



Oxidative decolorization of triphenylmethane dyes by chloramine-T in alkaline medium catalyzed by Pd(II): A comparative spectrophotometric kinetic and mechanistic approach

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ARTICLE INFO

Article history:

Received 18 July 2008

Received in revised form

30 September 2008

Accepted 1 October 2008

Available online 14 October 2008

Keywords:

Triphenylmethane dyes

Chloramine-T

Pd(II) catalysis

Oxidation-kinetics

ABSTRACT

Triphenylmethane dyes viz., p-rosaniline, crystal violet and ethyl violet (henceforth abbreviated as Dye) have been extensively used as colorants in textile industries. Effluents containing these dyes released by the industry causes significant environmental problems. Hence decolorization of dye effluents has acquired increasing attention. The oxidative decolorization of these dyes is of greater significance one understanding of their kinetic and mechanistic aspects in redox reactions is important. Consequently, Pd(II) catalyzed kinetics and oxidative decolorization of p-rosaniline, crystal violet and ethyl violet dyes by chloramine-T (CAT) in NaOH medium were studied spectrophotometrically. The oxidation reaction follows the identical kinetics for all the three dyes and obeys the rate law: $\text{rate} = k[\text{CAT}]^a[\text{Dye}]^b[\text{OH}^-]^c[\text{Pd(II)}]^d$ where a and b are unity, and c and d are less than unity. Addition of p-toluenesulfonamide, the reduction product of CAT, retards the rate and the order was found to be less than unity. The reaction rate increased with increasing ionic strength of the medium. Addition of chloride ions show negligible effect on the rate of reaction. Oxidation products were characterized by GC-MS analysis. Proton-inventory studies with ethyl violet as a probe have been made in H₂O-D₂O mixtures. Activation parameters and decomposition constants have been deduced. An isokinetic relation is observed with $\beta = 423 \text{ K}$ indicating enthalpy as a controlling factor. The rate of oxidation of triphenylmethane dyes follows the order: p-rosaniline > crystal violet > ethyl violet. This trend may be attributed to inductive effects of alkyl amino groups. Further, the kinetics of Pd(II)-catalyzed oxidation of these dyes have been compared with uncatalyzed reactions (in the absence of Pd(II) catalyst) and found that the catalyzed reactions are nearly four times faster. The catalytic constant (K_C) for Pd(II) was also calculated for each dye at different temperatures and the values of activation parameters with respect to the catalyst have been evaluated. Chlorite ion (OCl^-) has been postulated as the reactive oxidizing species. The observed results have been explained by a general mechanism, and the related rate law has been obtained. Furthermore, the simple and elegant method developed for the decolorization of triphenylmethane dyes in the present work can be adopted for treating the aforesaid dyes present in industrial effluents to minimize the toxicity caused by these dyes.

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1. Introduction

The diverse nature of the chemistry of N-metallo 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 [1]. As a result, these reagents react with a wide range of functional groups affecting an array of molecular transformations. Sodium N-chloro

p-toluenesulfonamide (p-CH₃C₆H₄SO₂NCINa·3H₂O), well known as chloramine-T (CAT), is a very important member of this class of compounds. Generally, CAT undergoes a two electron change in its reactions, the products being p-toluenesulfonamide and sodium chloride [2,3]. CAT is a source of positive halogen and this reagent has been exploited as oxidant for a variety of substrates in both acidic and alkaline medium [1,4–10]. The nature of active oxidizing species and mechanism depends on the nature of halogen atom, the groups attached to the nitrogen and reaction conditions. The species responsible for such oxidizing character may be different depending on the pH of the medium. The redox potential of the system is pH dependent [3] and decreases with increase in pH of the

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medium (1.138, 0.778, 0.614 and 0.50 V at pH 0.65, 7.00, 9.70 and 12.0, respectively). Extensive literature survey reveals that there are very few reports on the kinetics of oxidation of organic dyes by CAT [11–13]. Interestingly, no information is available about the oxidative behaviour of any N-haloamines towards triphenylmethane dyes from the view point of their kinetic and mechanistic aspects. In this background, it was considered to be desirable to study the oxidation chemistry of triphenylmethane dyes brought about by CAT to explore the kinetic and mechanistic features of these redox reactions.

Dyes are classified as azo dyes, triarylmethane dyes, anthroquinone dyes, nitro dyes and indigo dyes according to the type of chromophores present in their structures. Triphenylmethane dyes are important groups of triarylmethane dyes, in which a central carbon is bonded to three aromatic rings, one of which is in the quinoid form (the chromophore) and the auxochromes are $-NH_2$, $-NR_2$, etc. In general, triphenylmethane dyes, besides their many uses as coloring matters, find use in medicine since they are bactericidal. Triphenylmethane dye derivatives viz., p-rosaniline, crystal violet and ethyl violet have been widely used as coloring agents in textile industries, leather dyeing, paper printing, photography, food industries, cosmetic industries and as a biological stain [14,15].

Effluents streams containing these dyes discharged by various dyeing industries causes significant environmental problems. With this view, several photocatalytic degradation procedures for the decolorization of these three dyes have been reported in the literature [15–17]. In spite of the available procedures, still there is a need for simple method, which offers advantages such as cost effectiveness, non-toxic and environmentally benign. In the light of the above considerations, we have undertaken a detailed study on the kinetics and mechanism of the oxidative decolorization reaction of p-rosaniline, crystal violet and ethyl violet with CAT in NaOH medium and Pd(II) catalyst. Consequently, the redox system developed can be adopted for treating these dyes present in industrial effluents to reduce the toxicity caused by dyes.

Platinum group metal ion catalyzed reactions have evinced prodigious interest because of their involvement in many important industrial processes such as oxidation, reduction, halogenation and alkylation of organic compounds [18,19]. Consequently, in recent years platinum group metal ions like Ru(III), Os(VIII), Ir(III), Rh(III) and Pd(II) are widely employed as catalysts because these elements show strong catalytic influence in many reactions. The use of palladium(II) chloride as a homogeneous catalyst has been reported by several workers [20–24]. In some cases the inhibition action has also been observed. In the present case, the catalytic effect of Pd(II) has been observed on the rate of oxidation of triphenylmethane dyes by CAT in alkaline medium. However, literature survey has revealed that there are no efforts being made so far from the kinetic and mechanistic view points of Pd(II) catalysis in CAT oxidation of organic dyes. Preliminary experimental results revealed that the reactions of chosen triphenylmethane dyes with CAT in NaOH medium in absence of catalyst were sluggish, but the reactions became facile in the presence of traces of Pd(II) catalyst. These facts stimulated our interest to carryout a detailed kinetic study on the Pd(II) catalyzed oxidation of the triphenylmethane dyes viz., p-rosaniline, crystal violet and ethyl violet by CAT in alkaline medium to explore the mechanistic aspects of the redox reactions. Such studies also highlight the role of Pd(II) in these oxidation reactions.

In the light of the above considerations, we report herein, the hitherto unreported results on the oxidation and mechanistic aspects of aforesaid dyes by CAT in presence of NaOH and Pd(II) catalyst. The main target of the present investigations are to: (i) elucidate a suitable mechanism, (ii) design a rigorous kinetic model,

(iii) asses relative reactivity of the dyes studied, (iv) ascertain the reactive species, (v) identify the oxidation products, (vi) compute thermodynamic parameters and isokinetic relationship, (vii) find the catalytic efficiency of Pd(II), (viii) compare the catalyzed reactivity with that of uncatalyzed one, and (ix) establish optimum condition to develop a simple procedure for the decolorization of these dyes.

2. Experimental

2.1. Materials

CAT (E-merk) was purified by the method of Morris et al. [25]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored stoppered bottles until further use. The concentrations of stock solutions were periodically determined. P-rosaniline and crystal violet (Sd. Fine-Chem Ltd., India), and ethyl violet (Sigma) were of acceptable grades of purity and used as received. Fresh aqueous solutions of dyes were prepared whenever required. A stock solution of PdCl₂ (Lancaster, England) was prepared by dissolving the sample in 0.1 mol dm⁻³ HCl. An allowance was made for the amount of HCl present in catalyst solution, while preparing for kinetic runs. Solvent isotope studies were made with D₂O (99.4%) supplied by the Bhabha Atomic Research Centre, Mumbai, India. All other chemicals used were of AnalaR grade and all solutions were prepared using double distilled water.

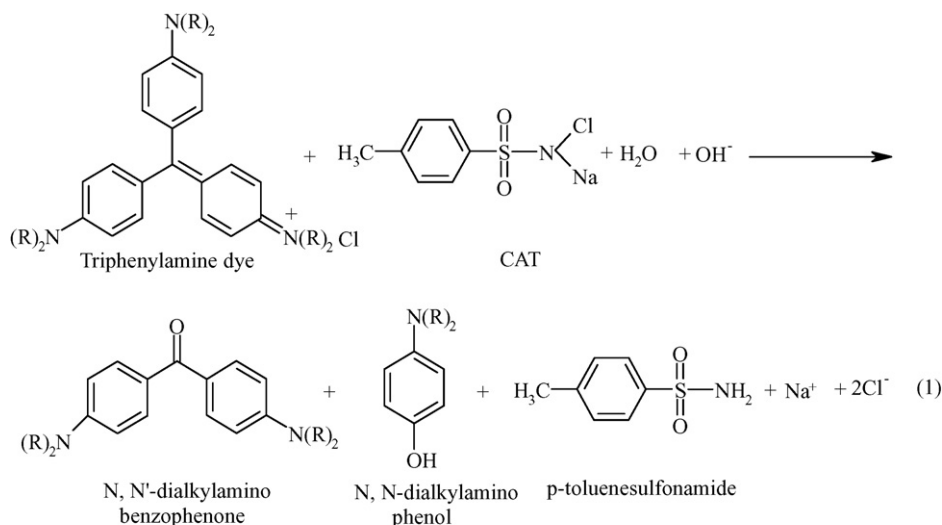
2.2. Kinetic measurement

The detailed kinetic runs were performed under pseudo-first-order conditions with a known excess of the [CAT]₀ over [Dye]₀ at 303 K using a UV-visible spectrophotometer (Digital Spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were carried out between 293 and 313 K. For this purpose, a Raaga Ultra Cold Chamber with digital temperature control (India) was used. A constant temperature was maintained with an accuracy of ± 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 dye, NaOH, Pd(II) and NaClO₄ solutions and water (to keep the total volume constant for all runs) were taken in separate tubes were thermostatted for 30 min at 303 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, 4 ml aliquot of the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at $\lambda_{max} = 546$ nm for p-rosaniline, 590 nm for crystal violet and 596 nm for ethyl violet for nearly three half-lives. The absorbance readings at $t=0$ and $t=t$ are D_0 and D_t . Plots $\log D_0/D_t$ versus time were made to evaluate the pseudo-first-order rate constants (k') which were found reproducible within $\pm 6\%$. Regression analysis of the experimental data was carried out on an $f_x - 100$ W scientific calculator to evaluate the regression coefficient, r .

2.3. Stoichiometry

Various ratios of the dye to CAT were equilibrated in presence of 1.0×10^{-3} mol dm⁻³ NaOH and 7.0×10^{-5} mol dm⁻³ Pd(II) catalyst for 24 h at 303 K. Determination of unreacted CAT in the reaction mixture showed that one mole of the dye consumed one mole of CAT in each case, confirming the following stoichiometry:



Here, R = -H for p-rosaniline, -CH₃ for crystal violet and -CH₂CH₃ for ethyl violet.

2.4. Characterization of products

The reaction mixture in the stoichiometric ratio in presence of NaOH and Pd(II) catalyst under stirred condition was allowed to progress for 24 h at 303 K. After completion of the reaction, the reaction mixture was neutralized with dilute HCl and the products were extracted with ethyl acetate. The organic products were identified by using TLC technique and separated by column chromatography. The purified compounds were recrystallized by methanol. The reduction product of CAT, p-toluenesulfonamide was identified [9] by paper chromatography using PhCH₂OH saturated with H₂O as the solvent with 0.5% vanillin in 1% HCl solution in EtOH as the spray reagent ($R_f = 0.905$).

The oxidation products of p-rosaniline were identified as N,N'-diamino benzophenone and p-aminophenol and for crystal violet were N,N'-dimethylamino benzophenone and p-N,N-dimethyl aminophenol. N,N'-diethylamino benzophenone and p-N,N-diethyl aminophenol were found to be the oxidation products of ethyl violet. These compounds were confirmed by gas chromatography coupled with mass spectral techniques. The mass spectra showed a molecular ion peak at 212, 109, 268, 137, 324 and 165 amu, clearly confirming N,N'-dimethylamino benzophenone, p-aminophenol, N,N'-dimethylamino benzophenone, p-N,N-dimethyl aminophenol, N,N'-diethyl amino benzophenone and p-N,N-diethyl aminophenol, respectively. It was also observed that there was no further oxidation of these products under the present reaction conditions.

3. Results and discussion

The detailed kinetic investigations were performed under pseudo-first-order conditions of $[CAT]_0 \gg [Dye]_0$. The kinetics of oxidation of triphenylmethane dyes (here after abbreviated as Dye) p-rosaniline, crystal violet and ethyl violet have been investigated with several initial concentrations of the reactants in the presence of NaOH and Pd(II) catalyst at 303 K. The similar oxidation behaviour was observed for all the three dyes studied in the present case.

3.1. Effect of reactant concentrations on the rate

With the oxidant in excess, at constant $[CAT]_0$, $[NaOH]$, $[Pd(II)]$, $[NaClO_4]$ and temperature, plots of log (absorbance) versus time

were linear ($r > 0.9880$), indicating a first-order dependence on the rate of $[Dye]_0$. The values of pseudo-first-order rate constants ($k' s^{-1}$) were listed in Table 1. Further, k' did not change with the change in $[Dye]_0$, confirming the first-order dependence on $[Dye]_0$. Under the same experimental conditions, an increase in $[CAT]_0$ increased the k' value (Table 1). Plots of $\log k'$ versus $\log [CAT]$ were linear ($r > 0.9976$) with unit slopes, showing a first-order dependence of the rate on $[CAT]_0$.

3.2. Effect of NaOH and Pd(II) concentrations on the rate

The rate increased with an increase in $[NaOH]$ (Table 2) and plots of $\log k'$ versus $\log [NaOH]$ were linear ($r > 0.9963$) with fractional slopes (0.74–0.82), showing a fractional-order dependence of the rate on $[NaOH]$. The reaction rate increased with increase in $[Pd(II)]$ (Table 2). Plots of $\log k'$ versus $\log [Pd(II)]$ were linear ($r > 0.9952$) with fractional slopes (0.64–0.84), confirming fractional-order dependence on $[Pd(II)]$.

3.3. Effect of p-toluenesulfonamide concentration on the rate

Addition of p-toluenesulfonamide ($ArNH_2$) to the reaction mixture retards the rate (Table 3). Plots of $\log k'$ versus $\log [ArNH_2]$ were linear ($r > 0.9881$) with negative slopes (0.16–0.30), indicating a negative fractional-order dependence on $[ArNH_2]$. It indicates

Table 1
Effect of reactant concentrations on the rate of reaction at 303 K^a.

$[CAT]_0 \times 10^3$ (mol dm ⁻³)	$[Dye]_0 \times 10^4$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)		
		p-rosaniline	Crystal violet	Ethyl violet
1.0	5.0	4.06	1.53	0.63
3.0	5.0	11.5	4.58	2.14
5.0	5.0	16.7	8.37	3.63
7.0	5.0	26.5	12.0	5.37
9.0	5.0	33.0	16.7	6.94
5.0	3.0	16.6	8.26	3.83
5.0	4.0	15.3	8.31	3.70
5.0	5.0	16.7	8.37	3.63
5.0	6.0	16.6	7.67	3.83
5.0	7.0	15.5	8.95	3.54

^a Experimental conditions: $[NaOH] = 1.0 \times 10^{-3}$ mol dm⁻³; $[Pd(II)] = 7.0 \times 10^{-5}$ mol dm⁻³; $\mu = 0.2$ mol dm⁻³.

Table 2
Effect of NaOH and Pd(II) concentrations on the rate of reaction at 303 K^a.

[NaOH] × 10 ³ (mol dm ⁻³)	[Pd(II)] × 10 ⁵ (mol dm ⁻³)	k' × 10 ⁴ (s ⁻¹)		
		p-rosaniline	Crystal violet	Ethyl violet
0.5	7.0	8.67	5.37	1.91
0.7	7.0	11.5	7.02	2.74
1.0	7.0	16.7	8.37	3.63
1.5	7.0	22.1	11.5	4.98
2.0	7.0	29.6	14.0	6.77
1.0	3.0	9.29	4.33	1.85
1.0	5.0	12.9	6.39	2.79
1.0	7.0	16.7	8.37	3.63
1.0	9.0	19.7	10.3	4.48
1.0	11.0	23.0	12.4	5.65

^a Experimental conditions: [CAT]₀ = 5.0 × 10⁻³ mol dm⁻³; [Dye]₀ = 5.0 × 10⁻⁴ mol dm⁻³; μ = 0.2 mol dm⁻³.

the involvement of ArNH₂ in a pre-equilibrium step prior to the rate-limiting step.

3.4. Effect of ionic strength on the rate

The effect of ionic strength (μ) of the medium was studied at 0.20 mol dm⁻³ by adding requisite amounts of NaClO₄, with all other experimental conditions held constant. The rate of the reaction increased with increase in ionic strength of the medium. The rate constants at 0.2 mol dm⁻³ NaClO₄ were found to be 16.7, 8.34 and 3.63 × 10⁻⁴ s⁻¹, whereas k' values in absence of the added electrolyte were found to be 13.9, 6.79 and 2.55 × 10⁻⁴ s⁻¹ for p-rosaniline, crystal violet and ethyl violet, respectively. This suggests the involvement of ionic species in the rate-limiting step of the proposed mechanism (Scheme 2). Hence, the ionic strength of the system was maintained at a constant value of 0.20 mol dm⁻³ using a concentrated solution of NaClO₄ for all kinetic runs in order to swamp the reaction.

3.5. Effect of chloride ion on the rate

Addition of Cl⁻ ions in the form of NaCl (1.0 × 10⁻³ to 3.0 × 10⁻³ mol dm⁻³) has negligible effect on the rate. It indicates that no free chlorine is formed in the reaction.

3.6. Effect of solvent isotope on the rate

Solvent isotope studies were made in D₂O medium, with ethyl violet as a probe. Values of k'(H₂O) and k'(D₂O) were 3.64 × 10⁻⁴ and 6.72 × 10⁻⁴ s⁻¹, giving a solvent isotope effect, k'(H₂O)/k'(D₂O) = 0.54. Proton-inventory studies were made with the same probe using H₂O–D₂O mixtures containing different atom fractions n of deuterium (Table 4).

Table 3
Effect of p-toluenesulfonamide concentration on the rate of reaction at 303 K^a.

[PTS] × 10 ³ (mol dm ⁻³)	k' × 10 ⁴ (s ⁻¹)		
	p-rosaniline	Crystal violet	Ethyl violet
1.0	13.9	7.67	3.31
3.0	9.87	6.71	2.68
5.0	8.17	6.07	2.33
7.0	6.52	5.65	2.10

^a Experimental conditions: [CAT]₀ = 5.0 × 10⁻³ mol dm⁻³; [Dye]₀ = 5.0 × 10⁻⁴ mol dm⁻³; [NaOH] = 1.0 × 10⁻³ mol dm⁻³; [Pd(II)] = 7.0 × 10⁻⁵ mol dm⁻³; μ = 0.2 mol dm⁻³.

Table 4
Proton-inventory studies for ethyl violet in H₂O–D₂O mixtures at 303 K^a.

H ₂ O–D ₂ O mixture (v/v)	Atom fraction of deuterium (n)	k' _n × 10 ⁴	(k' ₀ /k' _n) ^{1/2}
0	0.000	3.64	1.0000
25	0.248	4.47	0.9022
50	0.497	5.12	0.8432
75	0.745	5.85	0.7886
100	0.994	6.72	0.7362

^a Experimental conditions: [CAT]₀ = 5.0 × 10⁻³ mol dm⁻³; [Dye]₀ = 5.0 × 10⁻⁴ mol dm⁻³; [NaOH] = 1.0 × 10⁻³ mol dm⁻³; [Pd(II)] = 7.0 × 10⁻⁵ mol dm⁻³; μ = 0.2 mol dm⁻³.

3.7. Effect of temperature on the rate

The reaction was carried out at five different temperatures (293, 298, 303, 308 and 313 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log k' versus 1/T (r > 0.9972), activation energy (E_a) and other activation parameters (ΔH[‡], ΔS[‡], ΔG[‡] and log A) for the overall reaction have been computed. The rate constants at different temperatures and the calculated activation parameters are given in Table 5.

3.8. Polymerization study

Addition of the reaction mixture to the acrylamide monomer did not initiate polymerization indicating the absence of any free radicals produced during the course of reaction.

3.9. Reactive species of CAT

CAT (ArNCINa) acts as an oxidizing agent in both acidic and alkaline media. CAT behaves as a strong electrolyte in aqueous solutions and depending on the pH of the medium, CAT furnishes different types of reactive species (Eqs. (2–8)) in solutions [25–28].

**Table 5**
Effect of temperature and values of activation parameters for the oxidation of triphenylmethane dyes by CAT in the presence and absence of Pd(II) catalyst^a.

Temperature (K)	k' × 10 ⁴ (s ⁻¹)		
	p-rosaniline	Crystal violet	Ethyl violet
293	9.32 (1.72)	4.33 (0.66)	1.91 (0.51)
298	13.4 (2.76)	6.40 (1.23)	2.79 (0.76)
303	16.7 (3.83)	8.37 (1.84)	3.63 (0.95)
308	21.9 (6.82)	11.2 (2.59)	5.65 (1.53)
313	30.7 (8.95)	16.4 (4.04)	7.42 (2.19)
E _a (kJ mol ⁻¹)	41.7 (62.1)	50.5 (66.9)	57.4 (68.8)
ΔH [‡] (kJ mol ⁻¹)	39.2 (59.6)	48.0 (64.3)	54.8 (66.3)
ΔG [‡] (kJ mol ⁻¹)	90.2 (93.7)	92.3 (95.9)	94.0 (97.2)
ΔS [‡] (J K ⁻¹ mol ⁻¹)	-168(-112)	-146(-104)	-129(-101)
Log A	4.43 (7.34)	5.65 (7.79)	6.48 (7.90)

Values in the parentheses refer to the oxidation of dyes by CAT in absence of Pd(II)catalyst. Experimental conditions are same as catalyzed reactions without Pd(II) catalyst.

^a Experimental conditions for catalyzed reactions: [CAT]₀ = 5.0 × 10⁻³ mol dm⁻³; [Dye]₀ = 5.0 × 10⁻⁴ mol dm⁻³; [NaOH] = 1.0 × 10⁻³ mol dm⁻³; [Pd(II)] = 7.0 × 10⁻⁵ mol dm⁻³; μ = 0.2 mol dm⁻³.

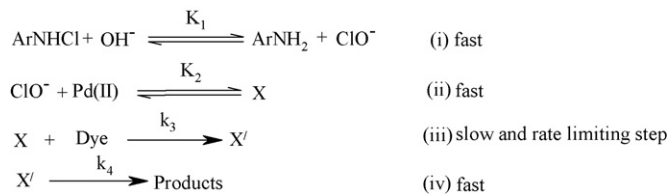


(Here Ar = CH₃C₆H₄SO₂⁻)

The possible oxidizing species in acidified CAT solutions are the conjugate acid ArNHCl, the dichloramine ArNCl₂, the hypochlorous acid HOCl and possibly H₂O⁺Cl. In alkaline solutions of CAT, ArNCl₂ and HOCl do not exist [29]. Hardy and Johnston [27] calculations have indicated that there is a considerable concentration of PhSO₂NHBr even in alkaline bromamine solutions. Because organic haloamines have similar chemical properties, we perhaps can extend the same argument to CAT also. Hence, it is likely that the predominant species in alkaline solutions of CAT are ArNHCl and ClO⁻. The rate is retarded by the reaction product, p-toluenesulfonamide (ArNH₂) indicating that it is involved in a pre-equilibrium step. The observed fractional-order dependence of rate on [OH⁻] and negative fractional-order dependence on [ArNH₂] can be rationalized by the mechanism shown in Scheme 1.

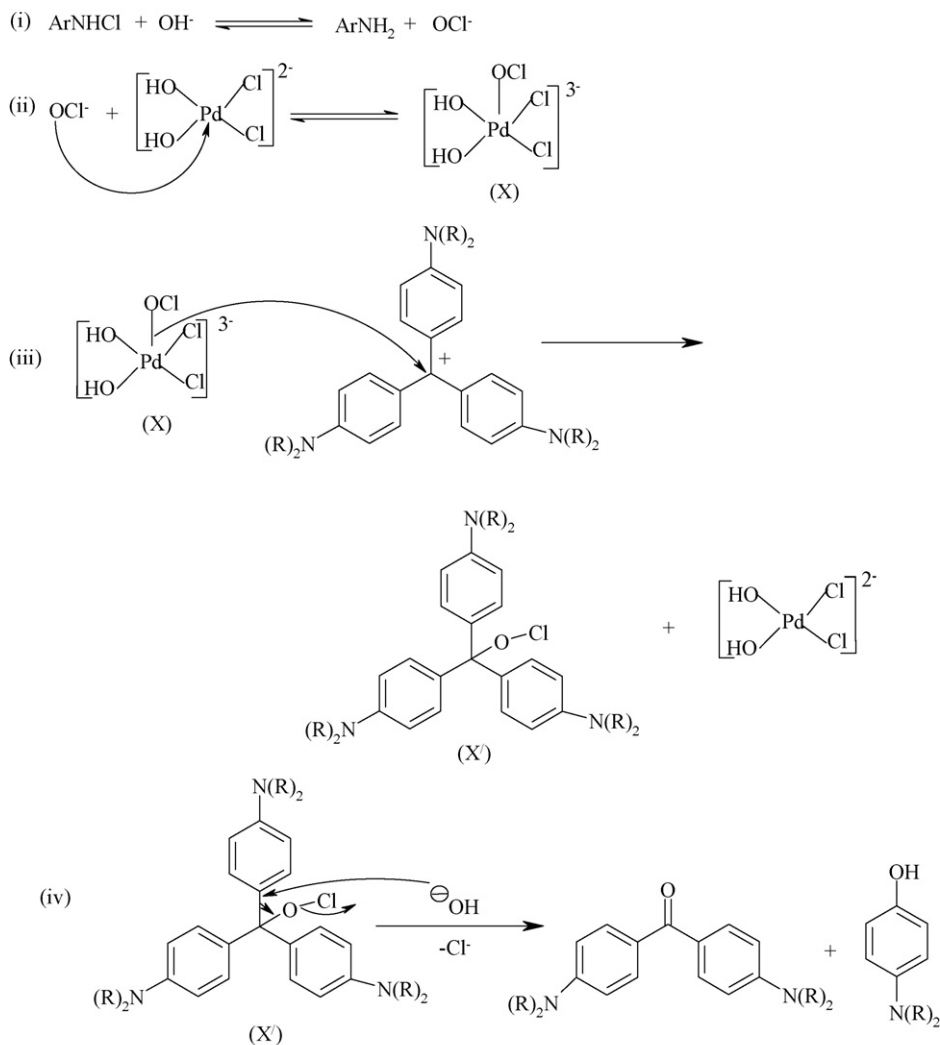
3.10. Reactive species of Pd(II) catalyst

Palladium(II) chloride catalysis and inhibition reactions have been reported in various redox reactions [20–24]. The redox reactions in the presence of Pd(II) have also shown a complex kinetics.



Scheme 1. A general scheme for the Pd(II) catalyzed oxidation of triphenylmethane dyes by CAT in alkaline medium.

Generally, the palladium complexes are somewhat less stable from both kinetic and thermodynamic sense, than their platinum analogs. It is known to form different complexes in alkaline solutions [22,30–32] and the possible complex species are [Pd(OH)Cl₃]²⁻, [Pd(OH)₂Cl₂]²⁻ and [Pd(OH)₄]²⁻. The species [Pd(OH)₄]²⁻ is not commonly found as it is insoluble. Further, the rate increases with increase in [OH⁻] and there was no effect of [Cl⁻] on the rate of reaction. This clearly rules out [Pd(OH)Cl₃]²⁻ species. In view of these facts, we assumed [Pd(OH)₂Cl₂]²⁻ complex ion as the reactive catalyst species in the present case. Existence of similar species has been employed in our earlier redox reaction involving Pd(II) catalysis [32].



Here, R = -H for p-rosaniline, R = -CH₃ for crystal violet and R = -C₂H₅ for ethyl violet

Scheme 2. Mechanistic interpretation for the Pd(II) catalyzed oxidation of triphenylmethane dyes by CAT in alkaline medium.

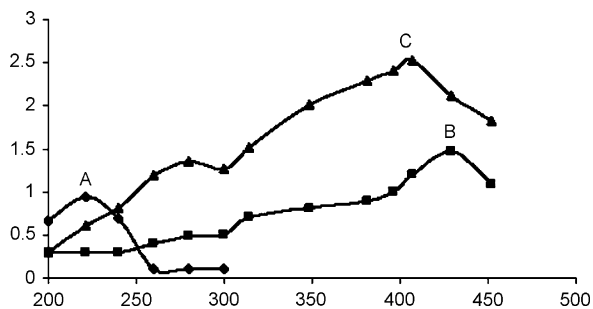


Fig. 1. UV-visible spectra of CAT (A), Pd(II) (B) and Pd(II)-CAT (C) complex.

3.11. Reaction scheme

Spectroscopic evidence for the complex formation between oxidant and catalyst was obtained from UV-visible spectra of CAT, PdCl₂ and the mixture of both. Absorption maxima in an aqueous medium appear at 220 nm for CAT, 429 nm for PdCl₂ in aqueous alkaline medium, and 407 nm for their mixture (Fig. 1). A hypsochromic shift of 22 nm from 429 to 407 nm of PdCl₂ suggests that the complexation reaction between CAT and PdCl₂ in the present case.

Considering the above facts and all the experimental results, the following reaction mechanism (Scheme 1) may be suggested for Pd(II) catalyzed oxidation of triphenylmethane dyes by CAT in alkaline medium.

In Scheme 1, X and X' represent complex intermediate species whose structures are shown in Scheme 2, where a detailed mechanistic interpretation of Pd(II) catalyzed oxidation of triphenylmethane dyes brought about by CAT in alkaline medium is depicted.

In a fast pre-equilibrium step (step (i)), the conjugate acid of CAT, ArNHCl interacts with hydroxyl ion to give the reactive oxidizing species, chlorite ion (ClO⁻) with the elimination of p-toluenesulfonamide (ArNH₂). This negatively charged chlorite ion combine with the metal centre of the active catalyst species, [Pd(OH)₂Cl₂]²⁻ and forms a metal complex anion X in a fast pre-equilibrium step (step (ii)). In the next slow/rate-limiting step, the lone pair of the oxygen atom of the metal complex anion attacks the carbocation centre of the substrate forms another intermediate species X' with the regeneration of catalyst [Pd(OH)₂Cl₂]²⁻. This complex X' in presence of OH⁻ ion undergoes decomposition with the loss of Cl⁻ to yield the final products.

3.12. Kinetic modeling

The total effective concentration of CAT is [CAT]_t, then

$$[\text{CAT}]_t = [\text{ArNHCl}] + [\text{ClO}^-] + [\text{X}] \quad (9)$$

Solving for [ArNHCl] and [ClO⁻] from steps (i) and (ii) of Scheme 1, one obtains:

$$[\text{ArNHCl}] = \frac{[\text{ArNH}_2][\text{X}]}{K_1 K_2 [\text{OH}^-][\text{Pd(II)}]} \quad (10)$$

$$[\text{ClO}^-] = \frac{[\text{X}]}{K_2 [\text{Pd(II)}]} \quad (11)$$

by substituting for [ArNHCl] and [ClO⁻] from Eqs. (10) and (11), respectively into Eq. (9) and solving for [X], we get:

$$[\text{X}] = \frac{K_1 K_2 [\text{CAT}]_t [\text{OH}^-][\text{Pd(II)}]}{[\text{ArNH}_2] + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{Pd(II)}]} \quad (12)$$

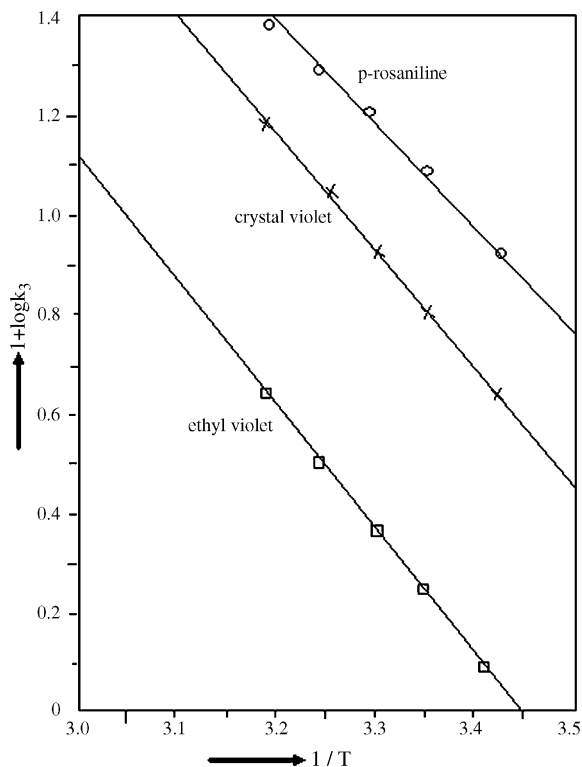


Fig. 2. Arrhenius plots of log k_3 versus $1/T$. Experimental conditions are as in Table 6.

From the slow and rate-limiting step (iii) of Scheme 1,

$$\text{rate} = k_3 [\text{X}][\text{Dye}] \quad (13)$$

By substituting for [X] from Eq. (12) into Eq. (13), the following rate law is obtained:

$$\text{rate} = \frac{K_1 K_2 k_3 [\text{CAT}]_t [\text{Dye}][\text{OH}^-][\text{Pd(II)}]}{[\text{ArNH}_2] + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{Pd(II)}]} \quad (14)$$

Rate law (14) is in accordance with the observed kinetic data.

Since $\text{rate} = k' [\text{CAT}]_t$, Eq. (14) can be transformed as

$$k' = \frac{K_1 K_2 k_3 [\text{Dye}][\text{OH}^-][\text{Pd(II)}]}{[\text{ArNH}_2] + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{Pd(II)}]} \quad (15)$$

$$\frac{1}{k'} = \frac{[\text{ArNH}_2]}{K_1 K_2 k_3 [\text{Dye}][\text{OH}^-][\text{Pd(II)}]} + \frac{1}{K_2 k_3 [\text{Dye}][\text{Pd(II)}]} + \frac{1}{k_3 [\text{Dye}]} \quad (16)$$

$$\frac{1}{k'} = \frac{1}{[\text{Pd(II)}]} \left\{ \frac{[\text{ArNH}_2]}{K_1 K_2 k_3 [\text{Dye}][\text{OH}^-]} + \frac{1}{K_2 k_3 [\text{Dye}]} \right\} + \frac{1}{k_3 [\text{Dye}]} \quad (17)$$

According to Eq. (17), in order to deduce decomposition constants (k_3) and activation parameters for rate-limiting step, the reaction has been studied in presence of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ p-toluenesulfonamide by varying [Pd(II)] in the temperature range of 293–313 K. From the intercepts of plots of $1/k'$ versus $1/[\text{Pd(II)}]$ ($r > 0.9891$) at each temperature, the values of decomposition constants for the rate-limiting step of the reaction were obtained. The activation parameters for the rate-limiting steps were deduced from plots of $\log k_3$ versus $1/T$ (Fig. 2; $r > 0.9952$) for each dye. All these data are tabulated and given in Table 6.

The proposed mechanism and the derived rate law are supported by the following experimental findings:

Table 6

Values of decomposition constants (k_3) at different temperatures and activation parameters for rate-limiting step calculated using k_3 values^a.

Temperature (K)	k_3 (s ⁻¹)		
	p-rosoaniline	Crystal violet	Ethyl violet
293	0.86	0.46	0.12
298	1.29	0.65	0.17
303	1.58	0.84	0.22
308	1.90	1.09	0.29
313	2.38	1.55	0.42
E_a (kJ mol ⁻¹)	41.4	48.4	51.0
ΔH^\ddagger (kJ mol ⁻¹)	38.9	47.8	50.4
ΔG^\ddagger (kJ mol ⁻¹)	73.1	77.9	82.3
ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	-112	-99.0	-105
Log A	7.33	8.28	8.15

^a Experimental conditions: [CAT]₀ = 5.0 × 10⁻³ mol dm⁻³; [Dye]₀ = 5.0 × 10⁻⁴ mol dm⁻³; [NaOH] = 1.0 × 10⁻³ mol dm⁻³; [Pd(II)] = 7.0 × 10⁻⁵ mol dm⁻³; [ArNH₂] = 1.0 × 10⁻³ mol dm⁻³; μ = 0.2 mol dm⁻³.

3.13. Proton-inventory studies

The proposed mechanism is also supported by the enhancement of rate in D₂O medium since OD⁻ ion a stronger base [33,34] than OH⁻ and implying fast pre-equilibrium hydroxyl ion transfer with specific base catalysis (step (i) of Scheme 1). The dependence of rate constant k'_n on n , the atom fraction of deuterium, in a solvent mixture containing H₂O and D₂O, is given [35,36] by Eq. (18):

$$\frac{k'_0}{k'_n} = \frac{\prod^{TS}(1-n+n\Phi_i)}{\prod^{RS}(1-n+n\Phi_j)} \quad (18)$$

Here Φ_i and Φ_j are the isotopic fractionation factors for isotopically exchangeable hydrogenic sites in the transition and reactant states, respectively. If it assumed that the reaction proceeds through a single transition state, Eq. (18) can be transformed into Eq. (19):

$$\left(\frac{k'_0}{k'_n}\right)^{1/2} = [1 + n(\Phi_j - 1)] \quad (19)$$

Eq. (19) indicates a linear relation between $(k'_0/k'_n)^{1/2}$ and n which is shown in Fig. 3 ($r = 0.9904$). The slope $(\Phi_j - 1) = -0.27$, from which the fractionation factor n is found to be 0.73. Kresge and Allred [37] obtained a value of 0.80 through NMR studies for the isotopic fractionation factor of OH⁻, and this was confirmed by Gold and Grist [38]. Considering the diversity of procedures employed, there is good agreement between the present and values reported for the fractionation factor of OH⁻. Hence, the formation of a simple transition state involving the participation of OH⁻ is supported.

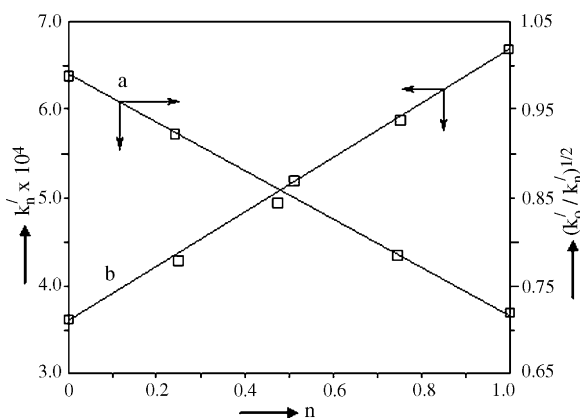


Fig. 3. Proton-inventory plots for the Pd(II) catalyzed oxidation of ethyl violet by CAT in H₂O–D₂O mixture. Experimental conditions are as in Table 4.

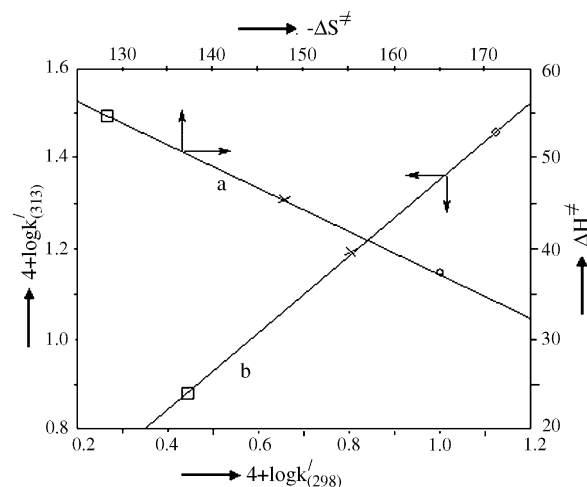


Fig. 4. Isokinetic plots of (a) ΔH^\ddagger versus $-\Delta S^\ddagger$ and (b) $\log k'_{(313K)}$ versus $\log k'_{(298K)}$. Experimental conditions are as in Table 5.

3.14. Isokinetic relationship

The moderate energy of activation found to support the proposed mechanism. The activation energy is highest for the slowest reaction and *vice-versa* (Table 6) indicating that the reaction is enthalpy controlled. This is ascertained by calculating the isokinetic temperature (β) from the slope of the linear plot of ΔH^\ddagger versus ΔS^\ddagger (Fig. 4; $r = 0.9999$). β is found to be 412 K. Further verification of the isokinetic relationship has been done by Exner criterion [39] by plotting $\log k'_{(313K)}$ versus $\log k'_{(298K)}$ (Fig. 4; $r = 0.9993$). The value of β was calculated from the equation $\beta = T_1 T_2 (q - 1) / (q T_2 - T_1)$, where q is the slope of the Exner plot. The value of β from this plot is 423 K, which is in agreement with the β calculated from ΔH^\ddagger versus ΔS^\ddagger relation. The values of β obtained from both the plots are much higher than the temperature range (293–313 K) employed in the present work indicates the enthalpy controlled pathways for the oxidation of triphenylmethane dyes by CAT and also signifies that all the three dyes are oxidized by a similar mechanism. Further, the large negative values of ΔS^\ddagger indicate the formation of a rigid associative transition state with few degrees of freedom in each case.

3.15. Relative reactivity of dyes

Data in Table 5 reveals that the rate of oxidation of triphenylmethane dyes by CAT in presence of NaOH and Pd(II) catalyst increased in the order: p-rosoaniline > crystal violet > ethyl violet. This trend may be attributed mainly to inductive effect of the alkyl amino groups. The hydrogen, methyl and ethyl groups present on amino group at para positions increase the stability of the tertiary carbocation by dispersing the positive charge and stabilizing the carbocation. The dispersive power of the groups increases in the order $-\text{N}(\text{C}_2\text{H}_5)_2 > -\text{N}(\text{CH}_3)_2 > -\text{NH}_2$, the stability of the carbocation also increases in the similar trend. Since the stability of carbocation increases in the order $-\text{N}(\text{C}_2\text{H}_5)_2 > -\text{N}(\text{CH}_3)_2 > -\text{NH}_2$, the reactivity decreases and hence the observed order of reactivity commensurate with the experimental observation, i.e., p-rosoaniline > crystal violet > ethyl violet.

3.16. Comparison of Pd(II) catalyzed and uncatalyzed reactions

It was thought worthwhile to compare the reactivity of these three triphenylmethane dyes with CAT in the absence of Pd(II) catalyst under identical experimental conditions in order to eval-

Table 7

Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values^a.

Temperature (K)	K_C (s^{-1})		
	p-rosaniline	Crystal violet	Ethyl violet
293	0.35	0.57	0.45
298	0.49	0.81	0.66
303	0.59	1.03	0.87
308	0.70	1.37	1.34
313	1.01	1.96	1.71
E_a ($kJ\ mol^{-1}$)	36.8	44.5	47.8
ΔH^\ddagger ($kJ\ mol^{-1}$)	34.2	42.0	45.3
ΔG^\ddagger ($kJ\ mol^{-1}$)	75.7	74.0	74.4
ΔS^\ddagger ($J\ K^{-1}\ mol^{-1}$)	-136	-105	-96.1
LogA	6.12	7.70	8.21

^a Experimental conditions: $[CAT]_0 = 5.0 \times 10^{-3}\ mol\ dm^{-3}$; $[Dye]_0 = 5.0 \times 10^{-4}\ mol\ dm^{-3}$; $[Pd(II)] = 7.0 \times 10^{-5}\ mol\ dm^{-3}$; $\mu = 0.2\ mol\ dm^{-3}$; $[NaOH] = 1.0 \times 10^{-3}\ mol\ dm^{-3}$.

uate the catalytic efficiency of Pd(II). Consequently, the reactions were studied at different temperatures (293–313 K) and from the Arrhenius plots of $\log k'$ versus $1/T$ ($r > 0.9950$), values of activation parameters for the uncatalyzed reactions were computed (Table 5). The rate of oxidation of triphenylmethane dyes in the absence of Pd(II) catalyst was found to be in the order: p-rosaniline > crystal violet > ethyl violet. A similar trend results in the presence of Pd(II) catalyst also. However, the Pd(II) catalyzed reactions were found to about four times faster than the uncatalyzed reactions. This was also confirmed by the activation parameters calculated (Table 5). Thus the observed rates of oxidation of triphenylmethane dyes by CAT in the presence of Pd(II) catalyst justify the need of a catalyst for a facile oxidation. Further, the results also suggests that Pd(II) has been an efficient catalyst in effecting the facile oxidation of chosen dyes by CAT in alkaline medium.

The difference in the activation parameters for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Pd(II) forms a complex (X) with the oxidizing species, which makes the oxidizing property of the oxidant more effective than in the absence of Pd(II) catalyst. Further, the catalyst Pd(II) alters the reaction path by stabilizing the transition state, which inturn provides an alternate pathway having lower activation energy for the reaction.

3.17. Catalytic activity

The catalyzed and uncatalyzed reactions proceed simultaneously [40] and correlated as,

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

Here k_1 is the observed pseudo-first-order rate constant obtained in the presence of Pd(II) catalyst, k_0 is that for the uncatalyzed reaction. K_C is the catalytic constant and x is the order of the reaction with respect to Pd(II). In the present investigations, x values for the standard run were found to be: p-rosaniline (0.64), crystal violet (0.77) and ethyl violet (0.84). Then the value of K_C is calculated using the equation.

$$K_C = \frac{k_1 - k_0}{[Pd(II)]^x} \quad (21)$$

The values of K_C have been evaluated for each substrate at different temperatures (293–313 K) and K_C was found to be varying with temperature. Further, plots of $\log K_C$ versus $1/T$ were found to be linear ($r > 0.9892$) and the values of energy of activation and other activation parameters for the catalyst were computed. All these results are summarized in Table 7. Further, for the standard

run at 303 K, plots of k' versus $[Pd(II)]$ (Table 2) were found to be linear ($r > 0.9906$) with an intercept equal to k_0 for all the three substrates. The values k_0 were found to be 4.05×10^{-4} , 1.70×10^{-4} and $0.90 \times 10^{-4}\ s^{-1}$ for p-rosaniline, crystal violet and ethyl violet, respectively. These values are comparable with the rate constants determined experimentally for the uncatalyzed reactions at 303 K (Table 5). This signifies that both uncatalyzed and catalyzed reactions proceed simultaneously.

4. Conclusions

The kinetics of oxidation of three triphenylmethane dyes namely, p-rosaniline, crystal violet and ethyl violet by CAT in alkaline medium catalyzed by Pd(II) catalyst follows identical kinetics with the rate law: $\text{rate} = k[\text{CAT}]^a[\text{Dye}]^b[\text{OH}^-]^c[\text{Pd(II)}]^d$ where a and b are unity, and c and d are less than unity. Addition of p-toluenesulfonamide retards the rate. An isokinetic relationship is observed with $\beta = 423\ K$, indicating that enthalpy factors control the reaction rate and all the three dyes are oxidized by a similar mechanism. Relative reactivity of these dyes follows the order: p-rosaniline > crystal violet > ethyl violet. Catalytic constants and the activation parameters with reference to catalyst were computed. Pd(II) catalyzed reactions were found to proceed nearly four times faster than the uncatalyzed reactions and justifies the use of Pd(II) catalyst for the facile oxidation of the selected dyes by CAT in alkaline medium. Plausible reaction mechanism and the related rate law have been deduced. The present redox system developed can be adopted for treating the chosen triphenylmethane dyes present in industrial effluents to reduce the toxicity caused by these dyes.

Acknowledgements

One of the authors (KNV) is grateful to the Bangalore University, Bangalore for awarding the Research Fellowship under Interdisciplinary Collaborative Research Project. The authors are also thankful to Prof. B.S. Sheshadri and Prof. M.A. Pasha for helpful discussions.

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