Oxidative Degradation of Brilliant Green by Potassium Iodate in Acidic Medium: A Kinetic and Mechanistic Study

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Brilliant green (BG), one of the triphenylmethane dyes, has been extensively applied and produced as a colorant for different industries like medical, paper/textile printing, food additive, cosmetics, *etc*. Dyes effluents discharged by these industries pose hazardous effects on environmental and human health *via* releasing toxic and carcinogenic contaminants during its deterioration. The present work evaluates kinetic and mechanistic aspects of oxidative degradation of brilliant green by iodate in acidic solution at 303 K. The influence of different factors such as concentration of various reactants (μ), free radicals, *etc*. has also been investigated to check feasibility of redox degradation for efficient, easy, low-cost and eco-friendly removal of brilliant green from aquatic medium. The experimental result shows a first-order rate dependence on [BG] and zero-order kinetics with respect to [KIO_3]. The reaction showed positive fractional order dependence on the rate for [H^+]. Variations in ionic strength of the medium and [Cl^-] did not bring about any noticeable change on the rate of reaction. It was found that the reaction rate declined with the decrease in the dielectric constant (D) of the medium in the oxidation of brilliant green. Additionally, the process was carried out at different temperatures to estimate the activation parameters and also to find rate controlling stages of the process. Finally, an appropriate mechanism, a plausible with the experimental observations, also supported by UV-Vis spectra has been proposed.

Keywords: Oxidative, Kinetics, Brilliant green, Potassium iodate, Acidic solution.

INTRODUCTION

Recently, it has been estimated that there are more than 1,00,000 different synthetic dyes are used in a wide range of anthropogenic activities and commercially available in the market [1] with a production exceeding 8,00,000 tons per year [2]. Global demand for coatings and paints is predicted to rise 3.7% per year to 57.7 million metric tons in 2020, valued at $193 billion and accumulation of nearly 10-15% of wasted dyes reach in the ecosystem through wastewater without proper treatment from various industries [3] causes negative impacts on natural environment as well as health due to their toxicity and ability to long sustain in the nature [4,5].

Brilliant green is a cationic (basic) odourless, golden green crystalline solid [6], triarylmethane dye of malachite green series and chemically known as 4,4-*bis* diethylaminotriphenyl methyl sulfate [7]. Generally, cationic dyes have most harmful

toxicants for whole natural environment because of their aromatic structure provide them a greater chemical stability [8], which not degradated easily. Due to genotoxic and carcinogenic nature of brilliant green, its use has been banned in many countries [9]. So its removal from the natural water bodies is imperative. Brilliant green is not only of biological interest but is also used in rubber, leather, paper/textile printing, pharmaceutical, plastic industries and as a biological stain [10] dermatological agents, veterinary medicine, saloon bars to dye hairs [11-13], coloured paper production [14], an additive to poultry feed [15] to inhibits spread of mould/intestinal parasites and fungus propagations [16]. If brilliant green comes in direct contact with the skin/an eyes, inhaled or swallowed then it causes many serious harmful health damages like redness, itching [8] vomiting and nausea. It is also strong irritant for respiratory tracts, induces cough and shortness of breath [6,17]. It is highly resistant to microbial degradation and can cause long term

adverse effects in the aquatic environment/ecosystem as it is very toxic to aquatic organisms due to their carcinogenic and mutagenic effects [15] on microorganisms [18,19]. Some degree of carcinogenicity, lack of attention, hypersensitivity, low frustration tolerance, *etc*. arises when brilliant green used as food additives [20], also toxify microbial environment, fish [21] and other aquatic organisms due to chelating metal ions by brilliant green. The sunlight penetration into water body blocked due to its colouring and inhibits the growth of useful biota [22], which slows down the photosynthetic activities of aquatic flora and fauna. Therefore, it is of great concern and interest that a quick/easy chemical analysis to develop an advanced elimination method for the degradation of brilliant green, which is convenient, efficient, sensitive/versatile and recyclable to remediate its accumulation in the environment. In the presence of cationic surfactant alkaline fading of brilliant green in aqueous solution is reported in literature [23,24]. Several works on the kinetics of oxidation of triphenylmethane dyes requires much more attention as depicted by the surveys using photocatalytic degradation [25-27] and oxidative degradation processes [28,29].

Potassium iodate (KIO_3) except in Europe and N. America (59.5% iodine) is the preferred source of iodine fortification for food and feed because of its stability [30]. It is a effective oxidizing agent and has application in food manufacturing which oxidizes gluten protein bonds in bread dough that adjust its strength, elasticity and tolerance almost immediately after mixing *i.e.* fast acting oxidizer [31]. So, it accelerate the reactions, which allow the bread to rise during backing. It is approved as a dietary iodine supplement for thyroxin hormones which is essential for good health/development and needed for effective thyroid gland operations which affects the body's metabolic and immunity functions. Radioactive KIO_3 used for protecting thyroid gland from damage and reducing risks of thyroid cancer. In spite of the various properties of KIO_3 [32-35], less information is available in the literature about this rarely used inorganic oxidant and their kinetic study.

However, literature surveys has revealed that there are no efforts being made so far from the kinetic and mechanistic view points of KIO_3 oxidation of brilliant green in homogeneous acidic medium. Thus, the order of reaction with respect to KIO_3 and brilliant green is determined and the effect of $[H^+]$, $[Cl^-]$, ionic strength, dielectric constant of medium and temperature, *etc*. on reaction rate were also studied. Moreover, the reactive species of KIO_3 was ascertained in-order to deduce the rate law consistent with the kinetic results and the estimate thermodynamic parameters and activation energy to find rate controlling stage of the reaction. And finally, a suitable reaction mechanism is also elucidated.

EXPERIMENTAL

Analytical reagent grade chemicals and triple distilled water were used throughout the investigation. Brilliant green (BG) [m.f. $C_{27}H_{34}N_2O_4S$] (Sd. Fine Chem, m.w. = 482.62) was of 99.8% pure and used without any further purification. By dissolving an accurately weighed quantity of dye in triple distilled water, stock dye solution was prepared and then successive dilution an experimental solution of the required concentration was obtained. Solvent studies *i.e.* dielectric constant (D) of the medium were varied with acetonitrile (Loba Chemicals). Perchloric acid ($HClO_4$), potassium nitrate (KNO_3), KCl and KIO_3 were used as supplied without further purification. KNO_3 was used to maintain the ionic strength (μ) and acrylamide to check the presence of the free radicals in reaction mixture. The reaction vessels were coated from outside with black paint to avoid any photochemical reaction.

Kinetic measurements: A kinetic analysis was conducted under the conditions of pseudo-first order at 303 K with $[KIO_3]$ >> [BG] by employing visible spectrophotometry (Digital Spectrophotometer 166, Systronics, India). In this study, the kinetic experiments were performed at 298–318 K. A Ragga Ultra Cold chamber having the digital control of temperature was employed for this experiment; this chamber maintained constant temperature with the accuracy of ±0.1 ºC. The pre-determined amounts of BG, water and $HClO_4$ were poured in glass-stoppered Pyrex boiling tubes. These tubes were placed in a water bath controlled with a thermostat and at 303 K, the water bath was pre-equilibrated. An appropriate amount of KIO_3 solution, which was equilibrated in the same water bath at the desired temperature, was spontaneously transferred into the reaction vessel for initiating the reaction. Then, 4 mL of the aliquot was pipetted out and transferred into a cuvette that was placed in the spectrophotometer. For BG, the absorbance was measured at λ_{max} of 622 nm for more than two half-lives. The plots of log absorbance versus time were prepared to estimate the pseudo-first-order rate constant (k_1); within ±4%, this rate constant was reproducible. Moreover, the reaction performed at various temperatures (303, 298, 313, 308 and 318 K) to determine the impact of temperature and calculate different activation and thermodynamic parameters. To investigate the effects of dissolved O_2 on the reaction rate, a kinetic run was performed in an inert atmosphere (*i.e.* in N_2 gas) to suppress parallel, unwanted chemical reactions, such as oxidation and hydrolysis, occurring with moisture available in air and oxygen. These reactions may alter results. No considerable difference was observed for the results obtained in the presence of O_2/air dissolved in the reaction mixture and in inert atmosphere.

Stoichiometry and product analysis: Different sets of the reaction mixture containing BG, $HClO_4$ with varying $[KIO_3]$:[BG] ratios were equilibrated for 72 h at 303 K under the conditions of $[IO_3^-]$ >> [BG]. The unconsumed KIO_3 in the reaction mixture was determined by iodometric titration. Estimation of unconsumed KIO_3 in each set revealed that for the oxidation of 1 mol of BG was consumed 1 mol of KIO_3, *i.e.* 1:1 ratio of oxidant and substrate (BG). Accordingly, the following stoichiometry equation may be formulated as shown in **Scheme-I**.

After reaction completion (monitored through TLC), the reaction product was extracted using ether. After ether layer evaporation, column chromatography was conducted on a silica gel with 60-200 mesh through gradient elution (from dichloromethane to chloroform). The product was further purified through recrystallization after the first separation. *p*-N,N-Diethylaminophenol and *N*,*N*-diethylaminobenzophenone were the

Scheme-I: Stiochiometric equation for oxidation of BG by KIO_3 in acidic medium
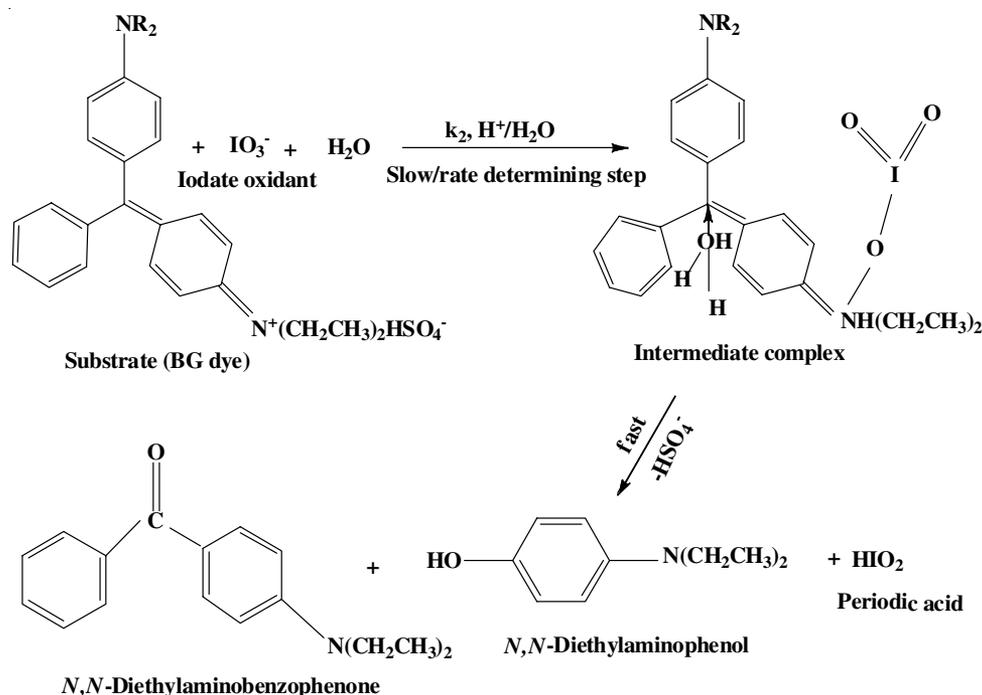
oxidation products of BG. The presence of compounds was confirmed through GC-MS and the spectra showed molecular ion peaks at 165 and 253 amu for p-N,N-diethylaminophenol and N,N-diethylaminobenzophenone, respectively. Under the reaction conditions, no further oxidation was observed for these products.

RESULTS AND DISCUSSION

For brilliant green (BG) oxidation through KIO_3, the kinetics was studied as a function of the initial reactant concentration at 303 K in an acidic medium. Under the condition of pseudo-first order of $[KIO_3] \gg [BG]$, when remaining reaction conditions were not changed, the plots of time *versus* log absorbance (Abs) were linear, which indicated the dependence of the first order on the rate of [BG]. The impact of BG was investigated between 1×10^{-5} and 5×10^{-5} mol dm^{-3}. For each kinetic run, the reaction rate constant was estimated using the plot of time *versus* log Abs (Fig. 1). This plot presents a straight line, indicating that under the selected condition, the reaction followed the pseudo-first-order kinetics. The rate constants of the pseudo-first order (k_1) are presented in Table-1. Furthermore, k_1 did not vary with changing [BG], which confirmed the dependence of the first order on [BG]. Under the aforementioned experimental conditions, with the increase in $[KIO_3]$ from 1×10^{-4} to 20×10^{-4} mol dm^{-3}, k_1 remained constant (Table-2), which showed the zero-order reaction for $[KIO_3]$. The influence of the ionic strength (μ) of media was investigated by adding the required amount of KNO_3 (1×10^{-3} to 9×10^{-3} mol dm^{-3}) when the remaining experimental conditions were maintained constant (Table-2). Different ionic strengths of the medium did not lead to considerable changes in the value of k_1 under these experimental conditions, which indicated that a non-ionic species was involved in the rate-determining step. The rate constant

TABLE-1
EFFECT OF KIO_3, BG AND KNO_3 CONCENTRATIONS ON THE RATE OF REACTION AT 303 K

$[BG] \times 10^5$ (mol dm^{-3})	$[KIO_3] \times 10^4$ (mol dm^{-3})	$[KNO_3] \times 10^3$ (mol dm^{-3})	$k_1 \times 10^3$ (s^{-1})
1.00			1.49
1.50			1.47
2.00			1.46
2.50			1.50
3.00			1.48
4.00			1.49
5.00			1.49
	1.00		1.49
	2.00		1.48
	3.00		1.49
	4.00		1.49
	5.00		1.42
	6.00		1.42
	8.00		1.41
	10.00		1.38
	12		1.34
	15		1.53
	20		1.38
		1.00	1.49
		2.00	1.46
		3.00	1.48
		4.00	1.49
		5.00	1.53
		7.00	1.42
		9.00	1.49

[a]Experimental conditions: $[HClO_4] = 1 \times 10^{-3}$ mol dm^{-3}

slightly increased from 0.27×10^{-3} to 3.60×10^{-3} with the increase in $[H^+]$ from 0.20×10^{-3} to 5×10^{-3} mol dm^{-3} (Table-3). The plots of log $[H^+]$ *versus* log k_1 were linear with the fractional slope of 0.832), which revealed the rate dependence of the fractional order on $[H^+]$ (Fig. 2). Chloride ion $[Cl^-]$ addition
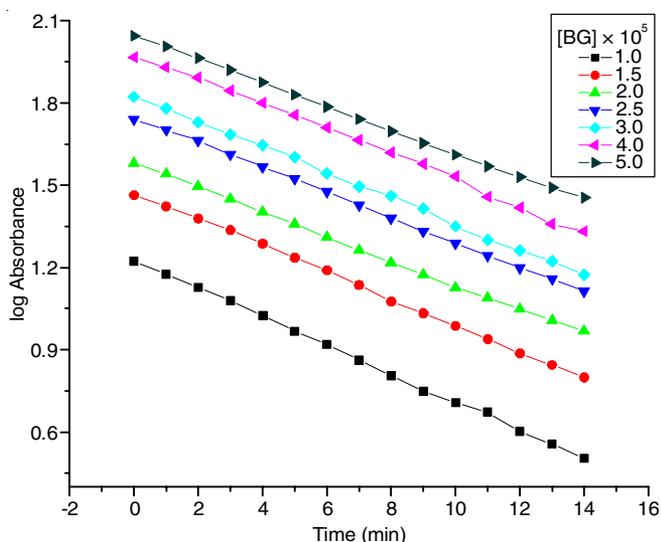
Fig. 1. First order plots of the oxidation of BG by KIO₃ in acidic medium. [BG] = 1 × 10⁻⁵, 1.5 × 10⁻⁵, 2 × 10⁻⁵, 2.5 × 10⁻⁵, 3 × 10⁻⁵, 4 × 10⁻⁵, 5 × 10⁻⁵ mol dm⁻³, [KIO₃] = 3 × 10⁻⁴ mol dm⁻³, [HClO₄] = 1 × 10⁻³ mol dm⁻³

Fig. 1. First order plots of the oxidation of BG by KIO_3 in acidic medium. [BG] = 1×10^{-5}, 1.5×10^{-5}, 2×10^{-5}, 2.5×10^{-5}, 3×10^{-5}, 4×10^{-5}, 5×10^{-5} mol dm⁻³, [KIO₃] = 3×10^{-4} mol dm⁻³, [HClO₄] = 1×10^{-3} mol dm⁻³
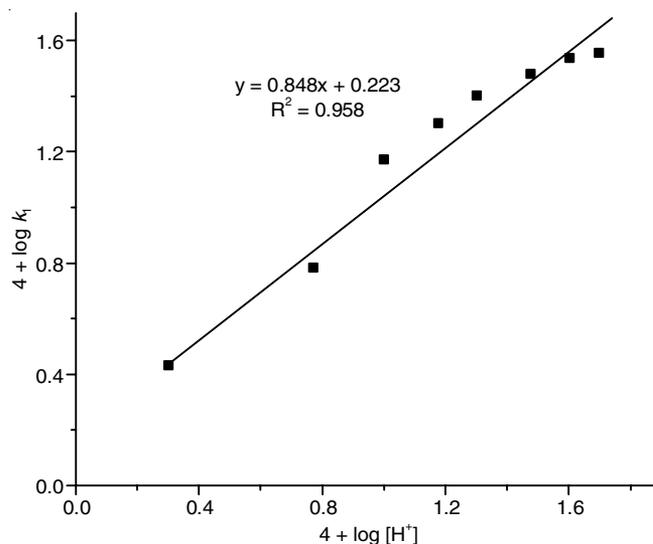

Fig. 2. Effect of [H⁺] on the rate constant (k_1) at 303 K. [H⁺] = 0.2×10^{-3}, 0.5×10^{-3}, 1×10^{-3}, 1.5×10^{-3}, 2×10^{-3}, 3×10^{-3}, 4×10^{-3}, 5×10^{-3} mol dm⁻³, [BG] = 3×10^{-5} mol dm⁻³, [KIO₃] = 3×10^{-4} mol dm⁻³

TABLE-2
EFFECT OF H⁺ CONCENTRATIONS AND
ACETONITRILE % ON THE REACTION RATE AT 303 K

[H⁺] × 10³ (mol dm⁻³)	CH₃CN (%)	D	$k_1 \times 10^3$ (s⁻¹)	$k_{cal} \times 10^3$ (s⁻¹)	$k_{rxn} \times 10^3$ (s⁻¹)
0.20			0.27	0.27	0.31
0.59			0.61	0.67	0.67
1.00			1.49	1.25	1.20
1.50			2.07	1.81	1.68
2.00			2.53	2.33	2.14
3.00			3.03	3.27	3.00
4.00			3.45	4.09	3.81
5.00			3.6	4.81	4.51
	0.00	73.60	1.49		
	5.00	71.80	1.11		
	10.00	70.00	0.77		
	20.00	68.20	0.50		
	30.00	66.50	0.36		

ᵃExperimental conditions: [BG] = 3×10^{-5} mol dm⁻³, [KIO₃] = 3×10^{-4} mol dm⁻³

Fig. 3. Effect of dielectric constant on the observed rate constant in the oxidation of BG by KIO_3 in acidic medium. [BG] = 3×10^{-5} mol dm⁻³, [KIO₃] = 3×10^{-4} mol dm⁻³, [HClO₄] = 1×10^{-3} mol dm⁻³

showed no important effect on the reaction rate. The reaction rate decreased with the decrease in the dielectric constant (D) of the medium (with the increase in acetonitrile percentage (CH₃C≡N) by volume) (Table-3; Fig. 3). This reaction was conducted in the temperatures range of 298-318 K without changing the other experimental conditions. The reaction rate
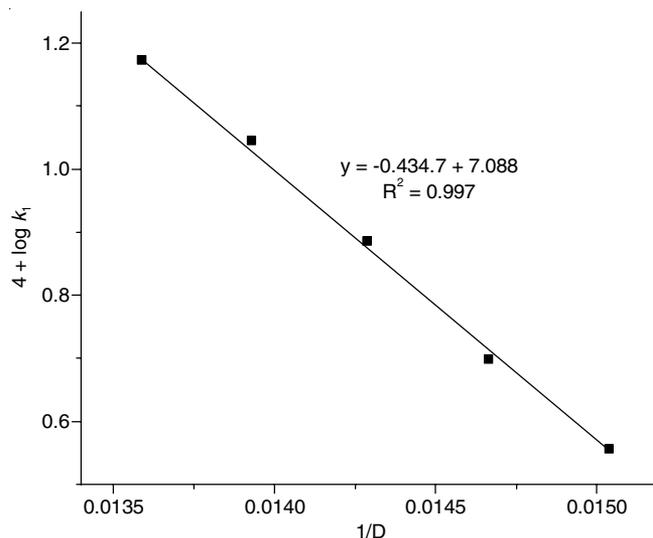
increased with the increase in temperature. By using the linear Arrhenius plot of 1/T *versus* log k_1 (Fig. 4), the activation energy E_a of 24.63 KJ mol⁻¹ was calculated using the intercept and slop. By employing the activation energy, other activation parameters, such as activation entropy ($\Delta S^{\#} = -217.70 \pm 0.16$ J K⁻¹ mol⁻¹), activation enthalpy ($\Delta H^{\#} = 22.12 \pm 0.12$ KJ mol⁻¹),

TABLE-3
EFFECT OF TEMPERATURE AND VALUES OF ACTIVATION PARAMETERS
FOR THE OXIDATION OF BG BY KIO₃ IN ACIDIC MEDIUM AT 303 K

Temp. (K)	$k_1 \times 10^3$ (s⁻¹)	E_a (KJ mol⁻¹)	ΔH (KJ mol⁻¹)	$\Delta S^{\neq}$ (JK⁻¹ mol⁻¹)	$\Delta H^{\neq}$ (KJ mol⁻¹)	log A
298	1.28					
303	1.49	24.63	22.12 ± 0.12	-217.70 ± 0.16	88.08 ± 0.12	1.42
308	1.71					
313	2.01					
318	2.41					

ᵃExperimental conditions: [BG] = 3×10^{-5} mol dm⁻³, [KIO₃] = 3×10^{-4} mol dm⁻³, [HClO₄] = 1×10^{-3} mol dm⁻³
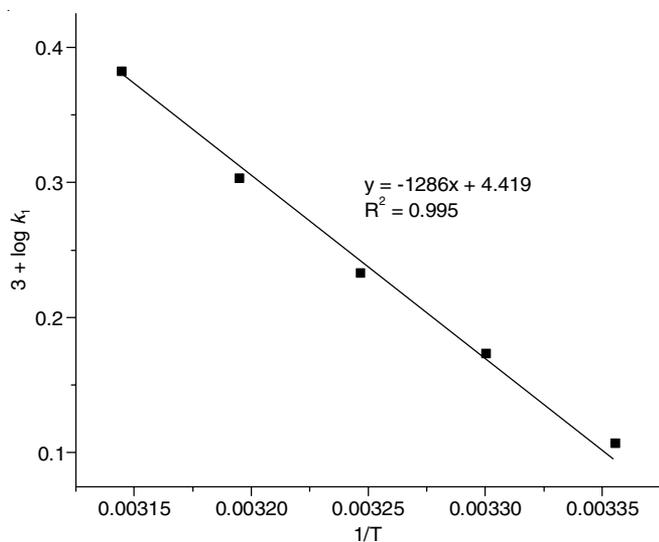
Fig. 4. Effect of temperature on the observed rate constant (k_1) in the oxidation of BG by KIO_3 in acidic medium. [BG] = 3×10^{-5} mol dm^{-3}, [KIO_3] = 3×10^{-4} mol dm^{-3}, [$HClO_4$] = 1×10^{-3} mol dm^{-3}

Arrhenius frequency factor (log A = 1.42), and Gibbs free energy of activation ($\Delta G^{\#}$ = 88.08 ± 0.12 KJ mol^{-1}), were calculated by using the Erying equation (Table-4).

TABLE-4 ACTIVATION PARAMETERS FOR TRIPHENYLMETHANE DYES WITH DIFFERENT OXIDANT, MEDIUM AND CATALYST (FOR ISOKINETIC TEMPERATURE)		
Dye + oxidant + medium + catalyst	$k_1 \times 10^3$ (s^{-1})	E_a (KJ mol^{-1})	Ref.
BG + CAT + H^+	1.40	41.31	[8]
BG + KIO_3 + H^+	1.49	24.63	Present work
p-Rosanilne + CAT + OH^-	3.83	62.10	[20]
p-Rosanilne + CAT + OH^- + Pd(II)	1.67	41.70	[20]
CV + CAT + OH^-	0.18	66.90	[20]
CV + CAT + OH^- + Pd(II)	0.84	50.50	[20]
EV + CAT + OH^-	0.09	68.80	[20]
EV + CAT + OH^- + Pd(II)	0.36	57.40	[20]

Analysis of free radicals: During the course of oxidation of BG no free radical was generated, which was confirmed by using acrylamide monomer. To the reaction mixture containing [BG] = 3.00×10^{-5} mol dm^{-3}, [$HClO_4$] = 1.00×10^{-3} mol dm^{-3}, [KIO_3] = 3.00×10^{-4} mol dm^{-3}, a known amount of acrylamide (say 20.0 mL) was added. Addition of different amount of acrylamide to the reaction mixture in an inert atmosphere did not initiate polymerization indicating the absence of free radicals (Table-2).

Reactive species of potassium iodate: In acidic medium, for oxidation of acetophenone [36], 1,2-propanediol [32], ferrocyanide [37], 1,3-dihydroxybenzene [38] and thiocyanate [39], IO_3^- has been used as an oxidant. Catalyzed oxidation of organic compounds been carried by using Os(VIII) [40] and Ru(III) [41] by an acidic solution of iodate. Some researchers used Ir(III) and Ru(III) as catalyst in alkaline medium for oxidation of organic or inorganic compounds through sodium or potassium iodate as oxidant [42-45]. In each case, IO_3^- parti-

cipates as the reactive species of sodium iodate or potassium iodate in the acidic/alkaline medium, which is well supported the existence of IO_3^- species in acidic medium. In the view of reported kinetic data and spectral evidences, it can be very easily concluded that the IO_3^- is the reactive species of KIO_3 for oxidation of BG by potassium iodate in the aqueous acid.

Spectrophotometric studies: The BG-imparted colour resulted from its structure, where the central carbon is bonded to three aromatic rings. Among these rings, one ring exhibits the quinoid form (chromophore), and the oxochrome is $–NR_2$. The changes occurring in the absorption spectra of BG (3×10^{-5} mol dm^{-3}) at 303 K in the acidic medium ($HClO_4 = 1 \times 10^{-5}$ mol dm^{-3}) at different times during oxidation in KIO_3 (3×10^{-4} mol dm^{-3}) are shown in Fig. 5. The decrease in the absorption peak of BG indicates the rapid degradation of BG at the λ_{max} of 622 nm. The decrease in the absorbance intensity of the bond during oxidation indicates the loss of conjugation at λ_{max}. This decrease suggests that for oxidative attack, central carbon, which is attached to an aromatic ring (in the quinoid form), is the most active site [29].
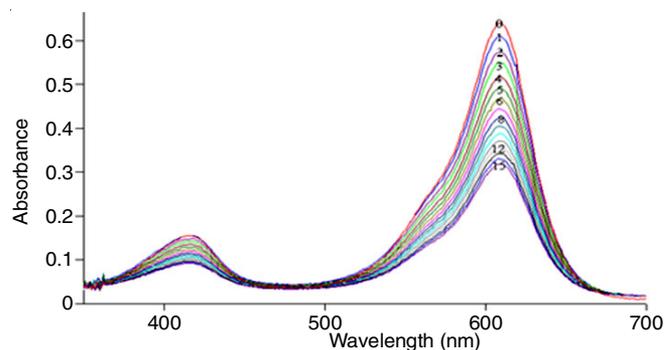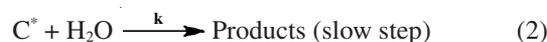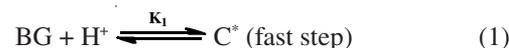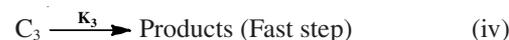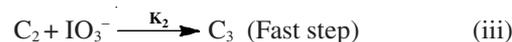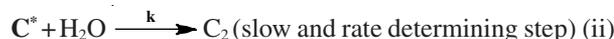

Fig. 5. Spectral changes during oxidative degradation of BG by KIO_3 in acidic medium: [BG] = 3×10^{-5} mol dm^{-3}, [KIO_3] = 3×10^{-4} mol dm^{-3}, [$HClO_4$] = 1×10^{-3} mol dm^{-3}

Reaction mechanism and derivation of rate law:

$$BG + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} C^* \text{ (fast step)} \qquad (1)$$

$$C^* + H_2O \xrightarrow{k} Products \text{ (slow step)} \qquad (2)$$

or

$$BG + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} C^* \qquad (i)$$

$$C^* + H_2O \xrightarrow{k} C_2 \text{ (slow and rate determining step)} \qquad (ii)$$

$$C_2 + IO_3^- \xrightarrow{K_2} C_3 \text{ (Fast step)} \qquad (iii)$$

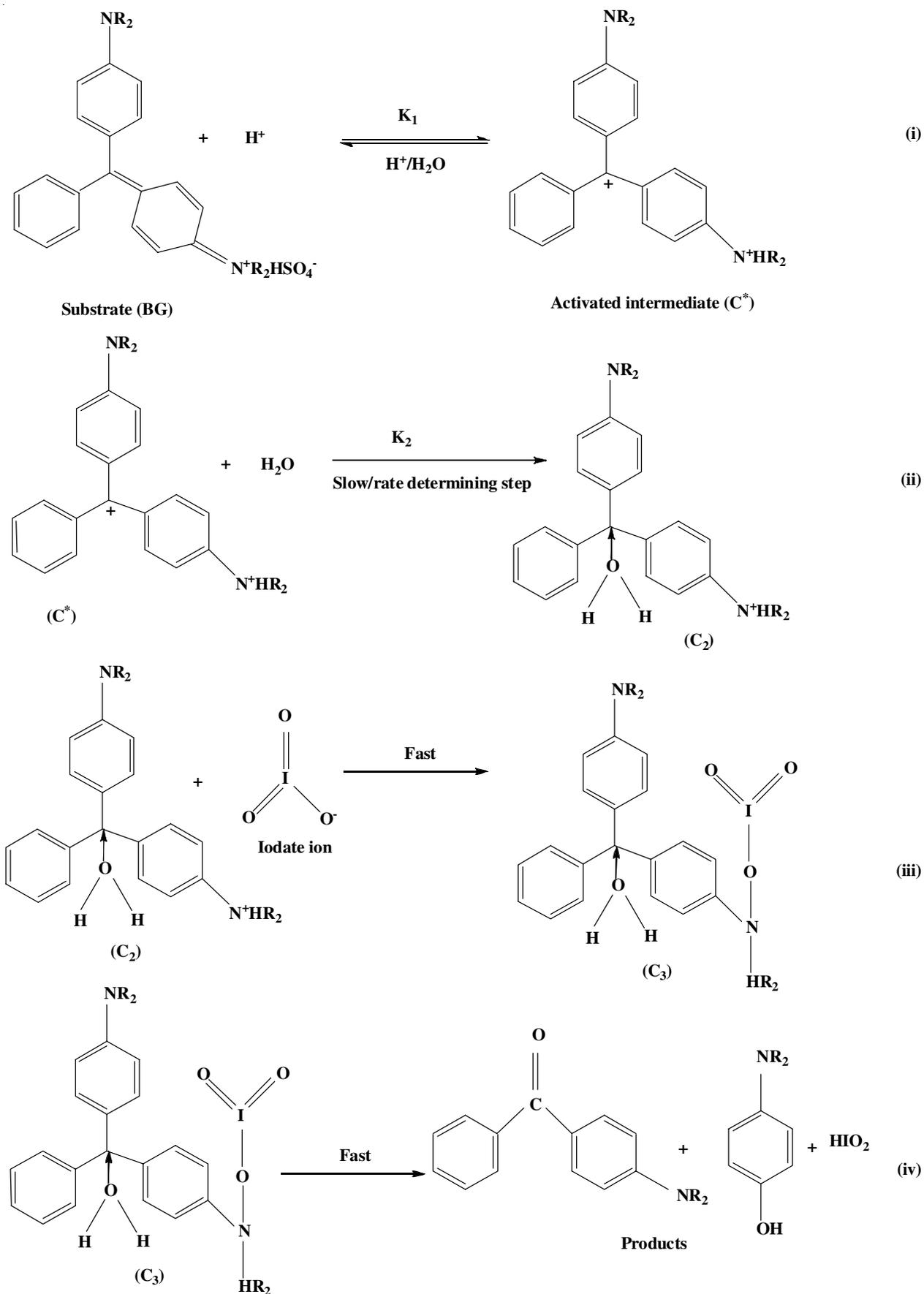$$C_3 \xrightarrow{K_3} Products \text{ (Fast step)} \qquad (iv)$$

Based on the experimental results, a mechanism (**Scheme-I**) was proposed for which all the observed orders in each constituent such as [KIO_3], [BG] and [$HClO_4$] may be accommodated.

In **Scheme-II**, the BG reacts with acid to form a BG-H^+(C^*) intermediate in a fast equilibrium step. In the next slow rate determining step, intermediate species (C^*) i.e. activated

Scheme-II: Mechanistic interpretation for the oxidative degradation of BG dye by CAT in acidic medium

complex reacts with H_2O molecule to form positively charged complex (C_2), which further reacts with the reactive species of oxidant IO_3^-, the reactive specie of potassium iodate oxidant *i.e.* IO_3^- possesses nucliophillic character to bind itself to $-N$ of C_2, by $-N-O-IO_2$ bond to the substrate (BG) and converted into a neutral complex(C_3) by fast step, finally C_3 followed by cracking ring structure to form end products *via* step iv. Taking all steps in **Scheme-II** for the oxidation of BG by KIO_3, the following rate law (eqn. 3) may be written:

$$\text{Rate} = \frac{-dc}{dt} = k[C^*] \quad (3)$$

Value of equilibrium constant can be calculated as:

$$K_1 = \frac{[C^*]}{[BG][H^+]} \quad (4)$$

So rate becomes as:

$$\text{Rate} = kK_1[BG][H^+] \quad (5)$$

At any time in the reaction, the total concentration of BG, that is $[BG]_T$ can be expresses as:

$$[BG]_T = [BG] + [C^*] \quad (6)$$

Substitution of the value of [C] in eqn. 6, eqn. 7 is obtained:

$$[BG]_T = [BG] + K_1[BG][H^+] \quad (7)$$

$$[BG]_T = [BG] (1 + K_1[H^+]) \quad (8)$$

By rearranging eqn. 8, eqn. 9 becomes as:

$$[BG] = \frac{[BG]_T}{1 + K_1[H^+]} \quad (9)$$

Substituting the expression for [BG], into eqn. 5, eqn. 10 is obtained.

$$\text{Rate} = \frac{kK_1[BG]_T[H^+]}{1 + K_1[H^+]} \quad (10)$$

By rearranging eqn. 10, eqn. 11 becomes:

$$k_1 = \frac{\text{Rate}}{[BG]_T} = \frac{kK_1[H^+]}{1 + K_1[H^+]} \quad (11)$$

By reversing eqn. 11, eqn. 12 becomes:

$$\frac{1}{k_1} = \frac{1}{kK_1[H^+]} + \frac{1}{k} \quad (12)$$

Eqn. 12 indicates that if a plot is made between $1/k_1$ and $1/[H^+]$ straight line with positive intercept on *y*-axis will be obtained (Fig. 6). This supports the proposed reaction scheme on the basis of which the rate law (eqn. 12) was derived. From the value of the intercept and slope of the plot, k was found to be $1.53 \times 10^{-2} s^{-1}$ and K_1 is $8.95 \times 10^1 M^{-1} s^{-1}$, respectively which provides relevant information's of experimental rate eqn. 12 and reaction mechanism too.

Effect of dielectric constant on the reaction rate and calculation of the size of activated complex (d_{AB}): The reaction was studied at different dielectric constant (D) of the medium with constant concentrations of all other reactants and a constant temperature 303 K, to find out the effect of the dielectric constant of the medium on the rate of reaction. Following
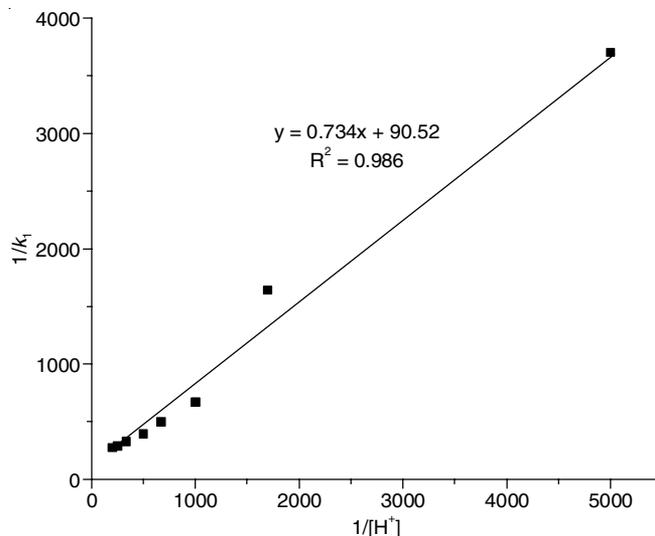

Fig. 6.   Graphical representation of $1/k_1$ and $1/[H^+]$. $[H^+] = 0.2 \times 10^{-3}$, 0.5×10^{-3}, 1×10^{-3}, 1.5×10^{-3}, 2×10^{-3}, 3×10^{-3}, 4×10^{-3}, 5×10^{-3} mol dm^{-3}, [BG] = 3×10^{-5} mol dm^{-3}, [KIO_3] = 3×10^{-4} mol dm^{-3}

equation gives the dependence of the rate constant on the dielectric constant of medium:

$$\log k_1 = \log k_0 - \frac{Z_A Z_B e^2 N}{2.303(4\pi\varepsilon_0)d_{AB}RT} \times \frac{1}{D} \quad (13)$$

where Z_A and Z_B are the charges of reacting ions, k_0 is the rate constant in a medium of infinite dielectric constant, T is the absolute temperature, d_{AB} refers to the size of activated complex and D is the dielectric constant of the medium. This equation suggests, a straight line can be attained with a slope of -434.7 (Fig. 3), if a plot is made between log k_1 *versus* 1/D. The proposed mechanism is supported by a negative dielectric effect. The effect on the rate of reaction by changing the solvent composition has been discussed in detail [46]. For the limiting case of zero angle approach in an ion-dipole system or between two dipoles, it has been shown that a general result for a reaction between a negative ion and a dipole or between two dipoles, a negative slope of a linear line in the plot of log k_1 *versus* 1/D is obtained. For a reaction between positive ion-dipole interactions, a positive slope is obtained [47]. In the present study, the former concept agrees with the observations. The reaction rate constant/order has been found to increase with decrease of particle diameter (reactants or activated complex) [48], also the apparent activation energy either increase [49] or decrease [48] with decrease of the particle diameter. The value of d_{AB} was evaluated using slope as 0.55 Å, which shows good agreement for present study.

In **Scheme-II**, the negligible effect of variation of ionic strength (μ) of the medium on the rate of oxidation of BG by KIO_3 is well explained. In the case of reaction between ions or between an ion and a neutral molecule or a neutral molecule forming ions, entropy of activation plays an important role. The transition state will be more highly charged ions, when reaction takes place between two similarly charged species and due to this, more solvent molecules will be required than for the separate ions, salvation of ions would lead to a decrease

in entropy in the formation of transition state. On the other hand, union will results in a lowering of the net charges, when reaction takes place between two ions of opposite charges and due to this some frozen solvent molecules will be released with an increase of entropy [50]. It is seen that the observed negative entropy of activation supports the rate limiting step of the proposed scheme on the basis of this information. The moderate value of entropy of activation $\Delta S^{\#}$ and E_a and other thermodynamic parameters also support the proposed mechanism. A highly solvated transition state is indicated by the high positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ (Table-3).

Multiple regression analysis (MRA) study: During the determination of the relationship between the independent variable [H$^+$] and dependent variable (pseudo-first-order variable rate constant k_1), for estimating whether the mechanism proposed is in accordance with the experimental kinetic data, the multivariate regression analysis was conducted using computer package STAT GRAPHICS. Using the multivariate regression analysis, the relationship between the concentration of H$^+$ and observed pseudo-first-order rate constant (k_1), without BG, was determined as:

$$k_1 = k\,[H^+]^{0.8} \tag{14}$$

where k is $3.79 \times 10^{-1}\ M^{-1} s^{-1}$. According to the R^2 statistics, the as-fitted model explained 96.35% of [H$^+$] variability. The value of adjusted R^2 statistics is 95.74%. The adjusted R^2 statistic is highly suitable for comparing models with different numbers of independent variables. The standard estimate error showed the standard residual deviation of of 0.083. This result supported the rate law validity presented in eqn. 10. The reactions proposed in the scheme were employed to calculate the rate on the basis of the multiple regression analysis by using eqn. 14. Thus, confirmed its validility. The rate law validity is presented in eqn. 10. The proposed mechanism of the reaction was proven using the similarity among the three rates (Table-3), namely calculated (from the rate law, k_{cal}), observed (experimental, k_{exp}) and predicted (from the multiple regression analysis, k_1) rates.

Comparative studies: Present experimental findings were compared with the results reported in literature for and non-catalysed BG oxidation by using CAT [29] in an acidic medium and the Pd(II)-catalyzed oxidation of triphenylmethane dyes, such as crystal violet (CV), *p*-Rosanilne and ethyl violet (EV) by employing CAT [28] in an alkaline medium. For the oxidant, the kinetic of zero order was observed in this study, that of the zero order [29] was observed in BG oxidation, that of the first order was observed in the Pd(II)-catalyzed oxidation of triphenyl methane dyes [28] by using CAT. The first-order kinetics reported previously [28,29] is similar to that obtained in this study for the used dye. For the medium, the kinetics of first order was observed for non-catalyzed BG oxidation, that of the fractional order oxidation was observed in this study and for the Pd(II)-catalyzed oxidation of triphenylmethane dyes by using CAT. Moreover, negligible impacts of [Cl$^-$] have been reported [28,29]. The same result was obtained in this study. The negligible effect of the ionic strength of reported medium [29] is similar to that reported in this study but different from that

obtained for Pd(II)-catalyzed oxidation of triphenylmethane dye by using CAT [28]. The dielectric constant negatively affected the reaction rate during BG oxidation through CAT and KIO$_3$. *p*-Toluenesulfonamide (PTS) addition, for triphenylmethane dyes, led to a delayed in the rate and showed no considerable effect on the rate of BG oxidation through CAT. From the presented activation energies and rate constants (Table-4), the order of relative reactivity of oxidants is as follows: KIO$_3$ for BG in acidic medium > CAT for BG in acidic medium > CAT for *p*-Rosanilne in the alkaline medium > CAT for CV in alkaline medium > CAT for EV in alkaline medium in the presence and absence of Pd(II). Studies conducted for triphenylmethane dyes by comparing the catalyzed and non-catalyzed reactions indicated that the catalyzed reactions are almost four-fold faster than the non-catalyzed reactions when all the remaining solution conditions were kept the constant (Table-5).

TABLE-5 CONSUMPTION OF KIO$_3$ IN THE OXIDATION OF BG IN ACIDIC MEDIUM AT 303 K				
[BG] × 10^5 (mol dm^{-3})	[KIO$_3$] × 10^4 (mol dm^{-3})			[KIO$_3$]:[BG]
	Initial	Final	Consumed	
0.50	5.00	4.49	0.51	1.02
1.00	10.00	8.96	1.04	1.04
3.00	30.00	26.94	3.06	1.02
[a]Experimental conditions: [HClO$_4$] = 1 × 10^{-3} mol dm^{-3}				

Conclusions

The following conclusions have been derived from the experimentally obtained kinetic data and spectroscopic information collected for the present investigation;

(i) The reactive species of potassium iodate oxidants considered as [IO$_3^-$].

(ii) Rate determining/slow step of the proposed reaction involves the interaction between a charged species and a neutral molecule of the reactants, resulting formation of activated complex C*, which is in tern it form more reactive complex C$_2$, then interaction of the C$_2$, with IO$_3^-$ give rise most reactive intermediate complex C$_3$ through fast steps and final products, all these species are well supported by (a) spectroscopic and kinetic data; (b) negative value of entropy of activation $\Delta S^{\#}$ (c) no effect of ionic strength (μ); and (d) the negative value of the dielectric effect of medium (*via* slop of linear line in the plot of log k_1 *versus* 1/D).

(iii) A first-order dependence on the rate of [BG], fractional order on [H$^+$], zero with respect to [KIO$_3$] and overall rate law and rate is as: rate (k_1) = k [BG] [H$^+$]$^{0.8}$

(iv) A positive values of Gibbs free energy of activation ($\Delta G^{\#}$) and enthalpy of activation ($\Delta H^{\#}$) indicate that transition state is highly solvated and endothermic nature over the studied temperature range of the process under investigation which reinforced the oxidation potential with rising temperature. This again ensures thermodynamic consistency of the proposed mechanism.

(v) Negative value of $\Delta S^{\#}$ suggested that during the course of present reaction, in rate determining step, the activated complex is neutral or singly charged (either + ve or - ve) species,

which dissociates into oppositely charged species or more than one smaller neutral molecules.

(vi) The oxidation products have been identified by TLC, column chromatography and GC-MS technique as *N,N*-diethyl-aminobenzophenone and *p-N,N*-diethylaminophenol and no further oxidation of these products have been found in present reaction conditions, also releasing no any harmful byproducts during course of above process which favoured its ecofriendly behaviour.

(vii) The smaller diameter (*i.e.* larger surface area) range of activated complex is $d_{AB} = 5.50$ nanometer, which also showed good agreement with the experimental findings.

(viii) The influence of co-contaminates/products studied by addition of $[Cl^-]$, acetonitrile and arylamide in reaction mixture has been showed insignificant effects and absence of free radicals.

(ix) Consistency in the values of three reaction rates (*i.e.* experimental k_{exp}, calculated k_{cal} and predicted from multiple regression analysis k_1) is well justified the validity of proposed reaction **Scheme-II**.

Considering above mechanism and the related rate law for oxidative degradation brilliant green (BG) dye by potassium iodate (KIO_3) showing an interesting option to degrade BG from effluent, so it can be implicated as a faster, simpler, effective, homogeneous, efficient, low-cost and modified kinetic method to remediate environmental water bodies from BG dye and other hazardous pollutants *via* this ecofriendly and greener way.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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