# Mechanistic aspects for the oxidation of brilliant green dye by chloramine-T in the presence of perchloric acid: a spectrophotometric kinetic approach

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**Abstract** The kinetics of a triarylmethane dye, brilliant green (BG), by sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) was studied spectrophotometrically in HClO<sub>4</sub> media at 303 K. Under identical experimental conditions, the rate law was -d [BG]/dt = k [BG] [H<sup>+</sup>]. Variations in ionic strength ( $\mu$ ) of the medium had no effect on the oxidation velocity. Addition of *p*-toluenesulfonamide, the reduction product of CAT and Cl<sup>-</sup>, had no significant effect on the rate of reaction. The values of rate constants observed at five different temperatures (298, 303, 308, 313, and 318 K) were utilized to calculate the activation parameters. The observed results have been explained by a general mechanism and the related rate law has been obtained. The process demonstrated in this study is cost effective, which holds great promise in potential application for pollutant control.

Keywords Oxidation kinetics · Brilliant green · Chloramine-T · Perchloric acid

#### Introduction

Pollution of water by dyes by many industries to color their products is a serious problem in the developed and developing countries. Brilliant green dye (BG— $C_{27}H_{33}N_2 \cdot HO_4S$ ), a triphenylmethane dye, is an odorless yellow-green to green powder which is toxic and has mutagenic and carcinogenic effects that affect aquatic biota and humans. It is also used extensively in textile dying and for the production of cover paper in the paper industry. About 0.8–1.0 kg of BG dye is consumed per ton of paper production [1, 2]. The removal of BG dye from

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wastewater is, therefore, a challenge to us. Several photocatalytic degradation procedures for the decolorization of triarylmethane dyes have been reported in the literature [3–5]. In spite of the available procedures, there is still a need for a simple method which is cost effective, non-toxic and environmentally benign. In the light of the above considerations, only a kinetic method can be the most effective for oxidative degradation of BG dye.

The diverse nature of the chemistry of N-metello N-arylhalosulfonamides (organic haloamines) is attributed to their ability to act as sources of halonium cations, hypohalite species and N-anions, which act as both bases and nucleophiles [6-10]. Sodium N-chloro p-toluenesulfonamide (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NClNa·3H<sub>2</sub>O), well known as chloramines-T (CAT), is an important member of this class of compounds. Generally, CAT undergoes a two-electron change in redox reactions, resulting in the formation of the reaction products *p*-toluenesulfonamide (PTS) and sodium chloride. CAT is a source of positive halogen, and this reagent has been exploited as an oxidant for a variety of substrates both in acidic and alkaline media [11, 12]. The species responsible for the oxidizing character may be different depending on the pH of the medium. The redox potential of the system is pH-dependent. CAT has been used as oxidant in neutral, acidic and alkaline media [13, 14]. It is also used as an antiseptic and antipyretic drug [15]. An extensive literature survey revealed that there are only a few reports on the kinetics of oxidation of organic dyes by CAT [16-19]. Interestingly, no information is available on the oxidative behavior of CAT towards BG dye from their kinetic and mechanistic aspects. The present study examines, in detail, the kinetic and mechanistic aspects for the oxidation of BG dye by CAT in the presence of  $HClO_4$  with the following objectives: (1) to determine the order of reaction with respect to oxidant and dye, (2) to ascertain the reactive species, (3) to study the effect of  $[H^+]$ ,  $Cl^-$  ion, ionic strength, dielectric constant of the medium, temperature, and one of the products of the oxidant on the reaction rate, (4) to study the stoichiometry and analysis of the product, and (5) to propose the rate law and the reaction mechanism in agreement with kinetic results.

## Experimental

## Materials

The stock solution of CAT (Loba Chem.) was prepared in water and standardized iodometrically. BG dye (Sd. Fine) was used without further purification. Aqueous solutions of desired strength were freshly prepared prior to use. Solvent studies were made with acetonitrile (Loba Chem.). All the other chemicals were of analytical reagent grade and were used as received. Double distilled water was used throughout the studies.

## Kinetic measurement

The detailed kinetic runs were performed under pseudo-first-order conditions with a known excess of the  $[CAT]_0$  over  $[BG]_0$  using a visible spectrophotometer (Digital

spectrophotometer 167; Systronics, India). In the present study, the kinetic experiments were carried out between 293 and 318 K. 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 BG, HClO<sub>4</sub> and water were taken in separate tubes and thermostated for 30 min at 303 K. The reaction was initiated by the rapid addition of a measured amount of CAT to the stirred reaction mixture. Absorbance measurements were made at  $\lambda_{max} = 622$  nm for BG dye for more than two half-lives. The absorbance readings at t = 0 and t = t are  $D_0$  and  $D_t$ . Plots of log  $D_0/D_t$  versus time were made to evaluate the pseudo-first-order rate constant  $k_{obs}$  which were found reproducible within  $\pm 4$  %.

## Stoichiometry

Stoichiometric experiments were conducted by mixing different amounts of BG dye and CAT at a molar ratio of 1:10 [BG]:[CAT] in the presence of  $4 \times 10^{-3}$  mol dm<sup>-3</sup> HClO<sub>4</sub> for 48 h at 303 K and the results are reported in Table 1. The results clearly demonstrate the consumption of 1 mol of CAT per mole of BG, confirming the following stoichiometry (Scheme 1).

## Characterisation of products

The reaction mixture in the stoichiometric ratio in the presence of  $HClO_4$  under stirred conditions was allowed to progress for 48 h at 303 K. After the completion of the reaction, the mixture was neutralized with dilute NaOH and products were extracted with ethyl acetate. The organic products were identified by using the TLC technique and separated by column chromatography. The reduction product, PTS (TsNH<sub>2</sub>), was detected by TLC [20]. Further confirmation was determined by its melting point, 139 °C, which was within close proximity to the reported temperature of 137–140 °C in previous studies [21]. PTS was quantitatively determined by its reaction with xanthydrol to yield the corresponding *N*-xanthyl-*p*toluenesulfonamide [16]. In a typical experiment, equal quantities of separated PTS and xanthydol (0.20 g) were dissolved in 10 ml of glacial acetic acid. The reaction mixture was stirred for 3 min at room temperature and allowed to stand for 90 min. The derivative was filtered, recrystallized with dioxane/water (3:1), and dried at room temperature. The mass of PTS was obtained with 80–85 % recovery in all the cases. *N*,*N*-diethylamino benzophenone and *p*-*N*,*N*-diethylamino phenol were found

$[BG] \times 10^5$ (mol dm <sup>-3</sup> )	[CAT] × $10^6$ (mol dm <sup>-3</sup> ): initial	[CAT] $\times 10^{6}$ (mol dm <sup>-3</sup> ): final	[CAT] × $10^6$ (mol dm <sup>-3</sup> ): consumed	[CAT]:[BG]
1.00	10.00	8.85	1.15	1.15
3.00	30.00	26.98	3.02	1.00
5.00	50.00	44.90	5.10	1.02

Table 1 Consumption of CAT in the oxidation of BG dye in acidic medium at 303 K

Experimental conditions:  $[HClO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 



Scheme 1 Stoichiometric equations for oxidation of BG dye by CAT in acidic medium

to be the oxidation products of BG dye. It was also observed that there was no further oxidation of these products under the present reaction conditions.

## **Results and discussion**

The detailed kinetic investigations were performed under pseudo-first-order conditions of  $[CAT]_0 \gg [BG]_0$ . The kinetics of oxidation of BG has been investigated with several initial concentration of the reactant in the presence of  $HClO_4$  at 303 K.

Effect of reactant concentrations on the reaction rate

With the oxidant in excess, at constant  $[CAT]_0$ ,  $[HClO_4]$  and temperature, plots of log absorbance (Abs) versus time were linear, indicating a first-order dependence on the rate of  $[BG]_0$  (Fig. 1). The values of pseudo-first order rate constants ( $k_{obs}$ ) were listed (Table 2). Further,  $k_{obs}$  did not change with the change in  $[BG]_0$ , confirming the first-order dependence on  $[BG]_0$ . Under the same experimental conditions, an increase in  $[CAT]_0$ , the value of  $k_{obs}$  remains constant (Table 2), showing a zero-order reaction with respect to [CAT]. The rate constant was found to increase slightly from  $0.2 \times 10^{-3}$  to  $1.4 \times 10^{-3} \text{ s}^{-1}$  with an increasing  $[H^+]$  from  $0.5 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup> (Table 3; Fig. 2).

Effect of PTS concentration on the reaction rate

The addition of PTS to the reaction mixture had no significant effect on the rate (Table 4).



**Fig. 1** First-order plots of the oxidation of BG by CAT in acidic medium.  $[BG] = 1.5 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-5}$ ,  $4 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $6 \times 10^{-5}$ ,  $7 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[CAT] = 4 \times 10^{-6}$  mol dm<sup>-3</sup>,  $[HCIO_4] = 4 \times 10^{-3}$  mol dm<sup>-3</sup>

$[CAT] \times 10^6 \text{ (mol dm}^{-3})$	$[BG] \times 10^5 \text{ (mol dm}^{-3})$	$k_{\rm obs} \times 10^3  ({\rm s}^{-1})$
0.50	4.00	1.40
1.00	4.00	1.41
1.50	4.00	1.40
2.00	4.00	1.39
3.00	4.00	1.40
4.00	4.00	1.40
5.00	4.00	1.41
6.00	4.00	1.40
4.00	1.50	1.40
4.00	2.00	1.41
4.00	2.50	1.40
4.00	3.00	1.39
4.00	4.00	1.40
4.00	5.00	1.40
4.00	6.00	1.41
4.00	7.00	1.40

Table 2 Effect of BG dye and CAT concentrations on the rate of reaction at 303 K

Experimental conditions:  $[HClO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 

#### Effect of ionic strength on the reaction rate

The effect of ionic strength ( $\mu$ ) of the medium was studied by adding requisite amounts of KNO<sub>3</sub>, with all other experimental conditions held constant. The rate of reaction remains constant with the increase in ionic strength of the medium. The rate

$[\mathrm{H^{+}}] \times 10^{3} \; (\mathrm{mol} \; \mathrm{dm^{-3}})$	$k_{\rm obs} \times 10^3  ({\rm s}^{-1})$	$k_{\rm cal} \times 10^3  ({\rm s}^{-1})$	$k_{\text{expected}} \times 10^3 (\text{s}^{-1})$
0.50	0.20	0.20	0.20
1.00	0.40	0.40	0.40
2.00	0.78	0.80	0.78
3.00	1.10	1.20	1.10
4.00	1.40	1.70	1.40

Table 3 Effect of H<sup>+</sup> concentration on the reaction rate at 303 K

Experimental conditions:  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ 

constant was found to be  $1.4 \times 10^{-3}$  (s<sup>-1</sup>) by using KNO<sub>3</sub> from  $5 \times 10^{-3}$  to  $20 \times 10^{-3}$  mol dm<sup>-3</sup>.

Effect of chloride ion on the reaction rate

The addition of  $Cl^-$  ions in the form of NaCl had a negligible effect on the rate, indicating that no free chlorine is formed in the reaction.

Effect of dielectric constant and temperature on the reaction rate

Rate constant values decreased with the increase in the acetonitrile %, that is, with decreasing dielectric constant or polarity of the medium (Table 4; Fig. 3). The reaction was carried out at different temperatures (298, 303, 308, 313, and 318 K), keeping other experimental conditions constant. The rate of reaction increased with an increase in the temperature. From the linear Arrhenius plots of log  $k_{obs}$  versus 1/T (Fig. 4), the activation energy  $(E_a)$  was calculated as  $41.31 \text{ kJ mol}^{-1}$ . Other activation parameters determined were enthalpy of activation  $(\Delta H^{\#} = 38.80 \pm 0.02 \text{ kJ mol}^{-1}).$  $(\Lambda S^{\#} =$ entropy of activation  $163.64 \pm 0.23 \text{ JK}^{-1}$ ), free energy of activation ( $\Delta G^{\#} = 96.45 \pm 0.12 \text{ kJ mol}^{-1}$ ), and the Arrhenius factor (log A = 4.27) (Table 5).

Polymerization study

In order to ascertain the presence of free radicals in the reaction, the reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. When the reaction mixture was diluted with methanol, no precipitate was found. On the basis of this, it can very easily be inferred that there is no possibility of the formation of free radicals in the reaction [22].

Reactive species of CAT

CAT acts as a mild oxidant both in acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions forming the reduction products, PTS and sodium chloride. The oxidation potential of the CAT-TsNH<sub>2</sub> redox couple



**Fig. 2** Effect of  $[H^+]$  on the rate constant  $(k_{obs})$  at 303 K.  $[H^+] = 0.5 \times 10^{-3}$ ,  $1 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $3 \times 10^{-3}$ ,  $4 \times 10^{-3}$ ,  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ 

[PTS] × $10^6 \text{ (mol dm}^{-3}\text{)}$	[CH3CN] (%)	D	$k_{\rm obs} \times 10^3  ({\rm s}^{-1})$
1.00			1.40
2.00			1.40
3.00			1.40
4.00			1.40
5.00			1.40
	0.00	73.60	1.40
	5.00	71.80	1.00
	10.00	70.00	0.60
	20.00	68.20	0.35
	30.00	66.50	0.19

Table 4 Effect of PTS and acetonitrile concentrations on the rate of reaction at 303 K

Experimental conditions: [BG] =  $4 \times 10^{-5}$  mol dm<sup>-3</sup>, [CAT] =  $4 \times 10^{-6}$  mol dm<sup>-3</sup>, [HClO<sub>4</sub>] =  $4 \times 10^{-3}$  mol dm<sup>-3</sup>

varies with pH of the medium ( $E_0$  is 1.14 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). Depending on the pH, CAT furnishes different types of reactive species in solutions. The suggested oxidizing species in acidified CAT solutions are TsNHCl, TsNCl<sub>2</sub>, HOCl, and H<sub>2</sub>OCl<sup>+</sup> [23, 24].

$$TsNCINa \rightleftharpoons TsNCI^{-} + Na^{+}$$
(1)

$$TsNCl^{-} + H^{+} \rightleftharpoons TsNHCl$$
(2)

$$2T_{s}NHCl \rightleftharpoons T_{s}NCl_{2} + T_{s}NH_{2}$$
(3)

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl$$
(4)

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**Fig. 3** Effect of dielectric constant on the observed rate constants in the oxidation of BG by CAT in acidic medium.  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[HCIO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 



**Fig. 4** Effect of temperature on the pseudo-first-order rate constant for the oxidation of BG by CAT in acidic medium.  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}, [CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}, [HClO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 

$$TsNCl_2 + H_2O \rightleftharpoons TsNHCl + HOCl$$
 (5)

$$HOCI \rightleftharpoons H^+ + CIO^- \tag{6}$$

Spectral changes of brilliant green during oxidation by CAT in acidic medium

The color of the BG dye is due to the structure, in which a central carbon is bonded to three aromatic rings, one of which is in the quinoid form (the chromophore) and the oxochrome is -NR<sub>2</sub>. The changes in the absorption spectra of BG dye  $(4 \times 10^{-5} \text{ mol dm}^{-3})$  solution during the oxidation process in CAT  $(4 \times 10^{-6} \text{ mol dm}^{-3})$  in acidic media HClO<sub>4</sub>  $(4 \times 10^{-3} \text{ mol dm}^{-3})$  at 303 K at different times

Temp. ( <i>K</i> )	$\begin{array}{c} k_{\rm obs} \times 10^3 \\ ({\rm s}^{-1}) \end{array}$	$E_{\rm a}$ (KJ mol <sup>-1</sup> )	$\Delta H^{\#}$ (KJ mol <sup>-1</sup> )	$\Delta S^{\#} (JK^{-1} mol^{-1})$	$\Delta G^{\#}$ (KJ mol <sup>-1</sup> )	logA
298	0.98					
303	1.40	41.31	$38.80\pm0.02$	$-163.64 \pm 0.23$	$96.45\pm0.12$	4.27
308	1.70					
313	2.20					
318	2.90					
E		IDC1	4 10-5	13 [CAT]	4 10-6	13

Table 5 Effect of temperature and values of activation parameters for the oxidation of BG dye by CAT in acidic medium at 303 K

Experimental conditions:  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[HClO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 

are shown in Fig. 5. The decrease of the absorption peak of the dye at  $\lambda_{\text{max}} = 622$  nm indicates a rapid degradation of the BG dye. The decrease is also meaningful with respect to the bond, i.e. central carbon attached to the aromatic ring (quinoid form) as the most active site for oxidative attack. The decrease in the absorption intensity of the band at  $\lambda_{\text{max}}$  during the oxidation also expresses the loss of conjugation.

Reaction mechanism and rate law

A general mechanism Scheme (2) was proposed to substantiate the observed kinetics during the oxidation of BG dye by CAT in acidic medium.

$$BG + H^{+} \stackrel{K}{\rightleftharpoons} C \text{ (fast step)} \tag{7}$$

$$C + H_2 O \xrightarrow{\kappa} products (slow step)$$
(8)

In Scheme (2), the BG dye reacts with acid to form a BG-H<sup>+</sup> (C) intermediate in a fast equilibrium step. In the next slow rate-determining step, intermediate species (C) reacts with  $H_2O$  to form products.

1.

According to the reaction, Scheme (2), and considering the fact that 1 mol of BG dye is oxidized by 1 mol of CAT, the rate of reaction can be expressed as:

$$Rate = -dc/dt = k K [BG] [H^+]$$
(9)

By reversing and rearranging Eq. 9, Eq. 10 becomes:

$$\frac{1}{k_{obs}} = \frac{[BG]}{rate} = \frac{1}{kK[H^+]}$$
(10)

Equation (10) indicates that, if we plot a graph between  $1/k_{obs}$  versus  $1/[H^+]$ , we get a straight line with positive intercepts at the *y*-axis (Fig. 6). This proves the validity of the rate law (Eq. 9) and the proposed reaction Scheme (2), on the basis of which the rate law (Eq. 9) has been derived. From the value of the intercept and slope of the plot, kK was found to be 0.407 s<sup>-1</sup>.



Fig. 5 Spectral changes during oxidative degradation of BG by CAT in acidic medium.  $[BG] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[HCIO_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ 

Effect of dielectric constant on the reaction rate

The effect of change of the solvent composition on the reaction rate was studied by varying the concentrations of acetonitrile from 0 to 30 % by volume, and the rate constants are listed in Table 4. The rate constant of the reaction decreased with increasing acetonitrile % from 0 to 30 %. The rate of oxidation was found to depend on the polarity of medium. When the polarity of solvent was increased, the rate of reaction decreased. In order to determine the effect of the dielectric constant (polarity) of the medium on the rate of reaction, the oxidative degradation of BG dye by CAT was studied for various concentrations of acetonitrile. The data clearly revealed that the rate constant values decreased with the increase in the acetonitrile %, that is, with decreasing dielectric constant or polarity of the medium.

The effect of the dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well known equation given below:

$$\log k_{\rm obs} = \log k_{\overline{0}} \frac{Z_{\rm A} Z_{\rm B} e^2 N}{2.303(4pe_0) d_{\rm AB} RT} \times \frac{1}{D}$$
(11)

Where  $k_0$  is the rate constant in a medium of infinite dielectric constant,  $Z_A$  and  $Z_B$  are the charges of the reacting ions,  $d_{AB}$  refers to the size of activated complex, *T* is absolute temperature, and *D* is the dielectric constant of the medium. A plot is made



Scheme 2 Mechanistic pathway for oxidative degradation of BG dye by CAT in acidic medium

between  $\log k_{obs}$  and 1/D, and a straight line having a negative slope was obtained (Fig. 3), indicating an interaction between a charged ion and a dipolar molecule. From the slope of the straight line, the  $d_{AB}$  value has been calculated and found to be 0.4 Å.

In Scheme (2), the negligible effect of the variation of ionic strength of the medium on the rate oxidation of BG dye is well explained. Entropy of activation plays an important role in the case of the reaction between ions or between an ion



**Fig. 6** Graphical representation of  $1/k_{obs}$  and  $1/H^+$  concentration. [HClO<sub>4</sub>] =  $0.5 \times 10^{-3}$ ,  $1 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $3 \times 10^{-3}$ ,  $= 4 \times 10^{-3}$ , [BG] =  $4 \times 10^{-5}$  mol dm<sup>-3</sup>, [CAT] =  $4 \times 10^{-6}$  mol dm<sup>-3</sup>

and a neutral molecule, or a neutral molecule forming ions. When the reaction takes place between two similarly charged species, the transition state will be a more highly charged ion, and, due to this, more solvent molecules will be required than for the separate ions, leading to a decrease in entropy. On the other hand, when the reaction takes place between two ions of opposite charges, their union will result in a lowering of the net charge and due to this some frozen solvent molecules will be released with an increase of entropy [25]. On the basis of this information, the observed negative entropy of activation supports the rate limiting step of the proposed scheme. The proposed mechanism is also supported by the moderate value of energy of activation and other parameters. The high positive values of  $\Delta H^{\#}$  and  $\Delta G^{\#}$  indicate that the transition state is highly solvated.

#### Multiple regression analysis

To discover the relationship between dependent, that is, pseudo-first-order variable rate constant  $k_{obs}$ , and one independent variable [H<sup>+</sup>] in order to arrive at a conclusion whether or not the proposed mechanism is well in accordance with our experimental kinetic data, we have been helped by a multivariate regression analysis using the computer package STAT GRAPHICS. With the aid of a multivariate regression analysis, a relationship between the observed pseudo-first-order rate constant  $k_{obs}$  and the concentration of H<sup>+</sup>, except BG dye, was determined.

$$k_{\rm obs} = k \left[ {\rm H}^+ \right] \tag{12}$$

where  $k_{obs}$  is 8.88 × 10<sup>-16</sup>. The *R*-squared statistic indicated that the model as fitted explains 100 % of the variability in [H<sup>+</sup>]. The adjusted *R*-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 0.0 %. The standard error of the estimate shows the standard deviation of the residuals to be 0.0. This supports the validity of the rate law given in Eq. 9. The

proposed reactions in Scheme 2 are also valid because these equations were used to calculate the rate based on the multiple regression analysis (Eq. 12). The similarity among the three rates, that is, the observed (experimentally), calculated (from rate law), and predicted (from regression analysis) results, clearly support the validity of the rate law expressed in Eq. 9, and hence, the proposed reaction mechanism.

#### Conclusion

In this study, BG dye was successfully degraded in acidic medium by the CAT oxidant, and it was found that the reaction of BG dye follows kinetics with the rate law:rate = k [BG] [H<sup>+</sup>]. The addition of PTS had no significant effect on the rate. Activation parameters for the overall reaction have been computed. A possible reaction mechanism and the related rate law have been deduced. The present redox system can be adopted for treating the chosen BG dye present in industrial effluents to reduce toxicity caused by BG dye. This novel approach could be used as a highly efficient and green technology for BG dye degradation.

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