Chemical Engineering Journal 163 (2010) 403–412

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

An efficient platinum-catalyzed oxidation process and mechanism for the facile conversion of benzoxazoles to aminophenols

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ARTICLE INFO

Article history:
Received 24 April 2010
Received in revised form 10 July 2010
Accepted 21 July 2010

Keywords:
Pt(IV) catalysis
Oxidation process
Benzoxazoles and aminophenols
Reaction mechanism
N-haloamines

ABSTRACT

An efficient platinum (IV)-catalyzed oxidation process has been developed for the facile conversion of benzoxazoles to aminophenols in good to excellent yields using sodium salt of N-haloarenesulfonamides (N-haloamines) at an alkaline pH. The general process involves the selective and preferential oxidation of a five membered oxazole ring of benzoxazoles using N-haloamines without affecting six membered ring. The detailed catalysis, mechanistic and kinetic investigations have been made for the oxidation reactions. Under similar experimental conditions, the reactions with different N-haloamines proceed with a common oxidation mechanism and follow an identical kinetics. As a result, the common oxidation mechanism which operates in all the reactions has been proposed and the related identical kinetic model was designed. To understand the detailed kinetics and mechanism of the reactions, the reactions have been subjected to changes in (i) dielectric permittivity, (ii) primary salt effect, (iii) effect of reduction products of N-haloamines and (IV) halide ion concentrations. Solvent isotope studies made in a mixture of H_2O–D_2O indicate the participation of OH^- ion in the formation of transition states. The reactions have also been carried out in the absence of platinum catalysts and the studies imply that the catalyst accelerates the reaction rates with 10–12-fold faster. The reactions were carried out at different temperatures and the activation parameters have been computed for both catalyzed and uncatalyzed reactions. The calculated isokinetic temperature (β) of 370 K obtained from enthalpy–entropy relationships and Exner correlations (365 K) was much higher than the experimental temperature of 313 K, and thereby it was concluded that the reactions were preceded under enthalpy control. The catalytic constants (K_C) were calculated for each N-haloamine at different temperatures and the corresponding activation parameters were deduced. Spectroscopic studies have been made for an intermediate complex formation between N-haloamine and Pt(IV). The catalytic method developed for the oxidation process was found to be very efficient and the involvement of cost-effective reagents makes the reaction simple and convenient for scaling the method for the industrial/technological operations with suitable modifications.

1. Introduction

The synthesis of aminophenols is an important task due to their valuable applications in both laboratory and industrial synthetic processes. The importance of 2-aminophenols recognized in their well-established anti-inflammatory, antiallergic and antioxidant activity [1], and their potential uses as reagents for the synthesis of dyes and pharmaceutically active heterocyclic compounds [2]. A number of sterically hindered 2-aminophenol derivatives have known to exhibit antiviral activity [3]. 2-Aminophenols are particularly useful in yielding ligands for metal-complex dyes when diazotized and coupled to phenols or aldehydes or resonant dye species. The amide derivatives of aminophenols have been used as depigmentation agents. Due to the versatile properties and pharmaceutical applications of these compounds, synthesis of 2-aminophenols is an important task by exploring convenient and efficient methodologies. One of the most relevant methods for the synthesis of 2-aminophenols involves the reduction of 2-nitrophenols [1,4]. However, there was not much attention paid towards the synthesis of these compounds by alternative methods other than the nitro group reductions. Hence, we felt it would be of keen interest to investigate the alternative method for the synthesis of aminophenols. In this regard we have developed an

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doi:10.1016/j.cej.2010.07.047

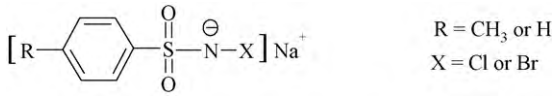


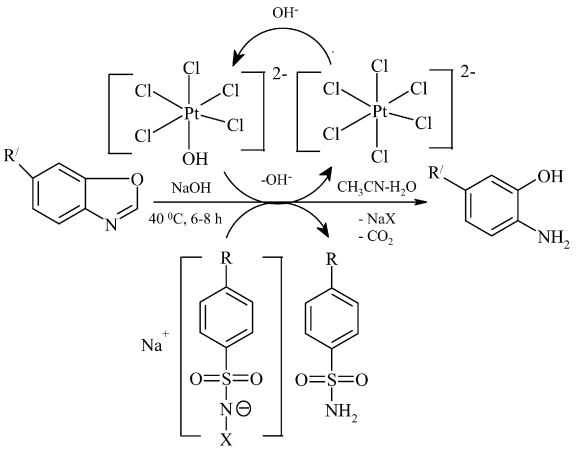
Fig. 1. Structure of N-haloamines.

easy and selective oxidation of benzoxazoles at oxazole ring to yield 2-aminophenols in good to excellent yields.

Oxidation of organic molecules plays a vital role in organic chemistry both at laboratory level and at industrial level. Oxidation reactions are important in the synthesis of many organic compounds, biomolecules and pharmaceuticals, because these reactions create new functional groups or modify existing functional groups in a molecule [5,6]. Several methods are available for the oxidation of organic molecules using different oxidants ranging from metal oxidants to atmospheric O_2. However, still there is a need for developing environmentally friendly methodologies and introducing safe, cost-effective and stable reagents for the oxidation of organic molecules. The development of new processes for the selective oxidations with environmentally friendly oxidants has potential practical applications in organic synthesis. In this regard, a large group of compounds entitled sodium N-haloarenesulfonamidates (organic haloamines) are widely used in fine organic synthesis [7] as an account of economical prospectus and simple reaction techniques.

The sodium N-haloarenesulfonamidates (Fig. 1; henceforth abbreviated as N-haloamines) are an interesting class of oxidants and reagents with polarizable N–X bond have remarkable applications in organic and analytical chemistry. The most blossomed applications of these compounds reside in their well-established oxidant, halogenating and analytical reagent properties [8–10]. Consequently, these reagents react with a wide range of functional groups and effect an array of molecular transformations [7,8]. The prominent members of N-haloamine class of compounds are chloramine-T (p-$CH_3C_6H_4SO_2NClNa{\cdot}3H_2O$ or CAT), chloramine-B ($C_6H_5SO_2NClNa{\cdot}1.5H_2O$ or CAB) and the corresponding bromine analogues, bromamine-T (p-$CH_3C_6H_4SO_2NBrNa{\cdot}3H_2O$ or BAT) and bromamine-B ($C_6H_5SO_2NBrNa{\cdot}1.5H_2O$ or BAB). Sodium N-haloarenesulfonamidates, due to their versatile properties have proved to be valuable reagents for a variety of functional group transformations [7–13]. Specially, N-haloamines act as good oxidants and reagents both in alkaline and in acidic media, and have been widely used for the oxidation and synthesis of a variety of organic and biomolecules [7–13].

Transition metal ions have been extensively used [11–15] as homogeneous catalysts for accelerating a variety of chemical reactions. In recent times, the studies on the use of transition metallic catalysts in many organic reactions have become vital and are of immense interest for the chemists to explore the catalysis mechanisms. Their catalytic activities are due to the existence of variable oxidation states and Levis acid characteristics due to partly filled d and/or f orbitals. Their ability to form both σ and π bonds with other moieties or ligands is one of the chief factors for imparting catalytic properties. Platinum (IV) chloride (chloroplatinic acid ($H_2(PtCl_6)$; Pt(IV)) has been widely used as a homogeneous catalyst in various redox and synthetic reactions [11,13,16–18]. The mechanism of Pt(IV) catalysis is quite complicated due to the formation of different intermediate complexes, free radicals and different oxidizing states of Pt(IV). Although many catalytic applications of platinum towards the oxidation and synthesis of various organic molecules have been reported [11,13,16–18], the applications of platinum catalysis towards the oxidation of heterocyclic compounds remain unexposed specially, on account of kinetic and mechanistic investigations. The wide range of applications of aminophenols, the usefulness of platinum catalyst in organic reactions and versatile properties of N-haloamines, instigate us to carry out the title reaction to develop a protocol for the synthesis of aminophenols from benzoxazoles with an interest of studying the reaction mechanism with kinetic interpretations. By keeping above points in mind, we are reporting a new method for the preparation of 2-aminophenols from benzoxazoles using N-haloamines and platinum catalyst (Scheme 1) with the following objectives: (i) to develop an efficient oxidation process for the facile conversion of benzoxazoles to 2-aminophenols, (ii) to elucidate a plausible mechanism and to deduce an appropriate rate law, (iii) to ascertain the various reactive species, (v) to assess the relative rates of oxidation of benzoxazoles towards N-haloamines, (vi) to find the catalytic efficiency of Pt(IV) and to compare the reactivity with that under uncatalyzed oxidation and (vii) to study the solvent isotope using D_2O.



Scheme 1. Pt(IV)-catalyzed oxidative conversion of benzoxazoles to 2-aminophenols.

The present method developed for the synthesis of 2-aminophenols from benzoxazoles offers many advantages including high conversions, short reaction times and the involvement of non-toxic reagents tuned the applicability of the process to industrial/technological operations with suitable modifications.

2. Experimental

2.1. General

Unless specified, all chemicals are commercially available and used as received without further purification. Melting points were determined on X-4 apparatus and were uncorrected. IR spectra were obtained using Shimadzu FTIR-8900 spectrometer. MS data were obtained on Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. Chloramine-T (E-Merck) and chloramine-B (Fluka) were purified by the method of Morris et al. [10] and Verger and Perlin [19], respectively. An aqueous solution of N-haloamines and benzoxazole by aqueous acetonitrile (1:1 water:acetonitrile) was employed for the kinetic study. Platinum chloride solutions were prepared in 2 mM HCl. Allowances were made for the amount of HCl present in catalyst solutions while preparing solutions for kinetic runs.

2.2. Representative procedure for the preparation of bromamine-T

Bromamine-T was prepared [20] by the partial debromination of dibromamine-T (DBT), which was obtained from the bromination of chloramine-T. The chloramine-T (20 g in 400 mL of water) was treated with liquid bromine (4 mL) under stirred condition at

room temperature. The resulting solid, DBT was filtered under suction, washed thoroughly with ice-cold water until all the absorbed bromine was removed and then vacuum-dried for 24 h. The so-obtained DBT (15 g) was dissolved in NaOH (4 M; 30 mL) with constant stirring at room temperature and the resultant aqueous solution was cooled in ice. The obtained pale yellow crystals of BAT were filtered under suction, washed quickly with the minimum amount of ice-cold water, and dried over P_2O_5. Bromamine-T was characterized and confirmed by IR and mass spectral analysis. Solutions of BAT were prepared in 1:1 ratio of acetonitrile:water and standardized by iodometric procedure and preserved in brown bottles to prevent photochemical deterioration.

2.3. Representative procedure for the preparation of bromamine-B

Bromamine-B was prepared [21] by the partial debromination of dibromamine-B (DBB), which was obtained as follows: Pure chlorine was bubbled through an aqueous solution of chloramine-B (30 g in 560 mL of water) and liquid bromine (6 mL) was added dropwise with constant stirring. The resulting yellow precipitate of dibromamine-B (DBB) was thoroughly washed with water, filtered under suction and dried in a desiccator. Dibromamine-B (31.5 g) was digested in batches with constant stirring in 50 mL of 4 mol dm^{-3} NaOH. The mass obtained was cooled in ice, filtered under suction and the product (BAB) was dried over anhydrous calcium chloride. Bromamine-B was characterized and confirmed by IR and mass spectral analysis. The purity of bromamine-B was assayed iodometrically to determine the active halogen content. Solutions of bromamine-B were prepared in 1:1 ratio of acetonitrile:water and standardized by iodometric procedure and preserved in brown bottles to prevent photochemical deterioration.

2.4. Reaction stoichiometry

Reaction mixtures with varying ratios of N-haloamine to benzoxazole in the presence of 1.0×10^{-3} mol dm^{-3} NaOH and 1.0×10^{-6} mol dm^{-3} catalyst were equilibrated at 313 K for 24 h. Determination of unreacted N-haloamines in reaction mixture showed that one mole of benzoxazole consumed two moles of N-haloamines, confirming the following stoichiometry:

$$\text{Benzoxazole}(0.01\,\text{M}) + \text{N-Haloamine}(0.1\,\text{M}) + \text{NaOH}(0.01\,\text{M}) + \text{Pt(IV)}(1 \times 10^{-6}\,\text{M}) \rightarrow \text{Products} \quad (1)$$

2.5. Representative oxidation procedure for the conversion of benzoxazoles to 2-aminophenols

The benzoxazoles (1 mmol) were completely dissolved in 10 mL acetonitrile:water (1:1) mixture and to these solutions, N-haloamines (2 mmol) in acetonitrile:water (1:1) mixture (10 mL) were added. The reactions were initiated by adding catalyst (0.2 mmol) and the mixtures were stirred at 313 K for 8 h in the presence of alkali. The reaction progress was monitored by TLC and GC. After completion of the reactions, the reaction mixtures were made acidic and the reduction products of N-haloamines, p-toluenesulfonamide (PTS) or benzenesulfonamide (BSA) were extracted with ethyl acetate and identified by TLC and confirmed by mass spectral analysis. The aqueous part of the reaction mixtures was neutralized with base and the products were extracted with dichloromethane. The dichloromethane layer was washed twice with water and dried over sodium sulfate. The products were subjected to GC–mass analysis and the qualitative and quantitative estimations by GC–MS analysis, offered 2-aminophenols around 95% yields. The reaction times and yields are given in Table 1.

2.6. Representative kinetic procedure for the oxidative conversion of benzoxazole to 2-aminophenol

The detailed kinetic experiments were made with respect to oxidative conversion of benzoxazole with four N-haloamines as model reaction. The reactions were carried out under pseudofirst-order conditions with a known excess of [Benzoxazole] over [N-haloamines] at 313 K. The reactions were carried out in stoppered pyrex boiling tubes those outer surfaces were coated black to eliminate photochemical effects. For each run, requisite amounts of solutions of benzoxazole, NaOH, catalyst and aqueous acetonitrile (1:1 water:acetonitrile) (to keep the total volume constant for all runs) were introduced in to the tube and thermostated at 313 K until thermal equilibrium was attained. A measured amount of N-haloamines solution, also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The progress of the reaction was monitored by iodometric determination of unreacted N-haloamines in aliquots (5 mL each) of the reaction mixture withdrawn at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudofirst-order rate constants (k') calculated from the linear plots of log [N-haloamine] vs. time were reproducible within ±3% difference.

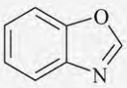
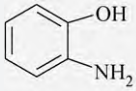
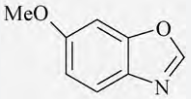
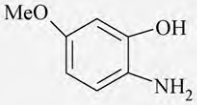
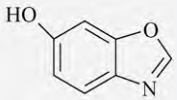
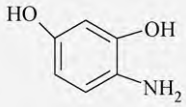
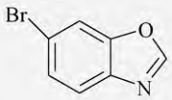
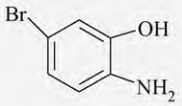
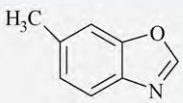
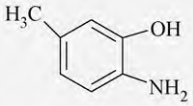
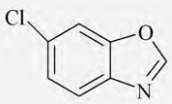
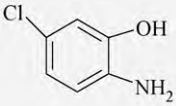
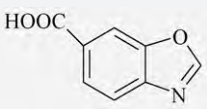
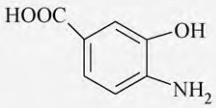
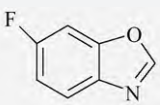
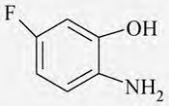
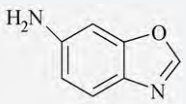
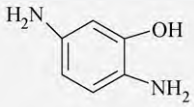
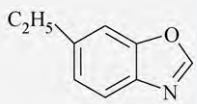
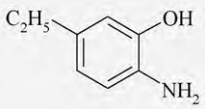
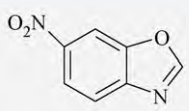
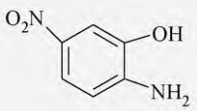
3. Results

3.1. Oxidative conversion of benzoxazoles to 2-aminophenols

Oxidative conversion of benzoxazoles to 2-aminophenols was achieved using catalytic amounts of platinum in acetonitrile–water (1:1) at 313 K by N-haloamines with 1:2 benzoxazoles:N-haloamines ratio in the presence of alkali. The products and the yields are summarized in Table 1. In general, substrates containing electron-donating moieties found to be more reactive and required shorter reaction times compared to substrates containing electron-withdrawing groups. The oxidation process proceeds with the formation of 2-benzoxazolones as the intermediates. Benzoxazoles first utilize 1 mole of N-haloamines to form 2-benzoxazolones. So formed, 2-benzoxazolones consume another mole of N-haloamines to yield ultimate and desired compounds, 2-aminophenol.

The reactions were studied in various solvents (acetonitrile, 1,2-dichloromethane, ethanol, and acetonitrile–water (1:1) mixture). The mixture of acetonitrile:water (1:1) was found to be the best solvent system, perhaps due to high dielectric constant and better solubilizing nature. Benzoxazoles are not very much soluble in water, but markedly soluble in acetonitrile–water mixture. Moreover, the organic haloamines furnish different species better in aqueous (water) medium rather than in pure organic solvents. For all these reasons acetonitrile:water with 1:1 ratio system was the better choice of solvent system in the present study. The reactions were found to be highly dependent upon pH of the system. To evaluate the effect of pH, the reactions were carried out at different pH values using NaOH. At neutral pH, the oxidation reactions were found to be very slow, however the reaction rates increase with an increase in pH (addition of NaOH). This behaviour of the reaction is attributed to the dissociation of N-haloamines in aqueous alkaline medium by furnishing different reactive species. This behaviour of dissociation of N-haloamines is well explained in Section 4. Due to the increase of reaction rates in the presence of NaOH, the reactions were carried out in NaOH.

Table 1
Pt(IV)-catalyzed oxidative conversion of benzoxazoles to 2-aminophenols.

Entry	Substrate	Product	Yield (%)	mp (°C)
1			95	176 (174)
2			96	315 (132)
3			96	218 (220)
4			84	137 (140)
5			97	160 (162)
6			94	146 (145)
7			92	213 (211)
8			93	40.0 (38)
9			96	164 (160)
10			95	230 (228)
11			93	130 (127)

mp given in parenthesis refers to authentic samples.

3.2. Kinetics of oxidative conversion of benzoxazole to 2-aminophenol

The kinetics of oxidation of benzoxazole by CAT, CAB, BAT, and BAB (henceforth abbreviated as N-haloamine) has been investigated at several initial concentrations of the reactants in the presence of NaOH and Pt(IV) catalyst at 313 K. Similar kinetic behaviour was observed with all the four N-haloamines under the identical experimental conditions.

With [Benzoxazole] in excess, at constant [NaOH] and temperature, plots of log[N-haloamine] vs. time were linear ($R^2 > 0.9900$) indicating a first-order dependence of rate on [N-haloamine]. The values of pseudofirst-order rate constants (k') are given in Table 2. Further, the values of k' are unaffected by variation of [N-haloamine]$_o$, confirming first-order dependence on [N-haloamine].

Table 2
Effect of varying reactant concentrations on the reaction rate at 313 K.

[N-haloamine] ($\times 10^3$ mol dm^{-3})	[Benzoxazole] ($\times 10^2$ mol dm^{-3})	k' ($\times 10^4$ s^{-1})			
		CAT	CAB	BAT	BAB
0.5	2.0	10.7	21.9	33.8	68.1
1.0	2.0	10.0	21.2	33.9	68.5
2.0	2.0	10.5	21.6	33.6	68.0
4.0	2.0	10.2	21.6	33.1	67.6
8.0	2.0	10.4	21.1	33.4	68.4
2.0	0.5	2.40	5.50	7.01	17.5
2.0	1.0	5.21	10.4	16.6	34.0
2.0	2.0	10.5	21.6	33.6	68.0
2.0	4.0	21.0	43.5	66.0	139
2.0	8.0	42.1	85.0	126	275

[NaOH] = 1.0×10^{-2} mol dm^{-3}; [Pt(IV)] = 1.0×10^{-6} mol dm^{-3}.

Table 3
Effect of varying NaOH and Pt(IV) concentrations on the reaction rate at 313 K.

[NaOH] ($\times 10^2$ mol dm^{-3})	[Pt(IV)] ($\times 10^6$ mol dm^{-3})	k' ($\times 10^4$ s^{-1})			
		CAT	CAB	BAT	BAB
0.25	1.0	5.50	12.0	16.1	34.6
0.5	1.0	8.12	17.2	23.5	51.2
1.0	1.0	10.5	21.6	33.6	68.0
2.0	1.0	14.2	30.0	41.1	89.4
4.0	1.0	18.6	40.1	53.9	117
1.0	0.25	3.75	7.87	12.7	24.2
1.0	0.5	6.01	12.6	20.4	38.7
1.0	1.0	10.5	21.6	33.6	68.0
1.0	2.0	16.7	35.0	56.7	107
1.0	4.0	27.0	56.7	91.8	174

[N-haloamine] = 2.0×10^{-3} mol dm^{-3}; [Benzoxazole] = 2.0×10^{-2} mol dm^{-3}.

Under the similar experimental conditions, an increase in [Benzoxazole] causes an increase in the k' values (Table 2). Plots of log k' vs. log[Benzoxazole] were linear (Fig. 2; $R^2 > 0.9909$) with unit slopes, showing a first-order dependence of the rate on [Benzoxazole]. Further, plots of k' vs. [Benzoxazole] were also linear ($R^2 > 0.9890$) passing through the origin, confirming the first-order dependence on [Benzoxazole]$_o$. Furthermore, the second-order rate constants $k'' = k'/$[Benzoxazole] are nearly the same for all the cases establishing a first-order dependence on the [Benzoxazole]. The rate of the reaction increases with an increase in [NaOH] (Table 3) and plots of log k' vs. log[NaOH] were linear (Fig. 3; $R^2 > 0.9900$) with slopes 0.4–0.45, indicating fractional-order dependence of rate on [NaOH]. Further, the rate of the reaction increases with increasing [Pt(IV)] (Table 3) and a plot of log k' vs. log[Pt(IV)] is linear (Fig. 4; $R^2 > 0.9899$) with slopes less than unity (0.7–0.72) indicating a fractional-order dependence of rate on [Pt(IV)].

Rate studies were carried out in H_2O–MeOH mixtures of different compositions (0–30%, v/v) with varying dielectric constant of the solvent medium. The rate was found to decrease with an

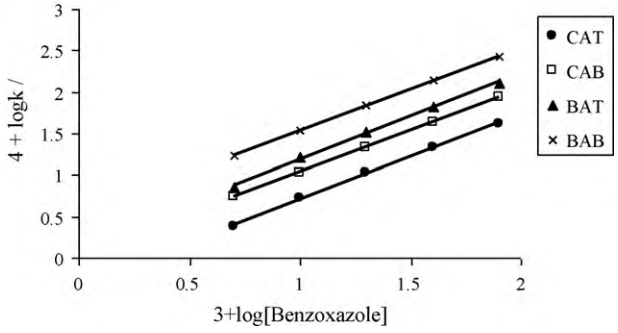


Fig. 2. Plots of log k' vs. log[Benzoxazole].

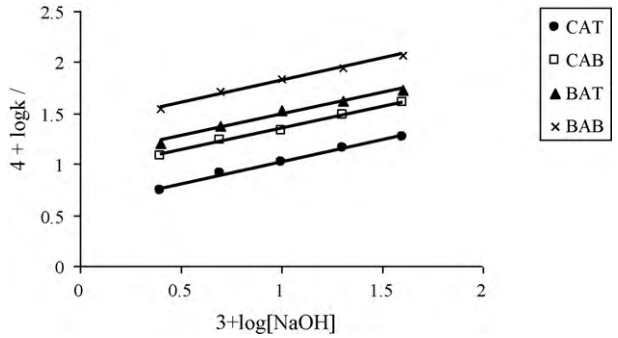


Fig. 3. Plots of log k' vs. log[NaOH].

Table 4
Effect of varying dielectric constant (D) of the medium on the rate of the reaction at 313 K.

% [MeOH] (v/v)	D	k' ($\times 10^4$ s^{-1})			
		CAT	CAB	BAT	BAB
0.0	76.73	10.5	21.6	33.6	68.0
10.0	72.37	9.10	20.0	30.1	63.1
20.0	67.48	8.20	18.0	27.2	55.0
30.0	62.71	7.21	15.0	23.0	47.2

[N-haloamine]$_o$ = 2.0×10^{-3} mol dm^{-3}; [Benzoxazole]$_o$ = 2.0×10^{-2} mol dm^{-3}; [NaOH] = 1.0×10^{-2} mol dm^{-3}; [Pt(IV)] = 1.0×10^{-6} mol dm^{-3}.

increase in MeOH content (Table 4) and plots of log k' vs. $1/D$ were linear (Fig. 5; $R^2 \gg 0.9901$) with negative slopes. Blank experiments performed with MeOH indicate that there was no oxidation of MeOH by any of the four N-haloamines under the experimental conditions. Rate studies in D_2O medium for CAT and BAB revealed that $k'(H_2O) = 10.5 \times 10^{-4}$ s^{-1} and 68.0×10^{-4} s^{-1}, and $k'(D_2O) = 14.8 \times 10^{-4}$ s^{-1} and 94.1×10^{-4} s^{-1} respectively. The formal solvent isotope effect ratio $k'(H_2O)/k'D_2O) = 0.70$ and 0.72 for these two N-haloamines. Solvent isotope studies were made using H_2O–D_2O mixtures for CAT and BAB; the results are given in Table 5. The corresponding solvent isotope plots for the rate constants (k'_n) in a solvent mixture containing deuterium atom fraction (n) are shown in Fig. 6.

The effect of the temperature on the reaction rate was studied by performing the kinetic experiments at various temperatures (303–323 K) under experimental conditions. From the linear Arrhenius plots of log k' vs. $1/T$ (Fig. 7; $R^2 > 0.9919$), the values of activation parameters (E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$) for the overall reaction were evaluated. These data are summarized in Table 6. Addition of p-toluenesulfonamide (PTS) or benzenesulfonamide (BSA), a reduction product of N-haloamines, (1.0×10^{-3} to 4×10^{-3} mol dm^{-3}), to the reaction mixture did not affect the rate

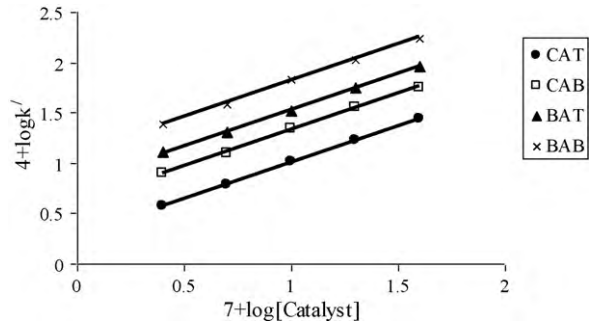


Fig. 4. Plots of log k' vs. log[Catalyst].

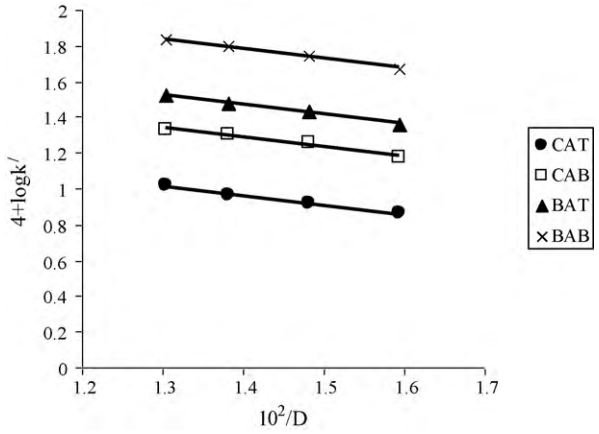


Fig. 5. Plots of $\log k'$ vs. $1/D$.

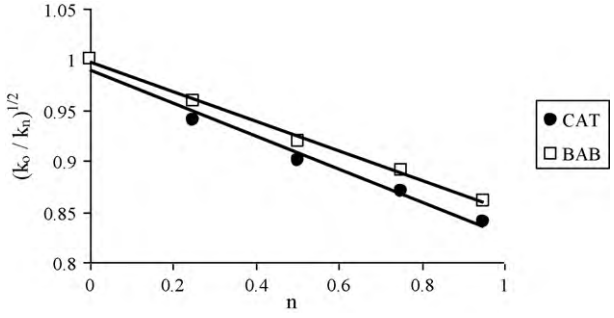


Fig. 6. Kinetic isotope studies plots.

significantly. This indicates that the reduction products of oxidants have not involved in any step prior to the rate-limiting step in the reaction process. The effect of ionic strength (I) of the medium on the rate was studied in a range of 0.10–0.50 mol dm^{-3} using $NaClO_4$ solution and found that the rate was unaffected by the addition of $NaClO_4$. At experimental conditions the addition of NaCl or NaBr (1.0×10^{-3} to 4.0×10^{-3} mol dm^{-3}) did not alter the rate of the reaction. These results indicate that there is no role for halide ions in the reaction. The addition of the reaction mixtures to aqueous acrylamide monomer solutions, kept in the dark, did not initiate polymerization, confirming the absence of any free radical species generated in the reaction sequence. The control experiments were also performed under similar reaction conditions without the oxidant.

Table 5
Solvent isotope studies for the oxidation of benzoxazole by CAT and BAB in H_2O–D_2O mixtures at 313 K.

Atom fraction of deuterium (n)	k'_n (s^{-1})		$(k'_o/k'_n)^{1/2}$	
	CAT	BAB	CAT	BAB
0.00	10.5	68.0	1.0	1.0
0.25	11.8	75.3	0.94	0.96
0.50	12.9	82.1	0.90	0.92
0.75	13.8	87.8	0.87	0.89
0.95	14.8	94.1	0.84	0.86

$[\text{N-haloamine}]_o = 2.0 \times 10^{-3}$ mol dm^{-3}; $[\text{Benzoxazole}]_o = 2.0 \times 10^{-2}$ mol dm^{-3}; $[NaOH] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[Pt(IV)] = 1.0 \times 10^{-6}$ mol dm^{-3}.

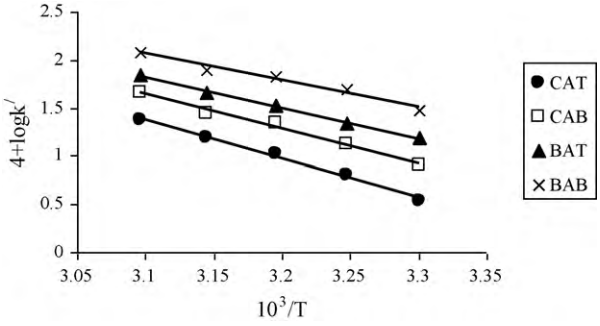


Fig. 7. Plots of $\log k'$ vs. $1/T$ for catalyzed reactions.

4. Discussion

4.1. Reactive species of N-haloamines

Investigations of Morris et al. [10], Bishop and Jennings [9], Pryde and Soper [22] and Hardy and Johnston [23] have shown the existence of similar equilibria in case of all N-metallo-N-arylhalosulfonamides (N-haloamines) in aqueous media. Depending on the pH, N-haloamines exhibits the following equilibria in aqueous solutions:

$$RNXNa \rightleftharpoons RNX^- + Na^+ \quad (2)$$

$$NX^- + H^+ \rightleftharpoons RNHX \quad (3)$$

$$2RNHX \rightleftharpoons RNH_2 + RNX_2 \quad (4)$$

$$RNX_2 + H_2O \rightleftharpoons RNHX + HOX \quad (5)$$

$$RNHX + H_2O \rightleftharpoons RNH_2 + HOX \quad (6)$$

$$HOX + H^+ \rightleftharpoons H_2OX^+ \quad (7)$$

$$HOX \rightleftharpoons H^+ + OX^- \quad (8)$$

Here R = $CH_3C_6H_4$ for CAT and BAT; C_6H_5 for CAB and BAB; X = Cl or Br.

In alkaline solutions of N-haloamines, RNX_2 does not exist, and the possible oxidizing species are RNX^- and OX^- anions, which could be transformed into more reactive species, RNHX and HOX during the course of the reaction in alkali retarding steps. Several workers have observed the retarding effect of OH^- ions on the rate of haloamines with a number of substrates [24–27] and have suggested that the reactivity of weakly alkaline solutions of haloamines is due to the formation of the conjugate acid RNHX from RNX^- in OH^- retarding step ($RNX^- + H_2O \rightleftharpoons RNHX + OH^-$). But in the present investigations, the OH^- ions increase the rate and as a result the equilibrium shifts in backward direction with furnishing species, RNX^- as the reactive oxidizing species ($RNHX + OH^- \rightleftharpoons RNX^- + H_2O$). In our earlier work [11–13], the positive influence of OH^- ion on the rate of haloamine reactions with a number of compounds has been observed and suggested RNX^- as the reactive oxidizing species. In the present investigations, the rate of the reaction is accelerated by OH^- ions clearly indicates that the anion RNX^- is the most likely reactive species of N-haloamines involved in the oxidative conversion of benzoxazoles to 2-aminophenols.

4.2. Reactive species of Pt(IV)

Pt(IV) has been used as homogenous catalyst for many reactions and its catalytic mechanism is well reported [11,13,16–18] in a variety of reactions. The chloroplatinic acid, $H_2(PtCl_6)$ is the starting material used in platinum (IV) catalysis. In aqueous solution,

Table 6
Temperature dependence and values of composite activation parameters for the oxidation of benzoxazole by N-haloamines in the presence and absence of Pt(IV)) catalyst.

	k' ($\times 10^4$ s^{-1})			
	CAT	CAB	BAT	BAB
Temperature (K)				
303	3.50[a] (0.26)[b]	8.01 (0.55)	15.5 (1.1)	30.1 (2.61)
308	6.50 (0.43)	13.5 (1.12)	22.1 (2.0)	50.2 (4.50)
313	10.5 (1.00)	21.6 (2.00)	33.6 (3.21)	68.0 (6.00)
318	15.5 (1.80)	28.6 (3.12)	45.0 (5.10)	79.9 (10.1)
323	24.1 (2.74)	45.0 (5.22)	70.1 (8.00)	120 (15.0)
E_a (kJ mol^{-1})	76.6 (101)	66.9 (92)	57.3 (82.6)	49.4 (71.0)
$\Delta H^{\neq}$ (kJ mol^{-1})	74.0 (98.0)	64.4 (89.5)	54.7 (79.0)	46.8 (67.0)
$\Delta G^{\neq}$ (kJ mol^{-1})	94.0 (100)	93.0 (99.0)	92.0 (98.0)	91.0 (97.2)
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−66.1 (−6.6)	−90.8 (−30.2)	−118 (−60.0)	−138 (88.0)

Values in parentheses refer to oxidation of benzoxazole in the absence of Pt(IV)) catalyst.
[a] $[\text{N-haloamine}]_o = 2.0 \times 10^{-3}$ mol dm^{-3}; $[\text{Benzoxazole}]_o = 2.0 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{Pt(IV)}] = 1.0 \times 10^{-6}$ mol dm^{-3}.
[b] Experimental conditions are the same as 'a' without Pt(IV) catalyst.

$H_2(PtCl_6)$ ionizes [18] as follows:

$$H_2[PtCl_6] \rightleftharpoons [PtCl_6]^{2-} + 2H^+ \quad (9)$$

In alkaline medium (pH > 8) $[PtCl_6]^{2-}$ changes to $[PtCl_5(OH)]$ [11,13,16–18] as:

$$[PtCl_6]^{2-} + OH^- \rightleftharpoons [PtCl_5(OH)]^{2-} + Cl^- \quad (10)$$

Further ligand (Cl^-) replacements from $[PtCl_5(OH)]^{2-}$ are also reported [16–18]:

$$[PtCl_5(OH)]^{2-} + OH^- \rightleftharpoons [PtCl_4(OH)_2]^{2-} + Cl^- \quad (11)$$

However, the dihydroxy platinum (IV) species is quite unstable [28] in aqueous solutions and therefore under the present experimental conditions $[PtCl_5(OH)]^{2-}$ acts as the reactive species of Pt(IV) in alkaline medium.

4.3. Complex formation studies between Pt(IV) and chloramine-T (CAT)

The existence of complex between Pt(IV) and CAT was evidenced from the UV–vis spectra of both Pt(IV) and Pt(IV)–CAT mixture, in which a shift of Pt(IV) from 360 nm to 345 nm was observed, indicating the formation of a complex.

The complex formation between metal ion Pt(IV) and CAT was given by the following equilibrium (Eq. (12)):

$$M + nS \overset{K}{\rightleftharpoons} (MS_n) \quad (12)$$

Here, M and MS_n are two metal species with different extinction coefficients. For the equilibrium (12), Ardon [29] has derived the following relation (Eq. (13)):

$$\frac{1}{\Delta A} = \frac{1}{[S]^n}\left\{\frac{1}{\Delta E[M_{Total}]K}\right\} + \frac{1}{\Delta E[M_{Total}]} \quad (13)$$

where K is the formation constant of the complex, $[S]$ is the concentration of CAT, ΔE is the difference in extinction coefficient between two metal species, $[M]_{Total}$ is the total concentration of metal species and ΔA is the absorbance difference between Pt(IV)–CAT mixture and Pt(IV) alone. Eq. (13) is valid when $[S]$ is much higher than $[M]_{Total}$. According to Eq. (13), a plot of $1/\Delta A$ vs. $1/[S]$ or $1/[S]^2$ should be linear with an intercept in case of 1:1 or 1:2 type of complex formation between M and S. The ratio of intercept to slope of this linear plot gives the value of K.

Platinum in aqueous alkaline acetonitrile medium containing CAT showed an absorption peak at 345 nm (λ_{max} for the complex). The complex formation studies were made at this λ_{max} of 345 nm. In a set of experiments, the solutions were prepared by taking different amounts of CAT (0.5×10^{-3} to 8×10^{-3} mol dm^{-3}) at constant amounts of H_2PtCl_6 (1.0×10^{-6} mol dm^{-3}) and NaOH (0.01 mol dm^{-3}) at 313 K. The absorbance of these solutions was measured at 345 nm. The absorbance of Pt(IV) in alkaline medium is also measured at same wavelength (345 nm). The difference of these absorbances (with and without CAT) gave the differential absorbance, ΔA. A plot of $1/\Delta A$ vs. $1/[CAT]$ was linear ($r = 0.9901$) with an intercept suggesting the formation of 1:1 complex between Pt(IV)–CAT. Further, the plot of $\log(1/\Delta A)$ vs. $\log(1/[CAT])$ was also linear ($r = 0.9871$). From the slope and intercept of the plot $1/\Delta A$ vs. $1/[CAT]$, the value of the formation constant, K, of the complex was deduced and found to be 6.12×10^2.

4.4. Benzoxazole oxidation mechanism and design of kinetic model

Based on the above discussion and the observed kinetic results, the general mechanism (Scheme 2) has been proposed for the platinum-catalyzed oxidative conversion benzoxazoles using N-haloamines in alkaline medium. In Scheme 2, Y and Y' represent the intermediate species whose structures are shown in Scheme 3. The detailed mechanism for the platinum-catalyzed oxidative conversion of benzoxazoles is depicted in Scheme 3.

The total effective concentration of N-haloamine is,

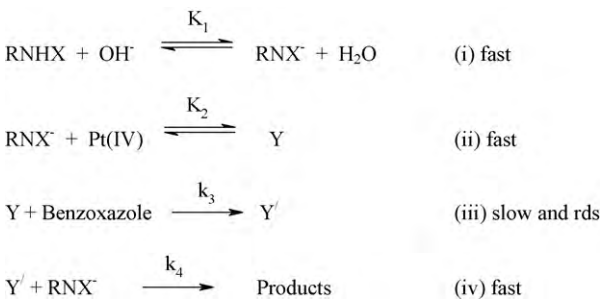
$$[\text{N-haloamine}]_t = [RNHX] + [RNX^-] + [Y] \quad (14)$$

By substituting [RNHX] and [RNX$^-$] with steps of (i) and (ii) of Scheme 2 in Eq. (14) and solving for [Y], we get:

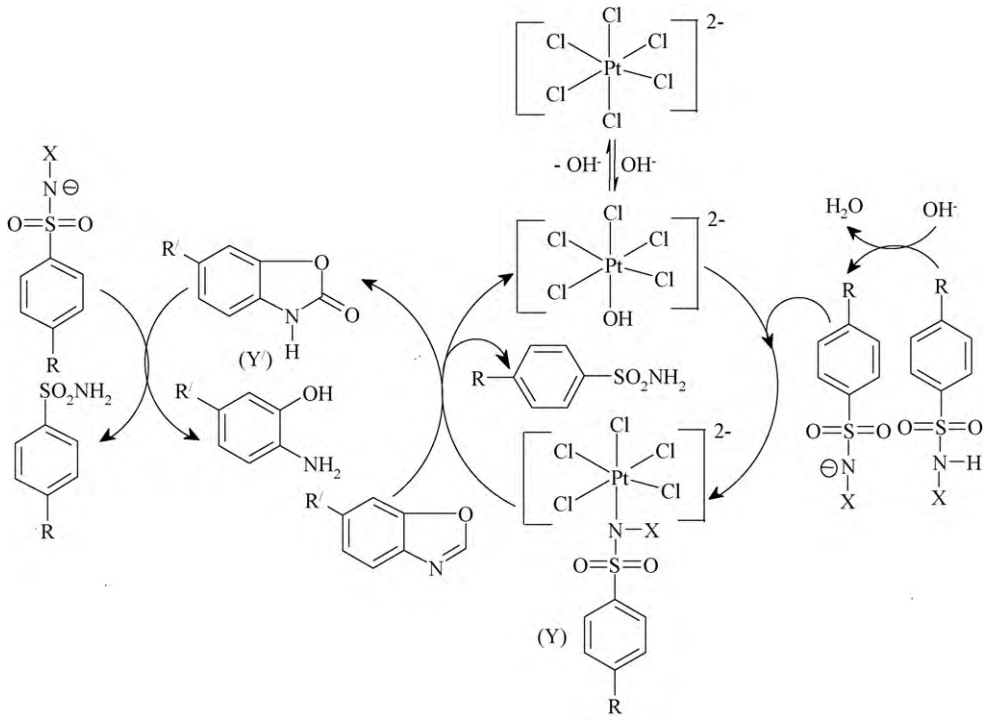
$$[Y] = \frac{K_1K_2[[\text{N-haloamine}]_t[Pt(IV)][OH^-]}{[H_2O] + K_1[OH^-] + K_1K_2[Pt(IV)][OH^-]} \quad (15)$$

From the slow step of Scheme 2,

$$\text{rate} = \frac{-d[\text{N-haloamine}]}{dt} = k_3[Y][\text{Benzoxazole}] \quad (16)$$



Scheme 2. General mechanistic scheme for oxidative conversion of benzoxazoles.



Scheme 3. Detailed mechanism for the Pt(IV)-catalyzed oxidative conversion of benzoxazoles to 2-aminophenols by N-haloamines.

By substituting [*Y*] from Eq. (15) into Eq. (16), the following rate law was obtained:

$$\text{rate} = \frac{K_6K_7k_8[[\text{N-haloamine}]_t[\text{Benzoxazole}][\text{Pt(IV)}][\text{OH}^-]}{[\text{H}_2\text{O}] + K_1[\text{OH}^-] + K_1K_2[\text{Pt(IV)}][\text{OH}^-]} \quad (17)$$

Scheme 2 and the kinetic model (17) are consistent with the observed experimental results and supported by the following facts.

4.5. Effect of dielectric permittivity

A decrease of reaction rate with a decrease in *D* (increase in MeOH content) of the medium supports the proposed mechanism. Amis and Jaffe [30] have shown that

$$\log k'_D = \log k' + \frac{Ze\mu}{2.303\,kTr^2D} \quad (18)$$

where k' is the rate constant in a medium of infinite dielectric constant and k'_D is the rate constant as function of dielectric constant *D*, *Ze* is the charge on the ion, μ is the dipole moment of the dipole, *k* is the Boltzmann constant, *T* is the absolute temperature and *r* is the distance of approach between the ion and dipole. Eq. (18) predicts a linear relation between $\log k'$ vs. $1/D$ (Fig. 5; $R^2 > 0.9911$). The slope of the line should be negative for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope is obtained for positive ion-dipole reactions. In the present investigations, plots of $\log k'$ vs. $1/D$ were linear with negative slopes (Fig. 5; $R^2 > 0.9911$) supporting the participation of negative ion and dipole in the rate-limiting step (Scheme 3).

4.6. Solvent isotope studies

It is interesting to note that the rates in D_2O medium are faster than those in H_2O. Since the OD^- is a stronger base than OH^- by a factor of 2–3, the solvent isotope effect of this magnitude is expected [31]. However, the observed inverse solvent isotope effect k' (D_2O)/k' (H_2O) of 1.40 for CAT and 1.32 and the normal kinetic isotope effect $k'_{OH^-}/k'_{OD^-} < 1$ could counter-balance the solvent isotope effect, which can be attributed to the fractional-order dependence of rate on [OH^-]. The solvent isotope studies in H_2O–D_2O mixtures could throw light on the nature of the transition state [32,33]. The dependence of rate constant k'_n on *n*, the atom fraction of deuterium in a solvent mixture, is given [33] by Eq. (19):

$$k'_o/k'_n = \pi(1 - n + n\Phi_i) \,/\, \pi(1 - n + n\Phi_j) \quad (19)$$

where Φ_i and Φ_j are isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition state (TS) and reactant state (RS) respectively and k'_o is the rate constant in pure H_2O. If the reaction proceeds through a single transition state [33], then the Eq. (19) takes the form given in Eq. (20):

$$\left(\frac{k'_o}{k'_n}\right)^{1/2} = [1 + n(\Phi_j - 1)] \quad (20)$$

From Eq. (20), a plot of $(k'_o/k'_n)^{1/2}$ vs. *n* should be linear. It is observed from Table 5 that such a plot is linear (Fig. 6; $R^2 > 0.9905$) with a slope of $(\Phi_j - 1) = -0.16$ and -0.14, giving values of 0.84 and 0.86 for the fractionation factor in the cases of CAT and BAB respectively. Considering the diversity of the procedure employed, it is reasonable to assume that there is an agreement between the *n* values obtained. Further, a comparison with the standard plots [34] clearly implies the involvement of a single or H–D exchange during the reaction sequence. The participation of OH^- ion in the formation of transition state is thus inferred.

4.7. Effect of temperature and computation on activation parameters

The reactions were carried out at range of temperatures (303–313 K) and the energy of activation (E_a) for each reaction has been calculated from the linear Arrhenius plots of $\log k'$ vs. $1/T$ (Fig. 7; $R^2 > 0.9909$). The values of other activation parameters ($\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$) for the overall reaction were also evaluated.

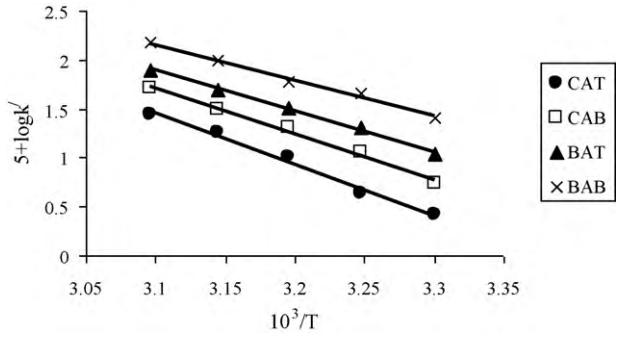


Fig. 8. Plots $\log k'$ vs. $1/T$ for uncatalyzed reactions.

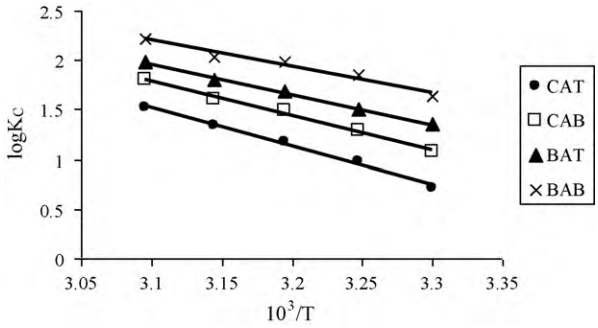


Fig. 9. Plot of $\log K_C$ vs. $1/T$.

These data are summarized in Table 6. Under comparable experimental conditions, the reactivity rates of N-haloamines towards benzoxazole in the presence of platinum catalyst follow the order: BAB > BAT > CAB > CAT (Table 2). The data in Table 6 also indicate that the energy of activation is highest for the slowest reaction and *vice-versa,* as expected, indicating that the reaction is enthalpy-controlled. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the oxidation of benzoxazole with all the four N-haloamines are linearly related ($R^2 = 0.9899$), with an isokinetic temperature of $\beta = 370$ K, indicating that a common mechanism operates in the oxidation of benzoxazole by all the said four N-haloamines. Further, the genuine nature of the isokinetic relationship was verified by the Exner criterion [35] by plotting log log $k'_{(303\,K)}$ vs. log $k'_{(313\,K)}$; this plot is linear ($V = 0.9881$). The value of β was calculated from the equation $\beta = T_1(1-q)/(T_1/T_2) - q$ where q is the slope of the Exner plot and $T_2 > T_1$. The value of β was found to be 365 K. The values of β evaluated from both the plots are much higher than the temperature range used in the present work (313 K). This indicates a common enthalpy-controlled pathway for all the reactions. The proposed mechanism is also supported by the moderate values of energy of activation and other thermodynamic parameters. The high positive values of the free energy of activation and of the enthalpy of activation suggest that the transition state is highly solvated, while the high negative entropy of activation indicates the formation of rigid associated transition states. The values of $\Delta G^{\neq}$ are almost the same in the cases of all the N-haloamines, suggesting that the oxidation of benzoxazole by N-haloamines proceeds by a common mechanism.

It was felt reasonable to compare the reactivity of these four N-haloamines towards benzoxazole in the absence of Pt(IV) catalyst under identical set of experimental conditions in order to evaluate the catalytic efficiency of Pt(IV). The reactions were studied at different temperatures (303–323 K) in the absence of Pt(IV). From the plots of $\log k'$ vs. $1/T$ (Fig. 8. $R^2 > 0.9899$), we evaluated the activation parameters for the uncatalyzed reactions (Table 6). The rate of reaction for uncatalyzed oxidation of benzoxazole increases in the order: BAB > BAT > CAB > CAT. A similar trend was also observed in the presence of Pt(IV) catalyst. However, the Pt(IV)-catalyzed reactions were found to be 10–12 times faster. This was also confirmed by the activation parameters calculated (Table 6). Thus the observed rates of oxidation in the presence of Pt(IV) catalyst justify the need of a catalyst for a facile oxidation of the benzoxazoles by the chosen N-haloamines in alkaline medium. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Pt(IV) forms a complex (Y) with N-halomines, which increases the oxidizing property of chosen N-haloamines than without Pt(IV).

4.8. Catalytic activity of platinum catalyst

For evaluating catalytic efficiency in terms of catalytic constant (K_C), the following general equation has been derived [36], which relates the reaction rates of both catalyzed and uncatalyzed reactions:

$$k_1 = k_o + K_C[\text{catalyst}]^x \quad (21)$$

where k_1 is the observed pseudofirst-order rate constant obtained in the presence of Pt(IV) catalyst, k_o is the pseudofirst-order constant for the uncatalyzed reaction, K_C is the catalytic constant and x is the order of the reaction with respect to Pt(IV). In the present investigations, x values for the standard run were found to be 0.70. Then the value of K_C is calculated using Eq. (21): The values of K_C have been evaluated for each oxidant at different temperatures (303–323 K) and K_C was found to vary with temperature. Further, plots of $\log K_C$ vs. $1/T$ were linear (Fig. 9; $R^2 > 0.9897$) and the values of energy of activation and other activation parameters for the catalyst were computed and were summarized in Table 7.

4.9. Reactivity of N-haloamines

One of the aspects of this research is pertaining to the reactivity studies of all the said four N-haloamines for oxidative conversion of benzoxazole. Under identical experimental conditions, the rates were found to be higher with bromamines compared to chloramines by a factor of 3 (Table 2) and the reactivity potential follows the order: BAB > BAT > CAB > CAT. This nature of reactivity difference is attributable to the difference in electrophilicities of the halo cations, Br^+ and Cl^+ involved in the oxidation process and is also related to the ease with which these species are generated in reactions. In these reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has the electronegativity of 2.7,

Table 7
Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values.

	K_C			
	CAT	CAB	BAT	BAB
Temperature (K)				
303	5.11	11.8	22.7	43.4
308	9.58	19.5	31.6	72.2
313	15.0	30.9	48.0	97.9
318	21.6	39.6	63.1	110
323	33.6	62.8	98.0	166
E_a (kJ mol^{-1})	71.2	62.8	56.5	49.4
$\Delta H^{\neq}$ (kJ mol^{-1})	68.5	60.2	53.9	46.8
$\Delta G^{\neq}$ (kJ mol^{-1})	69.0	68.0	67.0	65.5
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−3.9	−24.5	−41.0	−56.8

$[\text{N-haloamine}]_o = 2.0 \times 10^{-3}$ mol dm^{-3}; $[\text{Benzoxazole}]_o = 2.0 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{Pt(IV)}] = 1.0 \times 10^{-6}$ mol dm^{-3}.

while chlorine has a higher value of 2.8. As the electronegativity increases, the electropositive nature decreases, since the halo cations are the reactive species in these oxidation reactions and the electropositive nature is Br > Cl. This may also be due to the moderate differences in the van der Waal's radii of the bromine and chlorine. Therefore, the reactivity of bromamines is greater than that of chloramines. This is consistent with the observed order of reactivity: BAB > BAT > CAB > CAT in the present work. Hence, it can be generalized that bromamines are stronger oxidants compared to chloramines. A similar behaviour has been reported [37,38] in the oxidation of several other substrates using N-haloamines.

Further, the observed oxidation rates are lower in BAT and in CAT compared to the rates in BAB and in CAB, the ratios k' (BAB)/k' (BAT) and k' (CAB)/k' (CAT) were found to be around 2. This indicates the participation of a $-CH_3$ group in CAT and BAT, which exerts a strong inductive effect in enriching the electron density at the polar N–X bond, thereby reducing the electrophilicity of the X atom. This explains why the reactivity of benzenesulfonamide derivatives is higher than that of toluenesulfonamide derivatives of N-haloamines. It also substantiates the observed overall reactivity of BAB > BAT > CAB > CAT towards the oxidation of benzoxazoles in the present work.

5. Conclusions

Platinum-catalyzed oxidative conversion of benzoxazoles to 2-aminophenols was performed efficiently using N-haloamines at an alkaline pH. The catalytic oxidation preferentially takes place at oxazole ring with out effecting benzene ring. Catalyzed oxidations of benzoxazoles by CAT, CAB, BAT and BAB undergo with similar oxidation mechanism and follow the identical kinetic behaviour with the reactivity sequence: BAB > BAT > CAB > CAT. This effect is mainly attributed to electronic factors. Activation parameters were evaluated for both catalyzed and uncatalyzed reactions. Catalytic constants and activation parameters with reference to catalyst have been computed. Catalyzed reactions showed rates 10–12-fold faster than the uncatalyzed reactions. The observed results have been explained by a common oxidation mechanism with identical rate law. The present method developed for the synthesis of 2-aminophenols from benzoxazoles offers many advantages including high conversion, short reaction times and the involvement of non-toxic reagents tuned the method for the application in industrial/technological process with suitable modification. It can be concluded that Pt(IV) serves as an efficient catalyst for the oxidative conversion of benzoxazoles to aminophenols by N-haloamines in alkaline medium.

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