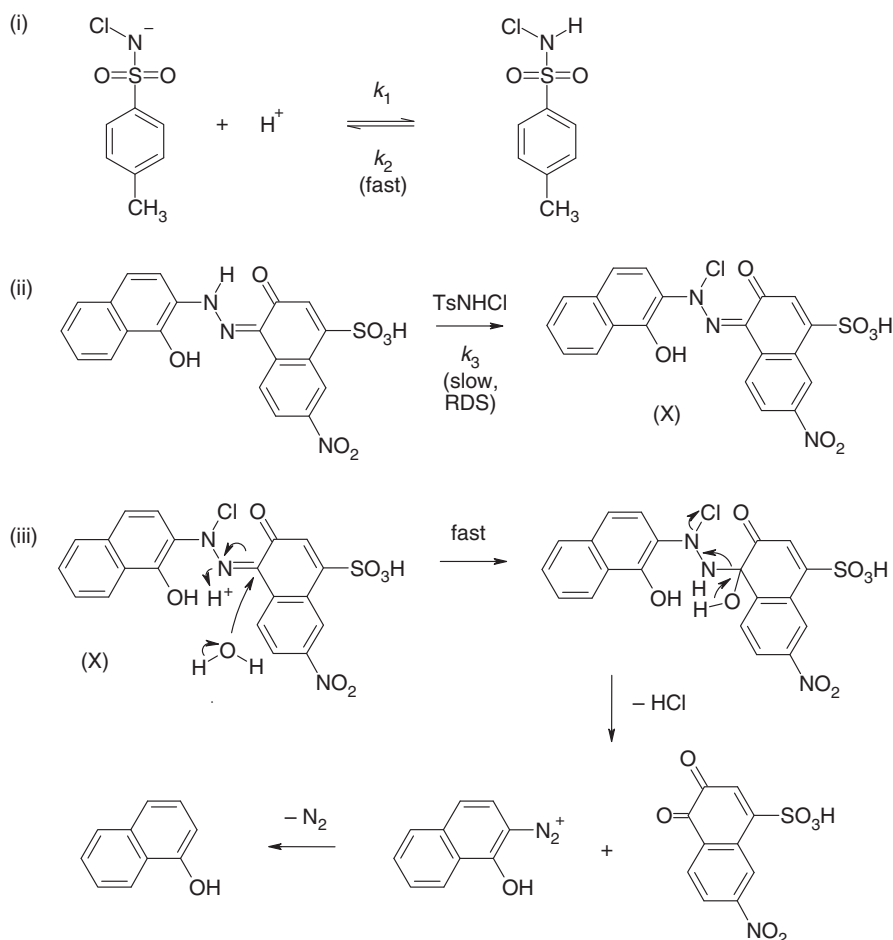
Scheme 3 A detailed reaction scheme for the oxidative decolorisation of EBT with CAT in acid medium

assume that OsO_4, which possesses tetrahedral geometry [29], is the active catalyst species that can effectively form a complex with the oxidant/substrate species.

The formation of the intermediate complex **X'** between oxidant and catalyst is demonstrated by spectroscopic measurements. Ultraviolet spectral measurements showed that CAT and Os(VIII) solutions have absorption bands at 230 and 320 nm, while a sharp band at 312 nm was noted for a CAT–Os(VIII) mixture (Figure 4). A hypsochromic shift of 8 nm from 320 to 312 nm for Os(VIII) suggests that complexation occurs between CAT and Os(VIII). Considering the above facts and experimental results, the following
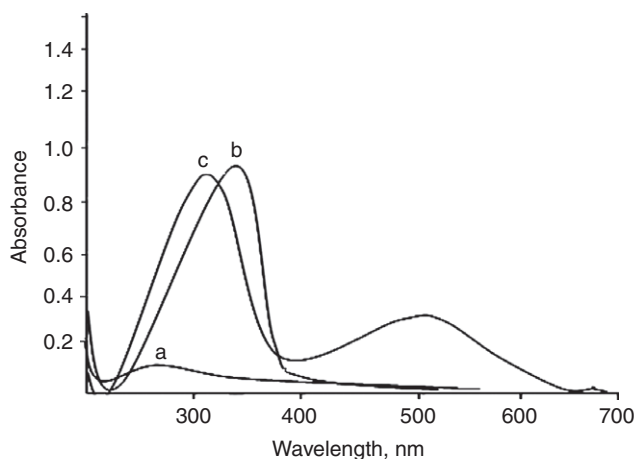

Figure 4 UV-vis spectra of (a) CAT, (b) Os(VIII), and (C) CAT + Os(VIII) mixture in alkaline medium

mechanism (Scheme 4) may be suggested for Os(VIII)-catalysed oxidative decolorisation of EBT with CAT in alkaline medium.

In Scheme 4, **X'** and **X''** represent the complex intermediate species. In the fast alkali accelerating step [step (i)], the conjugate acid TsNHCl loses a proton to give the anion TsNCl$^-$. In the next fast step [step (ii)], TsNCl$^-$ interacts with the OsO_4 catalyst to give the coordinate complex **X'**. In the next slow and rate-determining step [step (iii)], the anionic complex interacts with the substrate (EBT) to form another intermediate complex **X''**. Finally, complex **X''** undergoes decomposition through several steps in the presence of H_2O and OH^- ions and with the elimination of $TsNH_2$, OsO_4, Cl, and N_2, yielding the final products.

According to Scheme 4, the total effective concentration of CAT is
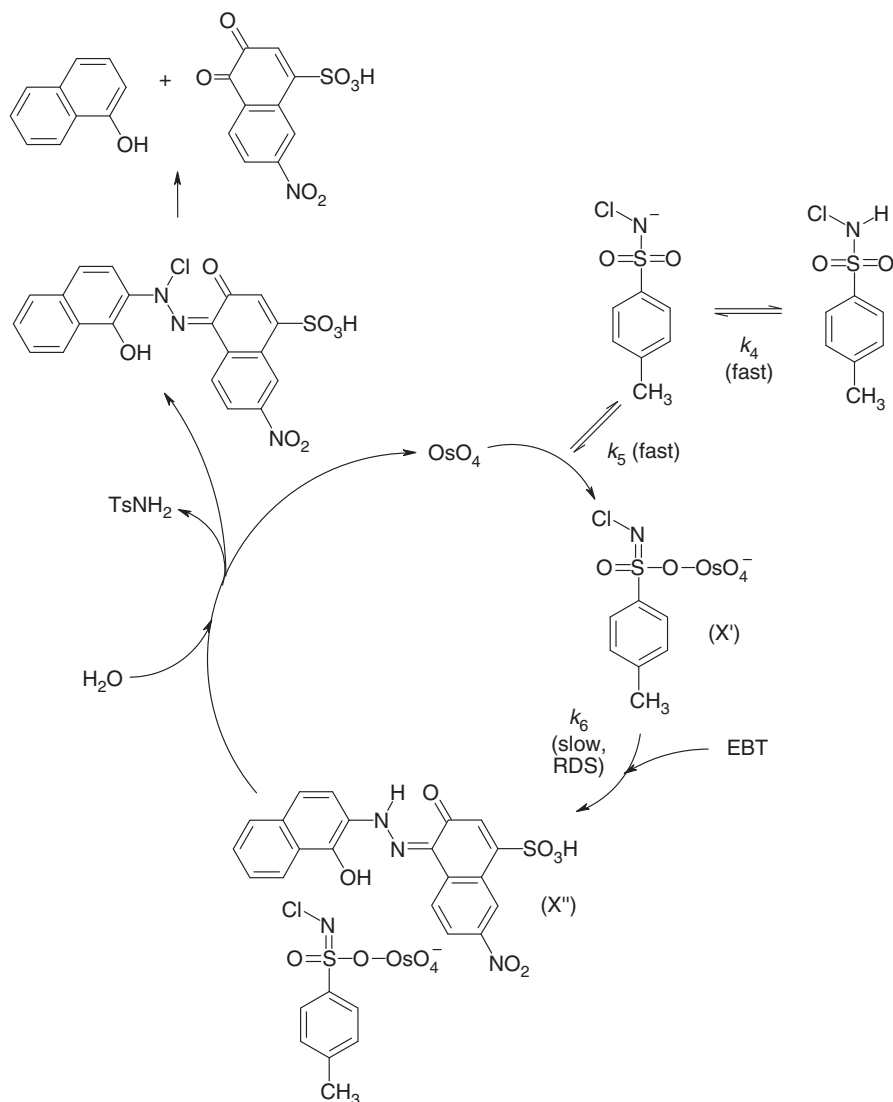
$$[CAT]_t = [TsNHCl] + [TsNCl^-] + \mathbf{X'} \tag{4}$$

From steps (i) and (ii) of Scheme 4, solving for [**X'**] yields:

$$[\mathbf{X'}] = \frac{k_4 k_5 CAT_t[OH^-][Os(VIII)]}{[H_2O] + k_4[OH^-] + k_4 k_5[OH^-][Os(VIII)]} \tag{5}$$

From the slow step of Scheme 4 it follows that:

$$\text{Rate} = [\mathbf{X'}][EBT] \tag{6}$$

By substituting [**X'**] from Eqn (5) into Eqn (6), the following rate law can be derived:

Scheme 4 A detailed reaction scheme for the oxidative decolorisation of EBT with CAT in alkaline medium catalysed by OsO$_4$

$$\text{Rate} = \frac{k_4 k_5 [\text{CAT}]_t [\text{EBT}][\text{OH}^-][\text{Os(VIII)}]}{[\text{H}_2\text{O}] + k_4 [\text{OH}^-] + k_4 k_5 [\text{OH}^-][\text{Os(VIII)}]} \quad (7)$$

Rate law (7) fits all experimental data well. The proposed mechanisms and derived rate laws are also substantiated by the experimental results discussed below.

A negative MeOH effect in both acid and alkaline media provides support for the proposed mechanisms. A change in the solvent composition by varying the MeOH content in MeOH–water affects the reaction rate. The effect of changing the solvent composition on the rate of the reaction has been described in detail in various well-known monographs [30–33]. For the limiting case of a zero angle of approach between two dipoles or an ion–dipole system, Amis [32] has shown that a plot of log k' *vs* 1/D gives a straight line, with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope results for a positive ion–dipole interaction. In the present investigations, such plots were linear with negative slopes (Figure 3), thus supporting the participation of two dipolar species in the rate-determining steps of Schemes 3 and 4.

The proposed reaction mechanisms are also evinced by the observed zero effect of ionic strength on the rate of the reaction. The primary salt effect on the reaction rates has been described by the Brönsted and Bjerrum theory [34]. According to this theory, for the reactions that involve uncharged reactant(s), the rate of the reaction is independent of the ionic strength of the solution. In the present investigations, in both cases, neutral molecules are involved in the rate-determining steps of Schemes 3 and 4. Hence, variation in the ionic strength of the medium does not alter the rate in either case, clearly confirming the above conclusion.

Moelwyn-Hughes [35] pointed out that the catalysed and uncatalysed reactions proceed in parallel, and the relationship is:

$$k_1 = k_0 + k_c [\text{catalyst}]^x \quad (8)$$

where k_1 is the pseudo-first-order rate constant obtained in the presence of Os(VIII) catalyst, k_0 is the pseudo-first-order rate constant for the uncatalysed reaction, k_c is the catalytic constant, and x is the order of the reaction with respect to Os(VIII), which is found to be 0.66 in the present study. Then, the value of k_c is calculated using the relationship:

$$k_c = \frac{k_1 - k_0}{[\text{Os(VIII)}]^{0.66}} \quad (9)$$

The values of k_c were evaluated at different temperatures (293, 298, 303, 308, and 313 K), and k_c was found to vary with temperature. Further, a plot of log k_c *vs* $1/T$ was linear ($R^2 = 0.9896$), and values of the activation parameters with respect to Os(VIII) catalyst were evaluated. All these results are given in Table 4.

Under an identical set of experimental conditions, the EBT–CAT reaction in alkaline medium was studied without Os(VIII) catalyst for comparison. Consequently, the reactions were studied at different temperatures, and from the linear Arrehenius plot ($R^2 = 0.9993$), values of the activation parameters for the uncatalysed reaction in alkaline medium were also computed (Table 4). As can be seen in Table 4, the Os(VIII)-catalysed reaction rate was found to be *ca.* sevenfold faster than the uncatalysed reaction rate. This was confirmed by the calculated values of the activation energy. Hence, it can be said that Os(VIII) is an efficient catalyst in the facile oxidative decolorisation of EBT with CAT in alkaline medium. It is also noted that the oxidative decolorisation reaction rate is *ca.* eightfold faster in acid medium than in alkaline medium.

The proposed reaction schemes and derived rate laws are supported by the moderate values of activation energy and other activation 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 values of the entropy of activation suggest the formation of a rigid activated complex with fewer degrees of freedom. The mechanism proposed and the rate laws derived are also consistent with the observed negligible effects of PTS and NaCl on the reaction rate in both media.

The chemical oxygen demand (COD) is a measure of oxidisable matter in dyestuff. Hence, it is an important parameter for industrial wastewater treatment. In the present study an attempt was made to determine the COD value by using the standard dichromate oxidation method [36]. Under the present experimental conditions, the COD of the EBT sample was found to be 460.8 mg l^{-1}. Importantly, in the present research, the optimum conditions for the oxidative decolorisation of EBT with CAT in acid and alkaline media have been established. The present method is simple, efficient, cost-effective, and environmentally benign, and also has the ability to be scaled up for industrial processes. Therefore, the present method is certainly an advantageous alternative technique in treating industrial and laboratory wastewater to resolve EBT dye.

Conclusions

The oxidative decolorisation kinetics of EBT with CAT has been studied in $HClO_4$ and NaOH media, with Os(VIII) as a catalyst in the latter medium. In acid medium, the experimental rate law was: $-d[CAT]/dt = k[EBT]^1[CAT]^1[HClO_4]^1$, which changes to: $-d[CAT]/dt = k[EBT]^1[CAT]^1[NaOH]^{0.82}[Os(VIII)]^{0.66}$ in the presence of alkali. The activation parameters for the overall reaction and also with respect to Os(VIII) catalyst (in alkaline medium) have been computed. It was observed that the decolorisation reaction is *ca.* eightfold faster in acid medium than in alkaline medium. In alkaline medium it was noted that the Os(VIII)-catalysed reaction is *ca.* sevenfold faster than the uncatalysed reaction, which justifies the use of Os(VIII) catalyst in the facile oxidative decolorisation of EBT with CAT in alkaline medium. Suitable mechanisms and appropriate rate laws have been worked out to account for the kinetics observed. The COD of EBT dye was also determined. This simple and economic redox system can be adopted for treating EBT dye present in industrial and laboratory wastewater to reduce the toxicity caused by this dye. Hence, this methodology is a valuable addition to the existing methods.

Acknowledgements

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