Research Article

Mechanistic investigation of osmium(VIII)catalyzed oxidation of brilliant green dye by chloramine-T in alkaline medium: a spectrophotometric kinetic study

Ajaya Kumar Singh[1] · **Shakila Bano**[1] · **Bhawana Jain**[1]

Received: 21 May 2019 / Accepted: 10 January 2020 / Published online: 21 January 2020
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Abstract

Wastewater generated by dyeing industries is of great threat to the globe and is major area of concern. In present paper, we deals with oxidation of brilliant green (BG) by catalytic route in alkaline medium at 298 K. Osmium(VIII) used as catalyst and the reaction showed first-order and zero-order behavior with respect to [BG] and [CAT] respectively. The reaction followed fractional-order kinetics with respect to [NaOH] and [Os(VIII)]. Negligible effect of [Cl^-], [PTS] and ionic strength of the medium on the rate of oxidation have also been noted. Decrease in the rate of reaction with decrease in the dielectric constant of the medium was also observed. Comparative studies between catalyzed and uncatalyzed reaction have also been reported. It is found that catalyzed reaction is four fold faster than uncatalyzed reaction. Activation parameter and catalytic constant (K_C) have also been calculated at different temperatures. GC–MS analysis identified the oxidation products of the BG i.e. *N*, *N*-diethylaminobenzophenone and p-*N*, *N*-diethylamino phenol while the stoichiometry of the reaction was found to be 1:1. On the basis of kinetic results, a plausible mechanism has been proposed and verified.

Keywords Oxidation · Kinetics · Brilliant green dye · Os(VIII) catalyst

1 Introduction

Harmful chemicals, dyes, oils etc. pollute the water. Among the pollutants of water, a major role is played by dyes. Most of the dyes released from the pharmacy and textile industries, as they are mutagenic and teratogenic can cause serious health hazards to humans and livestock [1]. Dyes released into aquatic environment decrease or stop capacity of water re-oxygenation by blocking sunlight thereby increasing BOD valueand it can also impart color to water [2, 12, 13]. Therefore these conditions generally disturb or prevent the growth of aquatic plants and animals [3, 4]. BG being carcinogenic in nature has been banned in many countries [5]. BG, besides being a compound of biological interest [6] has a major use in biological staining, modern textile and leather industries [7]. It is also used in antiseptic preparations active against gram-positive bacteria. It is irritating to skin, respiratory system and gastrointestinal tract [8, 9] and can cause serious damage to eyes. It can also produce serious health damage [10] on inhalation and it is also investigated as a mutagen in microorganism. BG causes some degree of carcinogenicity, hypersensitivity reactions, microbial and fish toxicity [11].

For the oxidation of variety of organic compounds, aromatic N-halosulphonamides, a group of mild oxidizing agents, have been extensively used [14–16]. These oxidants have strongly polarized N-linked halogens which are in the + 1 state. They undergo two electrons change which forms halide ions and corresponding sulphonamides. Sodium N-chloro-p-toluenesulphonamide (CAT or RNClNa) is a prominent member of this class of oxidant. In both acidic and alkaline media it behaves as an oxidizing

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✉ Ajaya Kumar Singh, ajayaksingh_au@yahoo.co.in | [1]Department of Chemistry, Govt.V.Y.T.PG. Autonomous College, Durg, CG 491001, India.

SN Applied Sciences (2020) 2:245 | https://doi.org/10.1007/s42452-020-2030-y

agent. It is versatile oxidizing agent and due to formation of its various oxidizing species depending upon pH of the medium, it has shown a variety of kinetics result [17–23]. Depending on the reaction conditions, it can behave as both electrophiles and nucleophiles [24]. Extensive literature survey depicts only tworeports on the kinetics of oxidation of triphenylmethane dyes by CAT [25, 26].

Transition metals due to theirmultiple oxidation state are known to catalyze many oxidation–reduction reactions [27]. In recent years either alone or binary mixtures, the use of transition metal ions, as catalysts in various redox processes have attracted considerable interest [28]. For different metal ion catalysts like Cr(III) [29], Ru(III) [30–40], Ir(III) [41–55], Pd(II) [52, 56–59] and Os(VIII) [59–63], Au(II) [64] different oxidizing agents have been used in the oxidation of organic compounds. The mechanism of the reaction relies upon the nature of the substrate, oxidant and moreover upon the ways in which transition metal complex ions play their role in order to promote the reactant molecules to the activated state before finally changing into products under experimental conditions. The main purpose of the present study are: (i) to confirm real reactive species of oxidant and catalyst (ii) to elaborate the plausible reaction mechanism (iii)to form compatibility of rate law with kinetic results and to calculate activation parameters (iv) to identify the oxidation products (v)to calculate thermodynamic parameters (vi) to find the catalytic efficiency of Os(VIII) and (vii) to compare and contrast the catalyzed reactivity with that of uncatalyzed one. Overall, the removal of BG dye from aqueous system is the main concern for both human health and ecosystem, thus it encouraging us the search for low cost and better efficient method which helps in removing color contaminant from waste water. So we have developed a catalytic transformation route for degradation of BG dye and its kinetic study to ensure its feasibility.

2 Experimental

2.1 Materials

During the experiment, all chemicals used were of reagent grade and water was triple distilled. BG (Sd. Fine Chem.) was used without any further purification and was 99.8% pure. Purification of CAT (E-Merck) was done by the method of Morris et al. [20]. Firstly, an aqueous solution of CAT was prepared then it was standardized iodometrically and finally stored in amber colored stoppered bottles until further use. By dissolving OsO_4 (Johnson Mathey) in 0.50 mol dm^{-3} NaOH a standard stock solution of Os(VIII) was prepared. The concentration was confirmed [69] by determining the unreacted $[Fe(CN)_2]^{4-}$ solution with standard Ce(IV) solution in an acidic medium. Without further purification KNO_3 and NaOH were used.

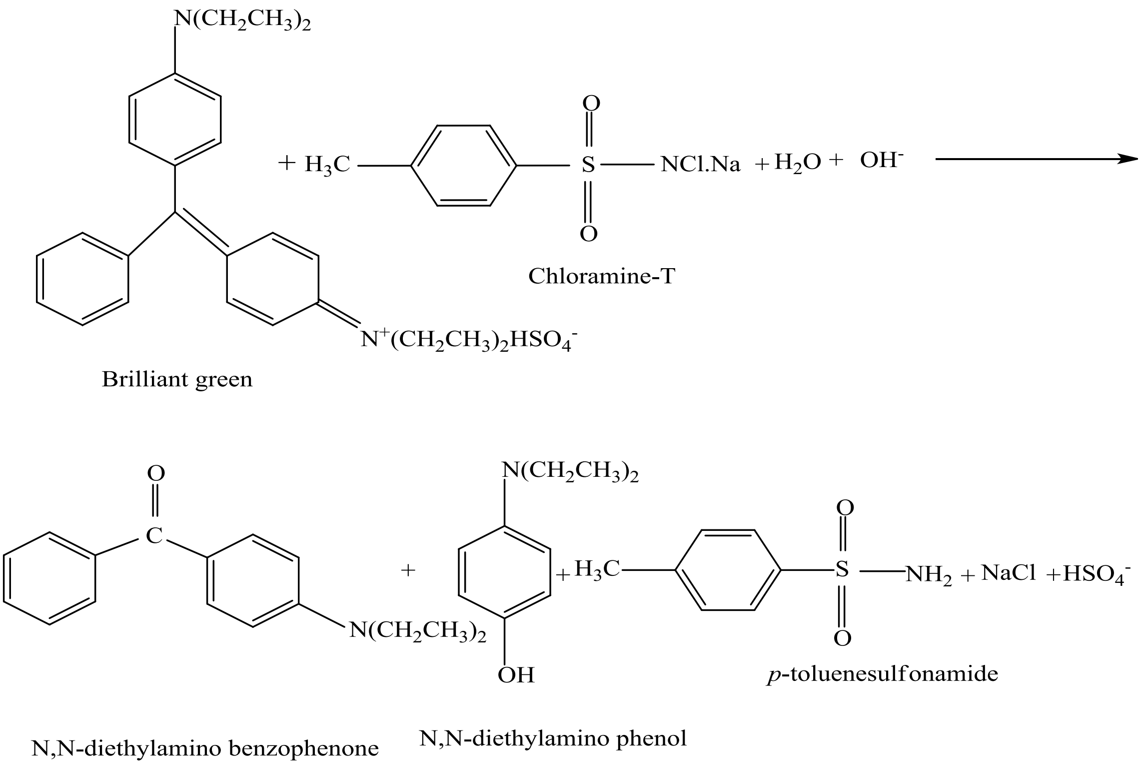
2.2 Kinetic measurements

By using an UV–visible spectrophotometer (Digital Spectrophotometer 166, Systronic, India) kinetic measurements were carried out. The kinetic experiments in the present study were carried out between 293 and 318 K. To conduct this experiment, a Ragga Ultra Cold chamber with digital temperature control (India) was operated, thereby keeping the temperature as constant with an accuracy ± 0.1 °C. In the present study, kinetic runs were performed under pseudo-first-order conditions with a known excess of the [CAT] over [BG] at 298 K. Glass-stoppered Pyrex boiling tubes whose outer surfaces coated black were used to perform the reactions to eliminate any photochemical effects. To keep the total volume constant for all runs, the oxidant as well as requisite amounts of BG, NaOH, Os(VIII) and water were taken in separate tubes and were thermostatted for 30 min at 298 K. To initiate the reaction, a measured amount of oxidant was rapidly added to the stirred reaction mixture. Instantly, 4 ml aliquot of the solution was pipetted into a cuvette positioned in the spectrophotometer. For nearly three half-lives, absorbance (Abs) measurements were made at $\lambda_{max} = 622$ nm for BG. To evaluate the pseudo-first-order rate constants (k_1) which were found reproducible within ± 5%, plots of log Abs versus time were made. To see the effect of temperature and to calculate the thermodynamic activation parameters, the reaction was also performed at various temperatures (298 K, 303 K, 308 K, 313 K and 318 K). In order to understand the effect of dissolved O_2 on the rate of the reaction kinetic runs were also carried out in N_2 atmosphere. No prominent difference in the results was observed under a N_2 atmosphere and in the presence of air.

2.3 Stiochiometry and product analysis

Different sets of reaction mixtures containing varying ratios of CAT to BG in presence of constant amount of NaOH and Os(VIII) were kept for 72 h in a closed vessel at 298 K. Estimation of unconsumed CAT in each set revealed that for the oxidation of 1 mol of BG, 1 mol of CAT was consumed. Accordingly, the following stiochiometry equation may be expressed as (Scheme 1).

The reaction mixture was neutralized with dilute HCl and the products were extracted with ethyl acetate after completion of the reaction. The organic products were identified and separated by using TLC technique and column-chromatography respectively. Methanol was used to recrystallize the purified compounds. p -toluenesulfonamide (PTS) was identified [65] as the reduction product



Scheme 1 Stiochiometric equation for Os(VIII) catalyzed oxidation of BG by CAT in alkaline medium

of CAT by paper chromatography using $PhCH_2OH$ saturated with H_2O as the solvent with 0.5% vanillin in 1% HCl solution in C_2H_5OH, as the spray reagent. Furthermore the result was confirmed by its melting point 139 ℃, which was within close proximity to the reported temperature of 137–140 ℃ in previous works [66]. *N*, *N*-diethylaminobenzophenone and p-*N*, *N*-diethylamino phenol were identified as oxidation products of BG. By gas chromatography coupled with mass spectral techniques (GC–MS) these compounds were confirmed. The mass spectra showed *N*, *N*-diethylaminobenzophenone and p-*N*, *N*-diethylamino phenol as oxidation products having molecular ion peak 253 amu and 165 amu respectively. It was also observed that under the present reaction conditions, there was no further oxidation of these products.

3 Results and discussion

The detailed kinetic investigations were performed under pseudo-first-order conditions of [CAT] ≫ [BG] (Table 1).

3.1 Dependence of rate on the concentration of BG

Under pseudo-first-order condition of [CAT] > [BG], the effect of BG was studied in the range (2.5×10^{-5} to 8×10^{-5}). The rate constants of the reaction in each kinetic run was determined by plotting of the log Abs versus time (Fig. 1, Table 2), which formed straight line and shows that the reaction under the chosen conditions follows pseudo-first-order kinetics.

Table 1 Consumption of CAT in the Os(VIII) catalyzed oxidation of BG in alkaline medium at 298 K

$[BG]\times10^5$ (mol dm^{-3})	$[CAT]\times10^4$ (mol dm^{-3})-Initial	$[CAT]\ 10^4$ (mol dm^{-3})-Final	$[CAT]\ 10^4$ (mol dm^{-3})-Consumed	CAT:BG
1.00	10.00	8.88	1.12	1.12
3.00	30.00	26.99	3.01	1.00
5.00	50.00	44.81	5.19	1.03

Experimental conditions: $[NaOH]=4\times10^{-3}$ mol dm^{-3}, $[Os(VIII)]=3.5\times10^{-4}$ mol dm^{-3}

3.2 Dependence of rate on the concentration of NaOH

The effect of NaOH was studied in the range of (1×10^{-4} to 10×10^{-4}) at constant concentrations of BG, CAT andOs(VIII). The rate constants increased with an increase in [NaOH] (Table 3) and plots of log k_1 versus log $[OH^-]$

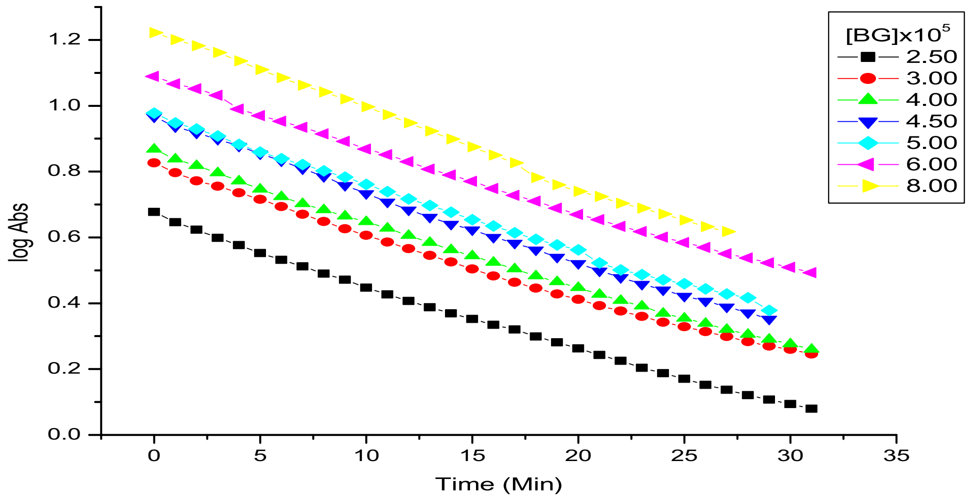


Fig. 1 First order plots of the oxidation of BG by CATin alkaline medium at 298 K. [BG] = 2.5×10^{-5}, 3×10^{-5}, 4×10^{-5}, 4.5×10^{-5}, 5×10^{-5}, 6×10^{-5}, 8×10^{-5} mol dm^{-3}, [CAT] = 3×10^{-4} mol dm^{-3}, [NaOH] = 4×10^{-3} mol dm^{-3}, [Os(VIII)] = 3.5×10^{-4} mol dm^{-3}

Table 2 Effect of BG, CAT, PTS and KNO_3 concentrations on the rate of reaction at 298 K

[BG] × 10^5	[CAT] × 10^4	[PTS] × 10^5	[KNO_3] × 10^3	$k_1 \times 10^4$
(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(s^{-1})
2.50				7.29
3.00				7.67
4.00				7.29
4.50				8.06
5.00				7.29
6.00				7.67
8.00				8.44
	2.00			8.44
	3.00			7.67
	4.00			6.90
	6.00			7.29
	8.00			7.67
	10.00			7.67
	12.00			7.29
		3.00		7.67
		6.00		8.06
		8.00		7.29
		12.00		7.67
		15.00		7.29
			1.00	7.67
			2.00	8.06
			3.00	6.9
			4.00	7.29
			5.00	7.29
			7.00	7.67
			9.00	7.29

Experimental conditions: [NaOH] = 4×10^4 mol dm^{-3}, [Os(VIII)] = 3.5×10^{-4} mol dm^{-3}

Table 3 Effect of NaOH, Os(VIII) concentrations and dielectric constant on the rate of reaction at 298 K

[NaOH] × 10^4	[Os(VIII)] × 10^4	CH_3CN %/(D)	$k_1 \times 10^4$	$k_{cal} \times 10^4$	$k_{exp} \times 10^4$
(mol dm^{-3})	(mol dm^{-3})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})
1.00			2.55	2.48	2.42
2.00			4.31	4.59	4.36
3.00			5.9	6.42	6.16
4.00			7.67	8.01	7.86
5.00			9.29	9.41	9.50
6.00			11.01	10.65	11.10
8.00			14.29	12.76	14.17
10.00			18.09	14.47	17.12
	1.16		3.28	3.13	3.31
	2.33		5.94	5.77	5.72
	3.5		7.67	8.01	7.86
	4.66		9.89	9.92	9.84
	5.82		11.53	11.5	11.72
	6.99		13.89	13.04	13.53
	9.32		16.05	15.48	16.95
	11.65		21.01	17.04	20.19
		0.00(73.6)	7.67		
		5.00.(71.8)	6.54		
		10.00(70.0)	5.67		
		20.00(68.2)	3.53		
		30.00(66.5)	2.57		

Experimental conditions: [BG] = 3×10^{-5} mol dm^{-3}, [CAT] = 3×10^{-4} mol dm^{-3}

were linear with fractional slope (0.848), showing a fractional-order dependence of the rate on [NaOH] (Fig. 2).

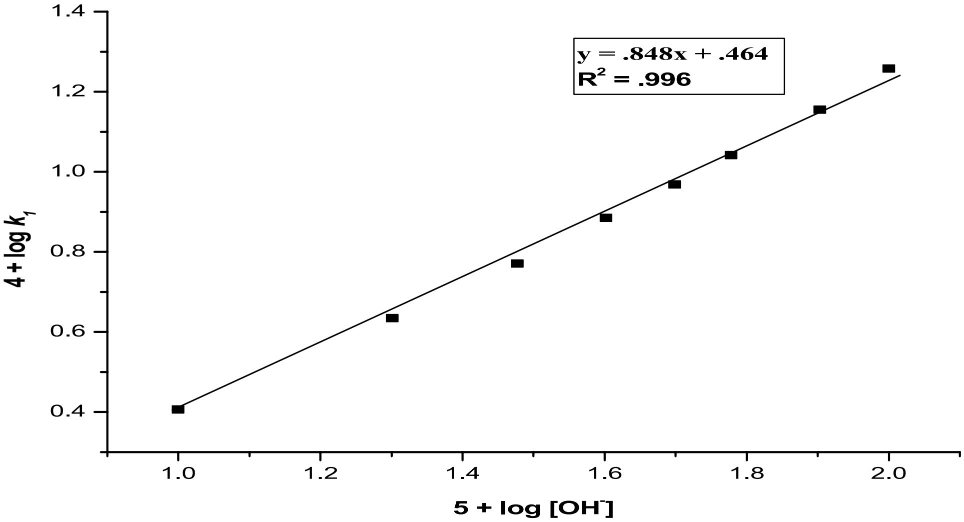


Fig. 2 Effect of [NaOH] on the rate constant (k_1) at 298 K. [NaOH] = 1×10^{-4}, 2×10^{-4}, 3×10^{-4}, 4×10^{-4}, 5×10^{-4}, 6×10^{-4}, 8×10^{-4}, 10×10^{-4} mol dm^{-3}, [BG] = 3×10^{-5} mol dm^{-3}, [CAT] = 3×10^{-4} mol dm^{-3}, [Os(VIII)] = 3.5×10^{-4} mol dm^{-3}

3.3 Dependence of rate on the concentration of CAT

The effect of CAT was studied in the range of (2×10^{-4} to 12×10^{-4}) at constant concentrations of BG, NaOH and Os(VIII). The value of k_1 remains constant (Table 2), showing a zero-order with respect to [CAT].

3.4 Dependence of rate on the concentration of Os(VIII)

To study the effect of Os(VIII) concentration on the rate of reaction, the reaction concentration varied in the range of (1.16×10^{-4} to 11.65×10^{-4}) at constant [BG], [CAT] and [NaOH] at 298 K. The result elucidates that rate of reaction increase with increasing [Os(VIII)] (Table 3). Plots of log k_1 versus log [Os(VIII)] were linear with fractional slope (0.783), confirming fractional-order dependence on [Os(VIII)](Fig. 3).

3.5 Dependence of rate on PTS and Cl$^-$ concentrations

To study the effect of PTS (reduction product of CAT) concentration on the rate of reaction, the reaction concentration varied in the range of (3×10^{-5} to 15×10^{-5}) at constant [BG], [CAT], [NaOH] and [Os(VIII)] at 298 K. The value of k_1 remains constant showing a zero-order with respect to [PTS] (Table 2). Variation of [Cl$^-$] did not bring about any significant change in k_1 values under the constant experimental conditions.

3.6 Dependence of rate on ionic strength

Keeping the other experimental conditions constant, the effect of ionic strength (μ) of the medium was studied in the range of (6×10^{-4} to 24×10^{-4}), using KNO_3 solution. It is observed that the μ had no effects on the rate of oxidation

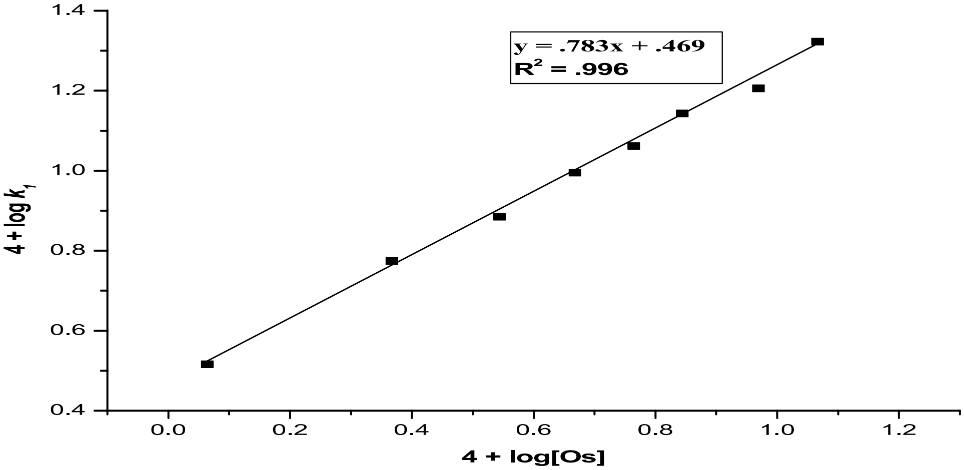


Fig. 3 Effect of [Os(VIII)] on the rate constant (k_1) at 298 K.[Os(VIII)] = 1.16×10^{-4}, 2.33×10^{-4}, 3.5×10^{-4}, 4.66×10^{-4}, 5.82×10^{-4}, 6.99×10^{-4}, 9.32×10^{-4}, 11.65×10^{-4} mol dm^{-3}, [BG] = 3×10^{-5}mol dm^{-3}, [CAT] = 3×10^{-4} mol dm^{-3}, [Os(VIII)] = 3.5×10^{-4} mol dm^{-3}

(Table 2), which indicates the involvement of a non-ionic species in the rate determining step.

3.7 Dependence of rate on the variation of temperature

The reaction was carried out at five different temperatures (298–313 K) while the other experimental conditions were kept constant. From the linear Arrhenius plots of log k_1 versus 1/T (Fig. 4), activation energy (E_a) and other activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and log A) for the overall reaction have been computed. The rate constants corresponding to different temperatures and the calculated activation parameters are given in (Table 4) for uncatalyzed and Os(VIII) catalyzed reaction.

3.8 Polymerization study

The reaction mixture with acrylamide was placed in an inert atmosphere for 24 h to test the presence of free radicals in the reaction. It is found that there is no precipitate in the reaction mixture, when the reaction mixture is diluted with methanol. This clearly indicates that the free radicals are not formed in the redox reaction under observation.

3.9 Reactive species of CAT

In both acidic and alkaline media, CAT (ArNClNa) acts as an oxidizing agent. In aqueous solutions CAT behaves as a strong electrolyte and it shows different types of reactive species (Eqs. 1–6) in solutions depending on the pH of the medium [20, 67, 68].

$$\mathrm{ArNClNa} \rightleftharpoons \mathrm{ArNCl^-} + \mathrm{Na^+} \tag{1}$$

Table 4 Effect of temperature and values of activation parameters for the oxidation of BG by CAT in alkaline medium in the absence and presence of Os(VIII) catalyst at 298 K

Temperature (K)	$k_1 \times 10^4$ (s^{-1})	k_{cat}, $\times 10^4$ (s^{-1})
	(Uncatalyzed)	(Catalyzed)
293	0.91 ± 0.22	4.90 ± 0.20
298	1.64 ± 0.15	7.67 ± 0.21
303	2.72 ± 0.19	12.28 ± 0.14
308	3.8 ± 0.25	16.50 ± 0.16
313	6.14 ± 0.13	22.60 ± 0.25
318	8.52 ± 0.11	29.60 ± 0.21
E_a (KJ mol^{-1})	68.64 ± 0.12	55.6 ± 0.14
$\Delta H^{\neq}$ (KJ mol^{-1})	66.16 ± 0.09	53.12 ± 0.13
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	−87.02 ± 0.16	−118.13 ± 0.11
$\Delta G^{\neq}$ (KJ mol^{-1})	92.09 ± 0.12	88.32 ± 0.08
log A	8.24 ± 0.18	6.62 ± 0.21

Experimental conditions: $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-4}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}

$$\mathrm{ArNCl^-} + \mathrm{H^+} \rightleftharpoons \mathrm{ArNHCl^-} \tag{2}$$

$$2\mathrm{ArNHCl} \rightleftharpoons \mathrm{ArNCl_2} + \mathrm{ArNH_2} \tag{3}$$

$$\mathrm{ArNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{ArNH_2} + \mathrm{HOCl} \tag{4}$$

$$\mathrm{ArNCl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{ArNHCl} + \mathrm{HOCl} \tag{5}$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^-} + \mathrm{ClO^+} \tag{6}$$

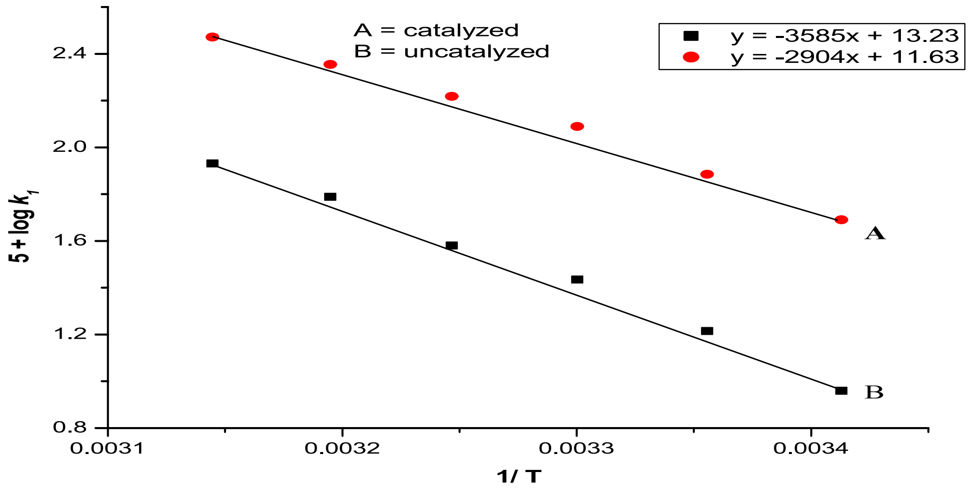


Fig. 4 Effect of temperature on the observed rate constant for the uncatalyzed and Os(VIII) catalyzed oxidation of BG by CAT in alkaline medium at 298 K.$[BG] = 3 \times 10^{-5}$mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-3}$ mol dm^{-3}, $[Os(VIII) = 3.5 \times 10^{-4}$ mol dm^{-3}

3.10 Reactive species of Os(VIII) catalyst

Osmium(VIII) has been reviewed as a catalyst in some redox reactions. At different OH^- concentrations Os(VIII) is known to form different complexes like $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$[69]. $[OsO_5(OH)]^{3-}$ is significant at higher concentration of OH^-. Since the rate of oxidation increased with increase in $[OH^-]$, hence at lower concentrations of OH^-, as employed in the present study, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction. Mechanistically most studies [70] propose that electron is being transferred between the substrate and catalyst in the rate determining steps leading to the products, followed by the rapid oxidation of Os (VI/VII) to Os(VIII) by main oxidants, resulting in zeroth order kinetics with respect to the main oxidant. In view of unit order in each osmium, substrate and oxidant, Os(VIII) is regenerated by Os(VI) intervention [71]. In some other reports [72], it is observed that with the regeneration of the catalyst, Os(VIII) forms complex with substrate, in view of apparent less than unit order in substrate concentrations which is oxidized by the oxidant. Hence the study of the behavior of Os(VIII) becomes prominent. First order dependency in [BG] and fractional order in $[OH^-]$, [Os(VIII)] and zero order in [CAT] was observed in the present investigation.

3.11 Spectral evidence for the Os(VIII) catalyzed oxidation of BG by CAT in alkaline medium

The color imparted by BG is due to its chemicalstructure which consists of a central carbon bonded to three aromatic rings, one of which is in the quinoid form (the chromophore) and the oxochrome is $-NR_2$. The changes in the absorption spectra of BG solution (3×10^{-5} mol dm^{-3}) during the oxidation process byCAT (3×10^{-4} mol dm^{-3}) in alkaline media (4×10^{-3} mol dm^{-3}) at 298 K at different times are shown in (Fig. 5). A rapid degradation of the BG is indicated by the decrease of the absorption peak of the dye at $\lambda_{max}=622$ nm. Decrease in Abs intensity of the bond at λ_{max} during oxidation also express loss of conjugation. The decrease also indicates that the most active site for oxidative attack is central carbon attached to the aromatic ring (quinoid form) [26].

3.12 Reaction scheme

On the basis of observed kinetic results and taking $[OsO_4(OH)_2]^{2-}$ as the most active species of OsO_4, the reaction steps in Scheme 1 are being proposed for the oxidation of BG by CAT in an alkaline medium catalyzed by Os(VIII).

$$S + OH^- \overset{K_1}{\rightleftharpoons} C_1 \tag{i}$$

$$C_1 + C_2 \overset{K_2}{\rightleftharpoons} C_3 \tag{ii}$$

$$C_3 \longrightarrow kC_4 \tag{iii}$$

According to the reaction Scheme 1 and considering the fact that 1 mol of BG is oxidized by 1 mol of CAT, the rate can be expressed as:

$$\text{rate} = k\left[C_3\right] \tag{7}$$

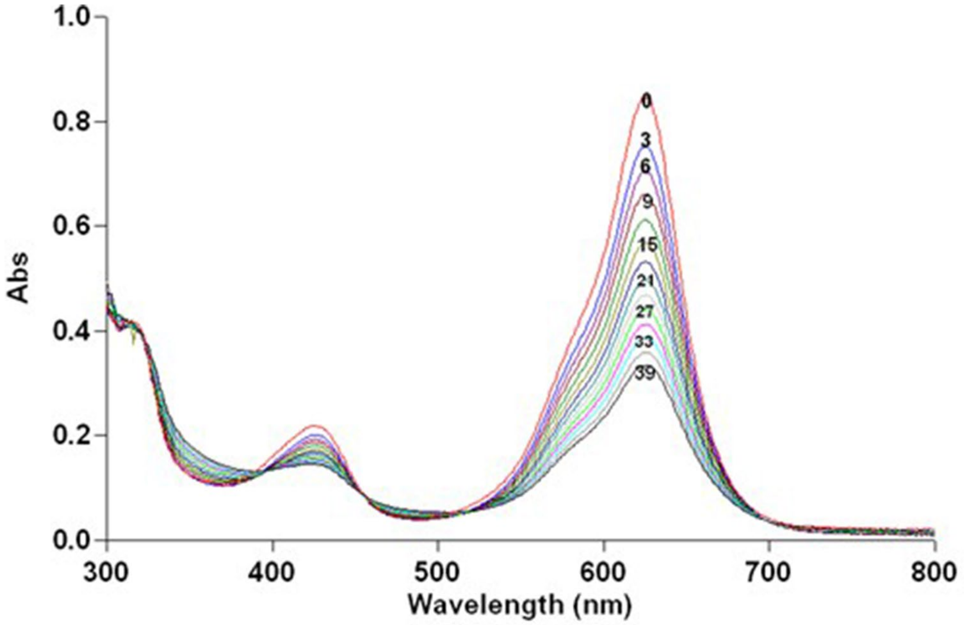


Fig. 5 Spectral changes during Os(VIII) catalyzed oxidative degradation of BG by CAT in alkaline medium at 298 K. $[BG]=3\times10^{-5}$ mol dm^{-3}, $[CAT]=3\times10^{-4}$ mol dm^{-3}, $[NaOH]=4\times10^{-3}$ mol dm^{-3}, $[Os(VIII)]=3.5\times10^{-4}$ mol dm^{-3}

On the basis of Scheme 1, equilibrium steps (i–ii), Eqs. 8 and 9 can be obtained in the following forms, and taking S as BG and C_2 as $[OsO_4(OH)_2]^{2-}$ respectively

$$\left[C_1\right] = K_1[S][OH^-] \tag{8}$$

$$\left[C_3\right] = K_2\left[C_1\right]\left[C_2\right] \tag{9}$$

Substitute the expression for $[C_1]$ (Eq. 8) into Eq. 9 to obtain the expression for Eq. 10

$$\left[C_3\right] = K_1K_2[S][OH^-]\left[C_2\right] \tag{10}$$

By substituting for $[C_3]$ from Eq. 10 into Eq. 7, we get

$$\text{rate} = kK_1K_2[S][OH^-]\left[C_2\right] \tag{11}$$

At any time in the reaction, the total concentration of S that is $[S]_T$, can be expressed as

$$[S]_T = [S] + \left[C_1\right] + \left[C_3\right] \tag{12}$$

By substituting for $[C_1]$ and $[C_3]$ from Eqs. 8 and 10, respectively into Eq. 12 and solving for [S], we get

$$[S]_T = [S] + K_1[S][OH^-] + K_1K_2[S][OH^-]\left[C_2\right] \tag{13}$$

$$[S]_T = [S] + \left(1 + K_1[OH^-] + K_1K_2[OH^-]\left[C_2\right]\right) \tag{14}$$

$$[S] = \frac{[S]_T}{1 + K_1[OH^-] + K_1K_2[OH^-]\left[C_2\right]} \tag{15}$$

Substitute the expression for [S] (Eq. 15) into Eq. 11 to obtain the expression for Eq. 16

$$\text{rate} = \frac{kK_1K_2[S]_T[OH^-][Os]}{1 + K_1[OH^-] + K_1K_2[OH^-][Os]} \tag{16}$$

Equation 16 is the rate law based on the observed kinetics orders with respect to each reactant involved in the reaction.

The rearrangement of Eq. 16 gives Eq. 17

$$\frac{\text{rate}}{[S]_T} = \frac{kK_1K_2[OH^-][Os]}{1 + K_1[OH^-] + K_1K_2[OH^-][Os]} \tag{17}$$

$$\frac{1}{k_1} = \frac{1}{kK_1K_2[OH^-][Os]} + \frac{1}{kK_2[Os]} + \frac{1}{k} \tag{18}$$

Equation 18 indicates that if a plot is made between $1/k_1$ vs 1/[Os] (Fig. 6) and $1/k_1$ vs $1/[OH^-]$ (Fig. 7), a straight line with positive intercept on y-axis will be obtained and this proves the validity of the rate law (Eq. 16) and the proposed reaction scheme 1, on the basis of which the rate law Eq. 16 has been derived. For the oxidation of BG the values obtained for k, K_1 and K_2 have been calculated and found as 3.52×10^{-3}, 96.27 and 22.7×10^3 respectively.

3.13 Effect of dielectric constant and calculation of the size of the activated complex

Given equation explains the dependence of rate constant on the dielectric constant of medium:

$$\log k_1 = \log k_0 - \frac{Z_A Z_B e^2 N}{2.303\left(4\pi\varepsilon_0\right)d_{AB}RT} \times \frac{1}{D} \tag{19}$$

where the rate constant in a medium of infinite dielectric constant is given by k_o, Z_A and Z_B are the charges of reacting ions, d_{AB} refers to the size of activated complex, T is absolute temperature and D is the dielectric constant of the medium. This equation shows that a straight line having slope equal to $-Z_AZ_Be^2N/2.303\,(4\pi\varepsilon_0)d_{AB}RT$ will be obtained if plot is made between $\log k_1$ versus 1/D (Fig. 8). A plot of $\log k_1$ versus 1/D gives a straight line, for the

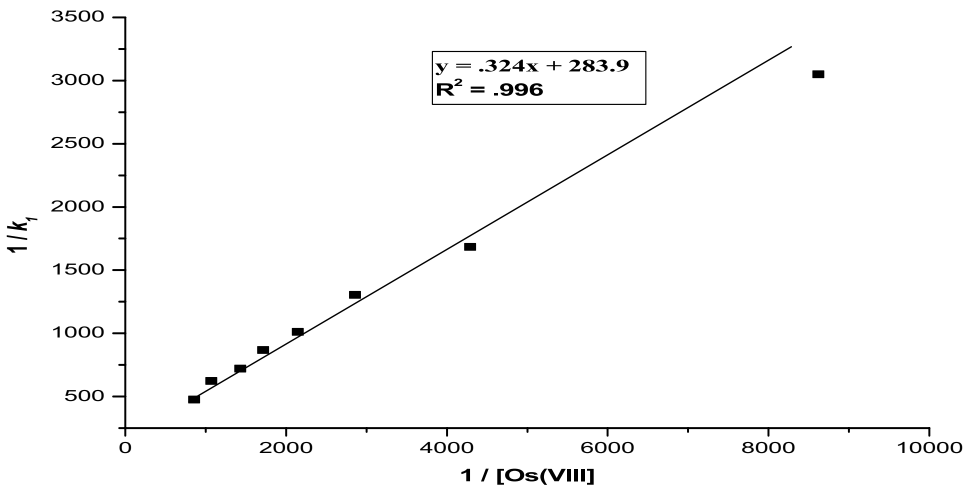


Fig. 6 Verification of rate law for $1/k_1$ and 1/[Os(VIII)] oxidation of BG by CAT in alkaline medium in the presence of Os(VIII) at 298 K. $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-3}$ mol dm^{-3}

Fig. 7 Verification of rate law for $1/k_1$ and $1/[OH^-]$ oxidation of BG by CAT in alkaline medium in the presence of Os(VIII) at 298 K. $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}

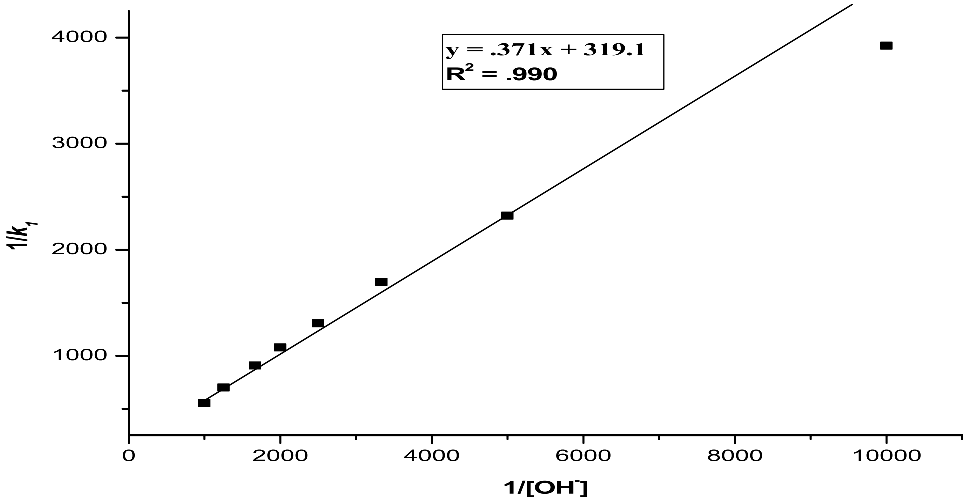
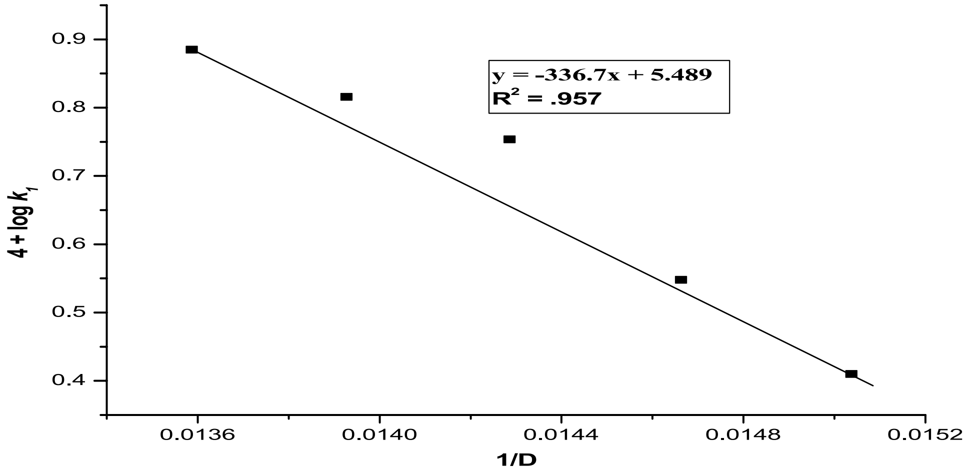


Fig. 8 Effect of dielectric constant on the observed rate constants in the Os(VIII) oxidation of BG by CAT in alkaline medium at 298 K. $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-3}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}



limiting case of zero angle approach between two dipoles or an ion dipole system, with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope for a positive ion–dipole interaction. The former concept agrees with the last observations. With the help of slope of straight line the value of d_{AB} has been evaluated and is found to be 0.73 A°. The proposed mechanism is also supported by the negative values of dielectric constant, moderate values of energy of activation and other thermodynamic parameters. Highly solvated transition state is indicated by the fairly high positive values of free energy of activation and enthalpy of activation. Formation of the compact activated complex with fewer degrees of freedom is suggested by large negative value of entropy of activation.

3.14 Comparision of Os(VIII) catalyzed and uncatalyzed reactions

In order to evaluate the catalytic efficiency of Os(VIII) it was thought worthwhile to compare the reactivity of BG with CAT in the absence of Os(VIII) catalyst under identical experimental conditions. Consequently, the reactions were studied at different temperatures (293–313 K) and values of activation parameters for the uncatalyzed reactions were computedfrom the Arrhenius plots of log k_1 versus 1/T ((Table 4) (Fig. 4). As compared to the uncatalyzed reactions, Os(VIII) catalyzed reactions were found to be about four times faster. This was also confirmed by the calculated activation parameters (Table 4). Thus the observed rates of oxidation of BG by CAT in the presence of Os(VIII) catalyst justify the need of a catalyst for a facile oxidation. Further, the results also suggests that Os(VIII) has been an efficient catalyst in effecting the facile oxidation of BG dye by CAT in alkaline medium. The reaction path is altered by the catalyst Os(VIII)by stabilizing the transition state, which inturn

Fig. 9 Graph between log K_C and 1/T. $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-3}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}

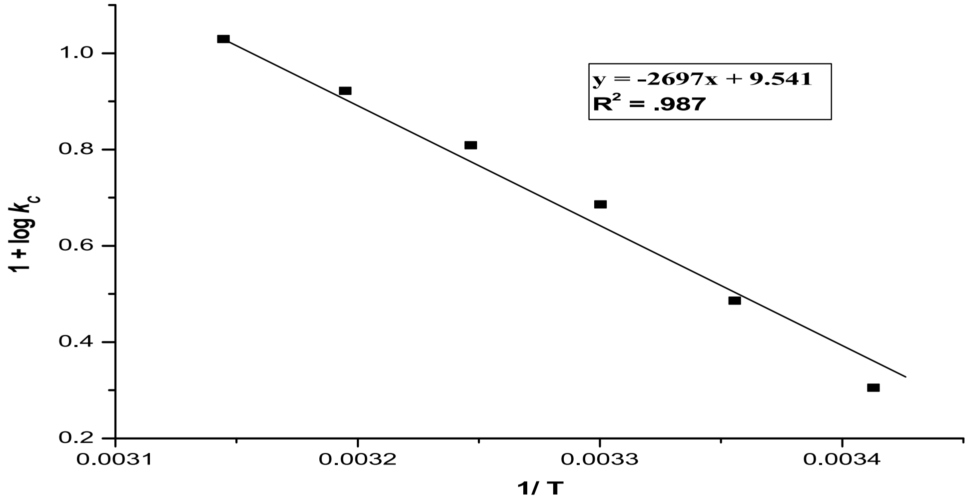


Table 5 Values of catalytic constant (K_C) at different temperatures and activationparameters calculated using K_C value

Temp.	K_C	E_a (KJ mol^{-1})	$\Delta H^{\neq}$ (KJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta G^{\neq}$ (KJ mol^{-1})	log A
293	0.202					
298	0.306	51.63 ± .12	49.16 ± .16	− 81.56 ± .11	73.46 ± .11	8.53
303	0.485					
308	0.644					
313	0.835					
318	1.07					

Experimental conditions: $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-4}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}

provides an alternative pathway having lower activation energy for the reaction.

3.15 Catalytic activity

As pointed out by Moelwyn-Hughes [73] in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

$$k_1 = k_0 + K_C[\text{catalyst}]^x \tag{20}$$

Here the observed pseudo-first-order rate constant obtained in the presence of Os(VIII) is represented by k_1, k_0 is that for the uncatalyzed reaction, K_C is the catalytic constant and × is the order of the reaction with respect to Os(VIII). × value for the standard run was found to be 0.783 in the present investigation. Then $K_C$value is calculated using the equation.

$$K_C = \frac{k_1 - k_0}{[\text{Os(VIII)}]^x} \tag{21}$$

The value of K_C was found to be varying with temperature when evaluated for BG at different temperatures (293–313 K). The values of energy of activation and other activation parameters for the catalyst were computedby plotting log K_C versus 1/T, which were found to be linear (Fig. 9). The summarized results are shown in Table 5.

Table 6 Correlation coefficient between variables

Variables	Correlation coefficient (r)
$[OH^-]$ and k_1	0.977
[Os(VIII)] and k_1	0.995
Temp. and k_1 (Uncatalyzed)	1.086
Temp. and K_C	0.993

Experimental conditions: $[BG] = 3 \times 10^{-5}$ mol dm^{-3}, $[CAT] = 3 \times 10^{-4}$ mol dm^{-3}, $[NaOH] = 4 \times 10^{-3}$ mol dm^{-3}, $[Os(VIII)] = 3.5 \times 10^{-4}$ mol dm^{-3}

3.16 Correlation coefficient

A correlation coefficient can be defined as a quantitative measure of some type of correlation and dependence, meaning statistical relationships between two or more random variables or observed data values. The correlation coefficient represented by r which means how closely data in a scatter plot fall along a straight line. If the value of r is near to one, it indicates that given data is expressed by a linear equation and data with values of r near to zero, show non linear relationship.

In our present study, the correlation coefficients between variables are given in Table 6. Allcalculated values are closely related to one indicating a positive linear relationship between variables.

3.17 Multiple regression analysis

In order to arrive at a conclusion, while discovering the relationship between dependent, that is, pseudo-first-order variable rate constant k_1 and two independent variable [OH$^-$] and [Os(VIII)], whether or not the proposed mechanism is well in accordance with our experimental kinetic data, a multivariate regression analysis using the computer package STAT GRAPHICS have proved to be very helpful. A relationship between the observed pseudo-first-order rate constant k_1 and the concentration of all the reactants of the reaction, except BG and CAT was determined with the aid of a multivariate regression analysis.

$$k_1 = k\,[\mathrm{OH}^-]^{.84}[\mathrm{Os(VIII)}]^{.78} \tag{22}$$

where k is 3.08×10^{-2}. The R-squared statistic indicated that the model as fitted explains 99.70% of the variability in [OH$^-$] and [Os(VIII)]. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.65%. The standard error of the estimate shows the standard deviation of the residuals to be .0155. This supports the validity of the rate law given in Eq. 16. The proposed reactions in Scheme (1) were used to calculate the rate based on the multiple regression analysis Eq. 22 and hence they are also valid. The validity of the rate law expressed in Eq. 16 and the proposed reaction mechanism is clearly supported by the similarity among the three rates that is, the observed (experimentally), calculated (from the rate law), and predicted (from regression analysis).

4 Comparative studies

An attempt has been made to compare our experimental findings with the results reported earlier for Pd (II) catalyzed oxidation of triphenylmethane dyes (p-Rosanilne, Crystal Violet (CV), Ethyl Violet (EV)) by CAT [25] in an alkaline medium and uncatalyzed oxidation of BG by CAT [26] in an acidic medium. As far as the kinetic order with respect to oxidant is concerned, it is zero-order [26] in the oxidation of BG, first-order in the Pd (II) catalyzed oxidation of triphenylmethane dyes [25] and zero-order in the present study. The reported [25, 26] first-order kinetics in [dye] seems to be similar with the present study as far as order with respect to dye is concerned. As far as the kinetic order with respect to medium is concerned, it is first-order in the uncatalyzed oxidation of BG, fractional-order in Pd (II) catalyzed oxidation of triphenylmethane dyes by CAT and in the present study. Negligible effects of [Cl$^-$] have also been noted in the reported [25, 26] and in present study. The reported [26] negligible effect of ionic strength of the medium seems to be similar with the present study, but dissimilar for Pd (II) catalyzed oxidation of triphenylmethane dyes by CAT [25]. The dielectric constant showed a negative effect on the reaction rate in the uncatalyzedoxidation of BG by CAT [26] and in the present study. Addition of p-toluenesulfonamide (PTS) retards the rate for triphenylmethane dyes [25] and had no significant effect on rate of uncatalyzed oxidation of BG by CAT [26] and in the present study.

5 Conclusion

The oxidation of BG by CAT experienced a slow reaction rate in alkaline media, but increased in rate in the presence of the Os(VIII) catalyst. The reactive species involved was only the $[\mathrm{OsO_4(OH)_2}]^{2-}$for the Os(VIII) catalyzed oxidation of BG by CAT. Os(VIII) catalyzed reactions were found to proceed nearly four faster than the uncatalyzed reactions and justifies the use of Os(VIII) catalyst for the facile oxidation of the BG by CAT in alkaline medium. The observed results were explained by plausible mechanisms and the related rate law was deduced. It can be stated that Os(VIII) acts as an efficient catalyst for the oxidation of BG by CAT in alkaline medium.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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