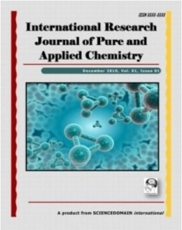

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Kinetics of Oxidation of Substituted Phenols by Potassium Bromate

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Authors' contributions

This work was carried out in collaboration with all authors AM designed the study, performed the statistical analysis, wrote the protocol, managed the literature survey and wrote the first draft of the manuscript. JKP managed the analyses of the study read and approved the final manuscript.

Short Communication

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ABSTRACT

Kinetic methods of analysis are now accepted as standard analytical procedures for several of reactions, especially oxidation types. Though the reaction of phenols and substituted phenols by potassium bromate is well understood as an oxidative type, there was a need to understand and more evidence required against the participation of Br_2 in the increasing rate of reaction with increasing acetic acid composition in the bromate oxidation of phenols. Present work explains the strange behaviour on the basis of formation of $HBrO_3$ that is favoured in acidic medium.

Kinetics of oxidation of 3, 4-Dimethyl phenol, 4-sec-butyl phenol and 4-tert-butyl phenol in aqueous acetic acid - water medium in the temperature range of 308K to 321K were investigated. The reaction obeys first order kinetics with respect to [oxidant], [substrate] and $[H^+]$. The active oxidising species was found to be $HBrO_3$. A suitable mechanism in conformity with the kinetic observation has been proposed. Various activation parameters such as energy of activation (58.59, 61, 43, 65.38 KJ/mol), enthalpy change [56.03, 58.87, 62.82 KJ/mol], free energy change (73.19, 77.17, 77.82 KJ/mol) and entropy of activation (-55.7, -59.45 and -48.78 J/mol/deg) for 3: 4-dimethyl phenol, 4-sec-butyl phenol, 4-tert-butyl phenol at 308K, were obtained. A rate law has been derived on the basis of the data. The order of reactivity among the methyl substituted phenols is 3, 4-

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dimethyl phenol > p-cresol > phenol. The order of reactivity among higher alkyl substituted phenols is 4-tert-butyl phenol $\approx$ 4-sec-butyl phenol > 4-ethyl phenol >phenol.

Keywords: 3, 4-dimethyl phenol; 4-sec-butyl phenol; 4-tert-butyl phenol; potassium bromate oxidation; kinetics.

1. INTRODUCTION

Oxidants like sodium periodate (Singh and Srivastava, 2008a; Srivastava et al., 2008b), N-bromoacetamide (Banerji and Negi, 1983; Singh et al, 1992), N-bromosuccinimide (Malvalang et al., 2001; Reddy et al., 2012) have been earlier used in oxidation of various organic compounds. Among these oxidants Potassium bromate has gained wide importance in the oxidation reactions of various substrates like primary alcohol (Farakas et al., 1949) secondary alcohol (Natarajan and Venkatasubramanian, 1969), cycloanols (Singh and Srivastava, 2005), aldehydes (Avasthi and Chatterji, 1970; Banerjee et al., 1979), ketones (Mahapatra and Moorthy, 1979), amino acids (Anandan and Subramanian, 1985), **α**–hydroxyketones' phenols (Natarajan and Venkatasubramanian, 1976; Natarajan and Venkatasubramanian, 1974), phenols (Sundaram and Vijayalakshmi, 1977) in presence of mercuric acetate (Subhash et al., 1982) and catalyst (Parimala et al., 1981; Sondhu et al., 1990; Singh and Srivastava, 1991).

A survey of the literature reveals that there are quite a few reports on the kinetics of oxidation of phenols by potassium bromate (Sundaram and Vijayalakshmi, 1977; Subhash et al., 1982; Parimala et al., 1981; Sundaram and Vijayalakshmi, 1981). Sundaram and Vijayalakshmi, (1977) have observed that during the oxidation of phenols by BrO_3^-, bromine was produced from bromide ions. The reaction was first order with respect to substrate and oxidant. The order with respect to sulphuric acid was two. The reaction was found to be ion-dipole type. There is no oxidation of phenol by molecular bromine though there is a possibility of formation of bromine from the ion. Subhash et al. (1982) have reported that Hg^{2+} ions oxidize phenol and catalyse the reaction. Hence mercuric acetate cannot be used to trap the ions. The reaction was retarded by electron withdrawing groups. The mechanism postulated involves the formation of a mercurated complex as the rate determining step followed by fast decomposition of the complex to quinine as the product. The kinetics of V (IV) catalysed oxidation of phenols by acid bromate was studied by Sundaram and Vijayalakshmi (1981) in binary solvent mixtures. The mechanism involves the attack of BrO_2^+ at the ortho carbon atom. It was found that mercuric acetate accelerates the reaction. However, there is a need to have more evidence against the participation of Br_2 in the bromate oxidation of phenols. Hence it may be worthwhile to investigate the kinetics of oxidation of various alkyl substituted phenols by $KBrO_3$ in aqueous acetic acid-perchloric medium in the absence of mercuric acetate. The kinetic results also lead to definite conclusions about the nature of the reactive species ($HBrO_3$) and mechanism of catalysis. The authors have made detailed study on the oxidation of substituted phenols by potassium bromate in acetic acid-perchloric acid medium and the results are reported in the communication.

2. EXPERIMENTAL DETAILS

2.1 Materials and Methods

Analytically pure chemicals were used in the present study. AnalaR acetic acid was heated under reflux for six hours with excess of Potassium dichromate and acetic anhydride in double distilled water. The solids separated were filtered off and the acid was distilled from an all glass distillation unit (Brafield and Ortan, 1927). The pure AnalaR sample of Potassium bromate was dried in an air oven at 110ºC, cooled and preserved in a desicator. The AnalaR grade of perchloric acid was used after standardization with sodium carbonate using methyl orange as indicator. For low acid concentration, stock solutions of perchloric acid were prepared and the required dilutions were used for obtaining the necessary acidity.

Pure AnalaR samples of 3, 4 – Dimethylphenol, 4 – tert-butylphenol, 4 – sec-butylphenol, phenol, p-cresol and 4 – ethylphenol were used as substrates. Potassium dichromate, potassium iodide, sodium thiosulphate, sodium carbonate, sodium perchlorate, starch and sulphuric acid used were AnalaR grade and used as such.

The substrate of required molarity was weighed and dissolved in 50% acetic acid (v/v). The oxidant of desired molarity was made up with a requisite amount of perchloric acid. The solvent mixture was made up for 50% acetic acid (v/v).The required ionic strength was maintained by adding sodium perchlorate.

2.2 Kinetic Techniques

The kinetic runs were performed in stoppered glass vessels in controlled temperature (±0.005ºC) thermostat. The kinetics of oxidation reaction between substituted phenols and potassium bromate in acetic acid – water acid medium was followed under first order condition by measuring the concentration of unreacted potassium bromate iodometrically as follows.

Suitable volumes of substrate and oxidant were taken in two different stoppered bottles and placed in the thermostat to attain the temperature of the bath. To initiate the reaction a suitable volume of the oxidant solution was pipetted into the bottle containing the substrate. The kinetics was followed by withdrawing desired portions of reaction mixture into a conical flask containing potassium iodide, sulphuric acid and ice and titrated against sodium thiosulphate using starch as indicator after suitable time intervals.

The preliminary investigation on substituted phenols revealed that they were oxidized by potassium bromate at a rate which could be measured and suitable for kinetic study. Therefore kinetic study of oxidation of substituted phenols by potassium bromate was undertaken. The stoichiometry calculations proved that 1 mole of the substrate reacted with 1 mole of the oxidant. The main products of this oxidation reaction were found to be quinone.

3. RESULTS AND DISCUSSIONS

The kinetics of oxidation of 4 - tertbutyl phenol, 4 – secbutyl phenol, 4 - ethyl phenol, 3,4 - dimethyl phenol, p – cresol and phenol by acid bromate has been investigated in aqueous acetic acid – perchloric acid medium.

The reactions were followed under pseudo first order conditions, using large excess of the substrate over the oxidant {[Substrate] = 0.01M [potassium bromate] = 5 x 10^{-4}M and [H^+] = 5 x 10 $^{-2}$M and the solvent composition was 1:1(v/v)} unless mentioned otherwise.

The pseudo first order rate constants were obtained by plotting log (a-x) values against time Vogel AI (1975). All the rate constants are reproducible within ±3%. The following aspects of bromate oxidation as enumerated in the succeeding paragraphs have been established.

3.1 Effect of Potassium Bromate Concentration

Several reactions were carried out in order to find the order of the reaction in bromate. All the experimental parameters were kept constant and the concentration of bromate was varied in each reaction and the reaction was followed iodometrically. Figs.1, 2 and 3 show the linear plots obtained for all the reactions. The rate constant k_1 was obtained and the results are summarized in Table 1. It can be deduced from the results obtained that the rate coefficients are independent of the initial concentration of bromate, which indicates that the reaction is first order with respect to bromate concentration.

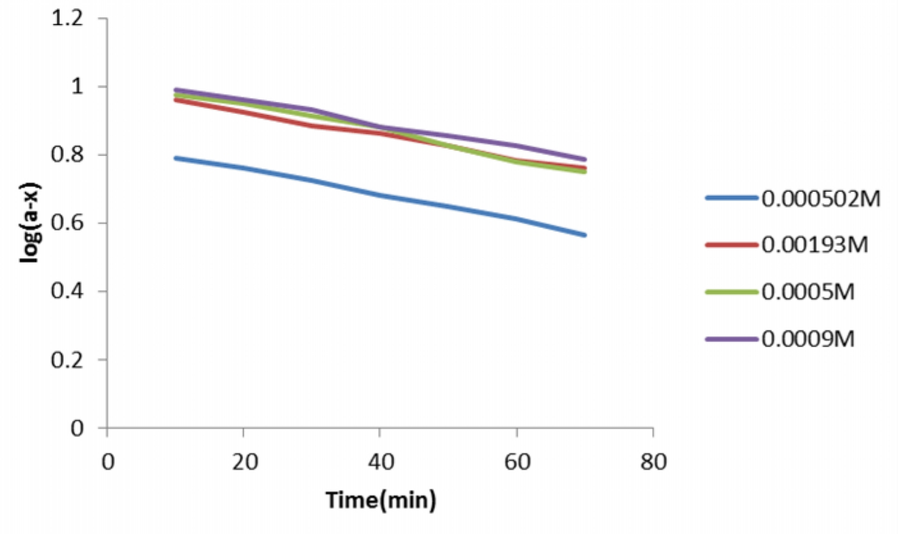


Fig. 1. Effect of [oxidant] on the oxidation of 3, 4- dimethylphenol [0.01M]. 50% HoAc(v/v) [$HClO_4$] = 0.05M temperature 308K

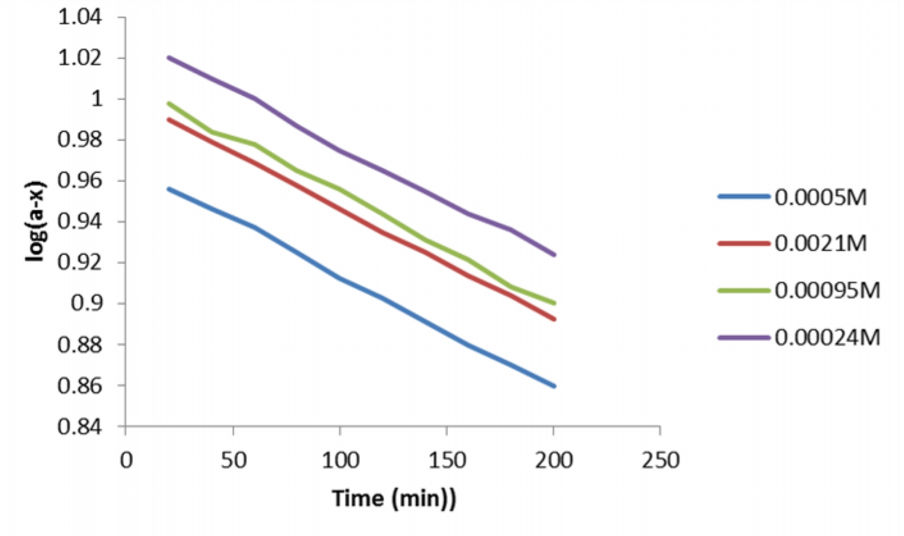


Fig. 2. Effect of [oxidant] on the oxidation of 4-Tert-butyl phenol [0.01M]. 50% HoAc(v/v) [$HClO_4$]=0.05M temperature 308K

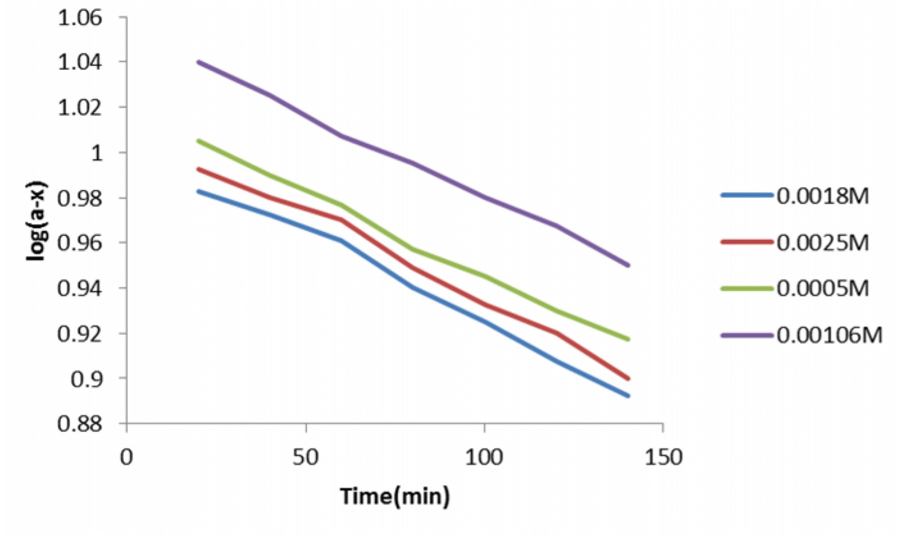


Fig. 3. Effect of [oxidant] on the oxidation of4- sec-butyl phenol [0.01M]. 50% HoAc(v/v) [$HClO_4$]=0.05M temperature 308K

Table 1. Effect of Bro_3^- on the reaction rate

Substrate	$10^4\left[BrO_3^-\right]M$	$10^3\ X\ k_1\ \text{min}^{-1}$
4 – tert – butyl phenol	2.48	1.30
	5.00	1.77
	9.52	1.29
	2.10	1.40
4 – sec-butyl phenol	2.50	1.65
	5.00	1.70
	1.06	1.63
	1.81	1.66
3:4 – dimethyl phenol	1.60	8.02
	5.00	8.06
	9.88	7.85
	19.40	8.29

[Substrate] = 0.01 M; Solvent = 50% aq. HOAc (v/v) [HC10$_4$] = 0.05 M; Temp = 308K

3.2 Effect of Substrate Concentration

Kinetic runs were carried out at different initial concentrations of substrate keeping the other conditions invariant. The k_1 values are summarized in Table 2. Fig. 4 shows the plot of log k_1 against log (substrate), indicating first order dependence with respect to [substrate]. Moreover the $k_2 = \left({}^{k_1}/_{[s]}\right)$ values computed for individual substrates studied are identical, confirming the first order dependence with respect to [substrate]. Hence the reaction follows first order in [oxidant] and first order in (substrate).

Table 2. Effect of [substrate] on the reaction rate

Substrate	**10^3X [sub] M**	**10^4k_1 sec $^{-1}$**	**K_2litre-mole $^{-1}$min $^{-1}$**
4 – tert-butyl phenol	2.50	3.25	0.13
	5.00	6.90	.14
	10.00	17.77	.17
	20.00	25.33	.13
4-sec-butyl phenol	5.00	8.00	.16
	10.00	17.00	.17
	20.00	32.17	.16
	30.00	47.58	.16
3, 4-dimethyl phenol	2.5	25.00	1.00
	5.0	45.20	0.90
	10.00	80.60	0.81
	20.00	18.40	0.92

[Bromate] = 0.0005 M; Solvent = 50% aq. HOAc (v/v); [HC10$_4$] = 0.05 M; Temp = 308K

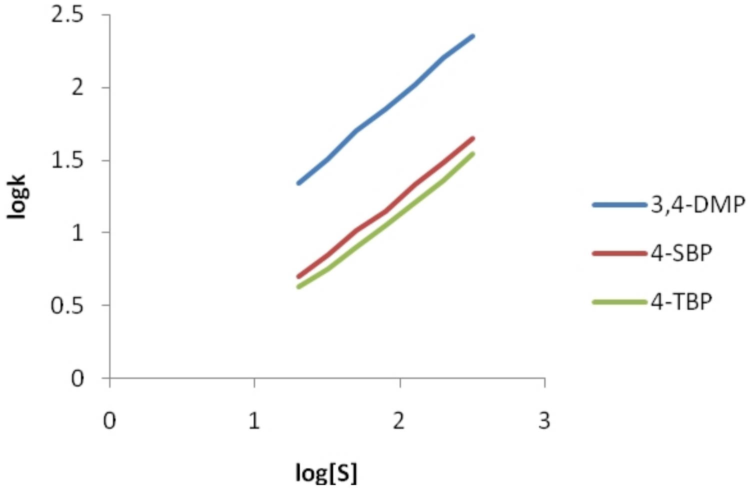


Fig. 4. Effect of [substrate] on the oxidation of 3, 4- Dimethyl phenol (DMP), 4-Tert-butyl phenol (4-TBP), 4- sec-butyl phenol (4-SBP).
50% HoAc (v/v) [$HClO_4$]=0.05M Temperature 308K [Oxidant]=0.0005M

3.3 Effect of Perchloric Acid Concentration

A series of reactions were carried out by changing the concentration of perchloric acid and keeping the other conditions constant. The rate constants increased with increase in perchloric acid concentration. The data is given in Table 3. A plot of log k_1 against log [H^+] gave a straight line with a slope of one (Fig. 5). The acid dependence proves that an equilibrium of the following type exists, the active species being $HBrO_3$:-

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3$$

Table 3. Effect of [H^+] on the reaction rate

Substrate	10^2 X [$HC10_4$] M	10^3 k_1 min $^{-1}$
4 – tert – butyl phenol	2.00	0.54
	5.00	1.77
	10.00	2.68
	20.00	4.80
4 – sec – butyl phenol	3.00	1.22
	5.00	1.70
	10.00	3.30
	20.00	6.30
3, 4 – dimethyl phenol	1.00	2.04
	2.00	4.10
	5.00	8.06
	10.00	15.60

[Substrate] = 0.01 M; Solvent = 50% aq. HOAc (v/v); [Oxidant] = 0.0005 M; Temp = 308K;

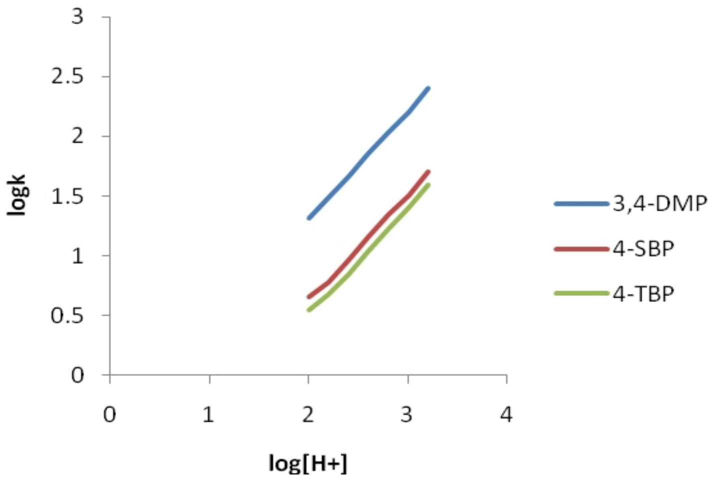


Fig. 5. Effect of [$HClO_4$] on the oxidation of 3, 4- Dimethyl phenol(DMP), 4 -Tert-butyl phenol (4-TBP), 4- sec-butyl phenol (4-SBP). 50% HOAc(v/v)
Temperature 308K [Oxidant] = 0.0005M [Substrate] = 0.01M pH range = 2.0 to 3.22

3.4 Effect of Solvent

The oxidation reactions were carried out in various water-acetic acid mixtures, maintaining other experimental conditions identical. The k_1 values obtained are given in Table 4. Increase in the percentage of acetic acid was found to increase the rate of reaction. The plot of log k_1 against 1/ ε is linear (Fig-6). Increase in HOAc and decrease in water content favours the formation of $HBrO_3$ or the above equation shifts to the right hand side. Also the plots of log k_1 against $\frac{£ - 1}{2£ + 1}$ are linear (Fig. 7).

Table 4. Effect of solvent composition on the reaction rate

Substrate	HOAc-H_2O%(v/v)	£	10^2X1/£	$10^3 k_1 min^{-1}$
4-tert-butyl phenol	40 – 60	49.6	2.02	0.64
	50 – 50	42.3	2.36	1.77
	60 – 40	35.1	2.85	3.78
	70 – 30	27.9	3.58	9.95
	80 – 20	20.6	4.85	38.36
4-sec-butyl phenol	40 – 60	49.6	2.02	1.18
	50 – 50	42.3	2.36	1.70
	60 – 40	35.1	2.85	2.95
	70 – 30	27.9	3.58	7.45
	80 – 20	20.6	4.85	25.33
3,4-dimethyl phenol	30 – 70	56.8	1.76	2.88
	40 – 60	49.6	2.02	4.87
	50 – 50	42.3	2.36	8.06
	60 – 40	35.1	2.85	16.71
	70 – 30	27.9	3.58	54.20

[Substrate] = 0.01 M; [$HC10_4$] = 0.05 M; [Oxidant] = 0.0005 M; [Temp] = 308K

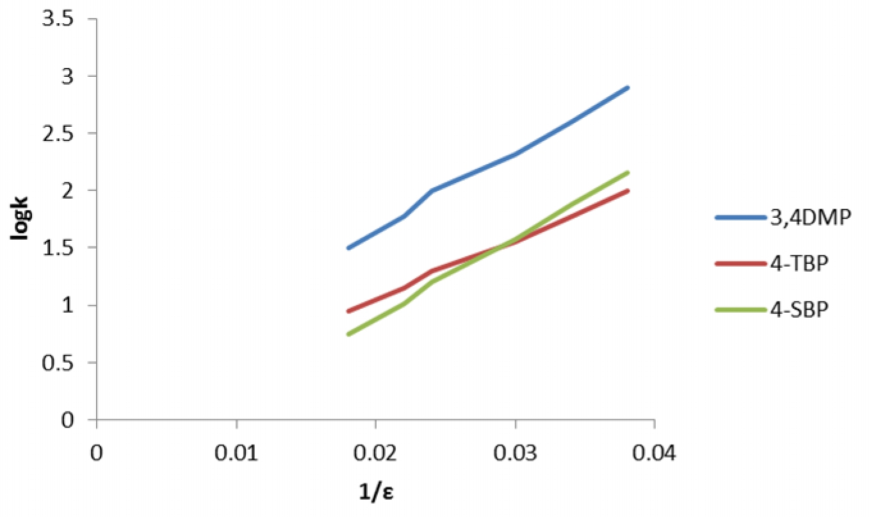


Fig. 6. Effect of [solvent] on the oxidation of 3, 4- Dimethyl phenol(DMP), 4-Tert-butyl phenol (4-TBP), 4- sec-butyl phenol (4-SBP). [$HClO_4$]=0.05M Temperature 308K [Oxidant]=0.0005M [Substrate]=0.01M

3.5 Effect of Addition of Salt

The effect of ionic strength on the reaction was investigated by carrying out the reaction in the presence of different amounts of $NaC1O_4$, maintaining all other conditions (Table-5).The results proves the effect of ionic strength on the reaction rate as negligible.

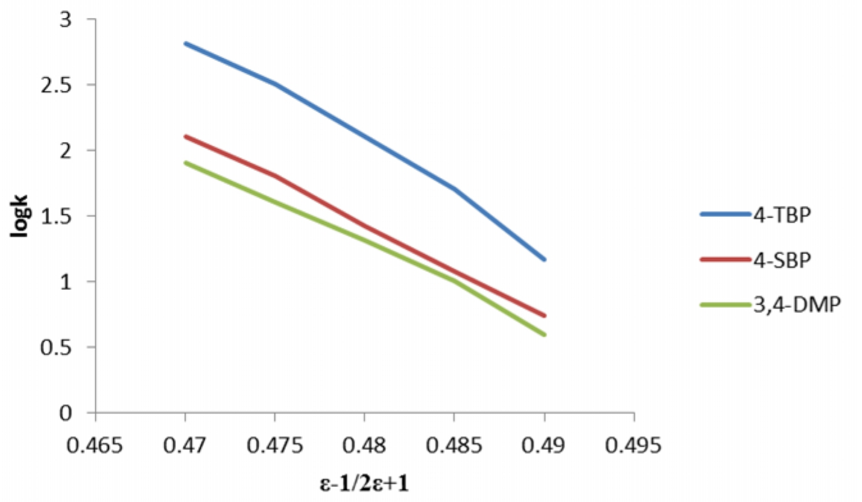


Fig. 7. Effect of [solvent] on the oxidation of 3, 4- Dimethyl phenol(DMP), 4-Tert-butyl phenol (4-TBP), 4- sec-butyl phenol (4-SBP). [$HClO_4$] =0.05M Temperature 308K [Oxidant] =0.0005M [Substrate]=0.01M

Table 5. Effect of adding salt on the reaction rate

Substrate	10^2 x Salt M	10^3k_1 min $^{-1}$
3,4-dimethyl phenol	2.5	7.16
	5.0	7.32
	10.00	7.67
	20.00	7.17
4-tert-butyl phenol	2.5	1.25
	5.0	1.21
	10.00	1.03
	20.00	1.23

[Substrate] =0.01M; [$HC10_4$] =0.05M; Temp =308K; [Bromate] = 0.0005 M; [Solvent] =50% aq. HOAc(v/v)

3.6 Effect of Addition of Mercuric Acetate

In order to determine whether molecular bromine is participating in the oxidation process, the reaction was carried out in the presence of mercuric acetate. From the rate constant in Table 6, proves there is no oxidation of phenol by Br_2 which excludes the possibility of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without bromated.

Table 6. Effect of addition of $Hg(OAc)_2$ on the reaction rate

10^3 x [HgO $(Ac)_2$] M	10^3 x k min $^{-1}$
0	8.06
1	12.5

[Substrate] = 0.01 M; [$HC10_4$] = 0.05M; Temp = 308K; [Oxidant] = 0.0005 M; Solvent = 50% aq. HOAc(v/v)

3.7 Order of Reactivity

Table 7 indicates that the order of reactivity among the methyl substituted phenols as 3, 4-dimethyl phenol > p-cresol > phenol. The order of reactivity among higher alkyl substituted phenols is p-tert-butyl phenol ≈ p-sec-butyl phenol > p-ethyl phenol > phenol.

Table 7. Rate constants for various phenols

Substrates	10^4 x k_1 min $^{-1}$
Phenol	6.60
p – ethyl	9.40
p – cresol	14.40
4-tert-butyl phenol	17.70
4-sec-butyl phenol	16.97
3,4 – dimethyl phenol	80.63

[Substrate] = 0.01 M; [$HC10_4$] = 0.05 M; Temp = 308K; [BrO_3] = 0.0005 M; Solvent = 50% aq. HOAc (v/v)

The oxidation of various alkyl substituted phenol by BrO_3^- has been found to be faster than that of phenol, as alkyl groups being electron donating in nature facilitate the oxidations. The oxidation of 3, 4 dimethyl phenols is faster than that of p-cresol, because the former has two electron donating methyl groups than in the case of p-cresol. The reactivity trend among the higher alkyl substituted phenols is in consonance with the inductive effect.

3.8 Effect of Temperature

The oxidations of the three substituted phenols were carried out at different temperatures while keeping other experimental parameters identical. The pseudo first order rate constants at different temperatures are given in Table 8. The substrates obeyed the Arrhenius relationship (Fig. 8). From the slopes of these plots, various activation parameters were evaluated. These are recorded in Table 9.

Table 8. Effect of temperature on the reaction rate

Substrate	Temp (°C)	10^3 x k_1 min^{-1}
4 – tert – butyl phenol	32	0.92
	35	1.77
	40	1.80
	45	3.00
4 – sec – butyl phenol	32	1.40
	35	1.70
	42	3.07
	45	3.56
3, 4 – dimethyl phenol	30	6.10
	35	8.06
	40	11.76
	45	18.48

[Substrates] = 0.01 M; [HC10$_4$] = 0.05 M; [Oxidant] = 0.0005 M; Solvent = 50% aq.HOAc(v/v)

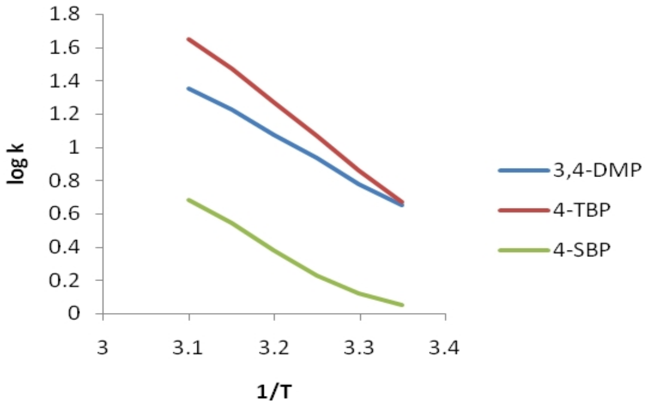


Fig. 8. Effect of temperature on the oxidation of 3, 4- Dimethyl phenol (DMP), 4-Tert-butyl phenol (4-TBP), 4 - sec-butyl phenol (4-SBP). [HClO$_4$] = 0.05M [Oxidant] = 0.0005M; [Substrate] = 0.01M

Table 9. Thermodynamic parameters at 308 K

Substrates	E_a	$\Delta H^{\pm}$	$\Delta G^{\pm}$	$\Delta S^{\pm}$
3,4-dimethyl phenol	58.59	56.03	73.19	-55.70
4-sec-butyl phenol	61.43	58.87	77.17	-59.45
4-tert-butyl phenol	65.38	62.82	77.82	-48.70

E_a, $\Delta H^{\pm}$ and $\Delta G^{\pm}$ are in KJ/mol and $\Delta S^{\pm}$ in J $mol^{-1} deg^{-1}$.

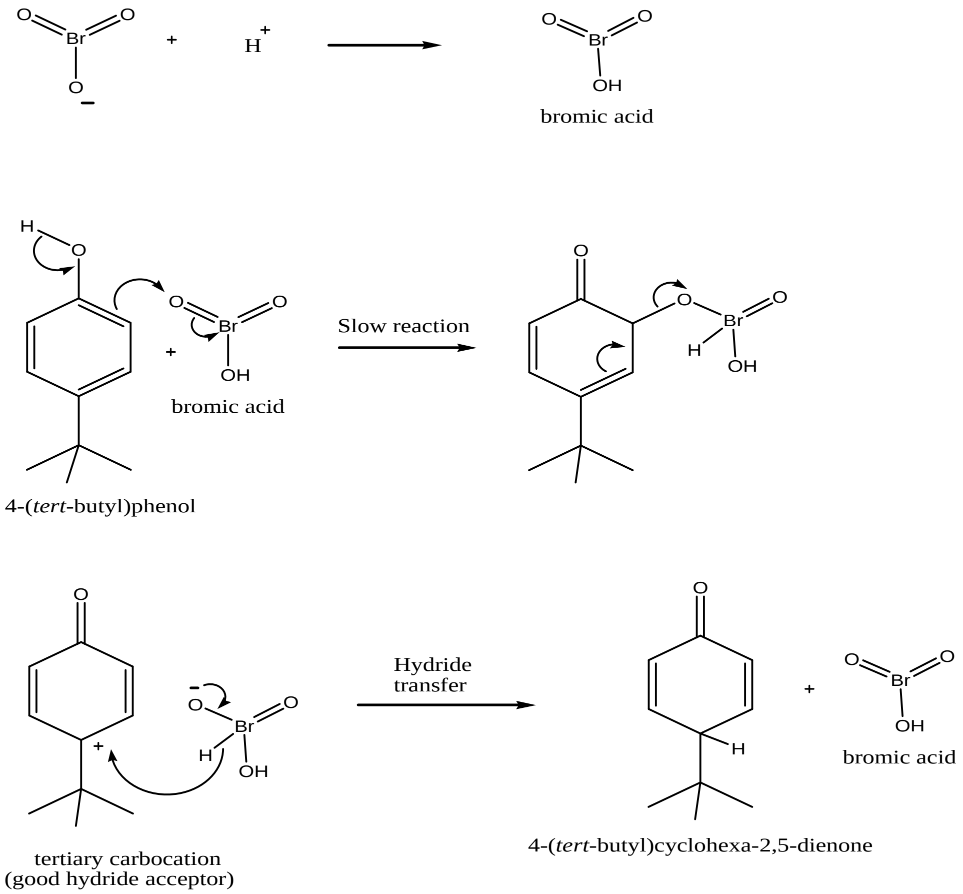
The high positive values of energy of activation ($\Delta G^{\pm}$) bulky transition state, while fairly high negative values of entropy of activation ($\Delta S^{\pm}$) suggests the formation of an activated complex with reduction in degree of freedom. The values of E_a suggest a fairly slow kinetics. Considering the first order kinetics with respect to the substituted phenols a mechanism consistent with above findings has been proposed in the relevant section.

3.9 Stoichiometry

To determine the stoichiometry of a reaction, 0.001 M of the substrate was mixed with 0.004 M of the oxidant with 50% aq. Acetic acid (v/v) and the concentration of the oxidant was determined after 1 hr, 2 hrs, 24 hrs, 48 hrs, 72 hrs and 96 hrs. Calculation shows that 1 mole of substrate reacts with 1 mole of the oxidant. The remaining of the stoichiometric mixtures was left for 15 days to ensure completeness of the reaction. The semisolid formed as product was found to be Quinone. The kinetics features observed in the present reaction are as follows:-

(i) The order with respect to oxidant is one.
(ii) The reaction is first order with respect to substrate.
(iii) The order with respect to acid is unity indicating that the active oxidant species is $HBrO_3$.
(iv) Increase in acetic acid increases the rate of reaction because the equilibrium $BrO_3^- + H^+ \rightleftharpoons HBrO_3$ shifts to the right thereby accelerating the rate of reaction.
(v) The stoichiometry was found to be 1:1. The products were the corresponding ortho-benzoquinones.

Hence we postulate a mechanism that involves the formation of a complex between the substrate and oxidant in the rate determining step which explains the first order dependence with respect to oxidant and substrate. The complex formed then breaks down in subsequent fast steps to give the product. The mechanism scheme which explains the above kinetic observation is given below:-



Scheme 1. Mechanism of formation of the oxidative species and subsequent participation in reaction, formation of a complex between the substrate and oxidant and then the product.

The rate law was deduced as 'rate law' = k [substituted phenols] [H$^+$] [BrO$_3^-$]

4. CONCLUSION

The kinetics of oxidation of 3, 4-dimethyl phenol, 4-sec-butyl phenol and 4-tert-butyl phenol has been investigated in aqueous HOAc – HC1O$_4$ acid medium. It has been found that the reaction is first order in [oxidant], [substrate] and [H$^+$]. The active oxidizing species was found to be HBrO$_3$. There was increase in the reaction rate with the increase in acetic acid composition. This observation was contrary to that expected for a dipole-dipole type of reaction. But it has been explained that this observation was due to the formation of HBrO$_3$ which is favoured by the increase in HOAc composition. The order of reactivity was found to be among higher alkyl substituted phenols as p-tert-butyl phenol $\approx$ p-sec-butyl phenol > p-ethyl phenol > phenol and that among the methyl substituted phenols as 3, 4 – dimethyl phenol > p-cresol > phenol. A plausible mechanism has been suggested which involves formation of a complex in the rate determining step.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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