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Full Paper

A Much-Needed Mechanism and Reaction Rate for the Oxidation of Phenols with ClO_2: A Joint Experimental and Computational Study

Carlos Alberto Huerta Aguilar,[A] *Jayanthi Narayanan,*[B]
Mariappan Manoharan,[C] *Narinder Singh,*[D,E]
and Pandiyan Thangarasu[A,E]

[A]Facultad de Química, Universidad Nacional Autónoma de México (UNAM),
Ciudad Universitaria, Coyoacán, 04510 México D.F., México.
[B]División de Nanotecnología, Universidad Politécnica del Valle de México,
Av. Mexiquense, C.P. 54910 Tultitlan, Estado de México, México.
[C]School of Science, Engineering and Mathematics, Bethune-Cookman University,
Daytona Beach, Florida 32114, USA.
[D]Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar,
Panjab 140001, India.
[E]Corresponding authors. Email: nsingh@iitpr.ac.in; pandiyan@servidor.unam.mx

The oxidation of phenols with chlorine dioxide, a powerful means to eliminate phenol pollutants from drinking water, is explored. Kinetic experiments reveal that 2,4,6-trichlorophenol exhibits a lower oxidation rate than other phenols because the chlorine atoms ($\sigma = 0.22$) at *ortho* and *para*-positions decrease the benzene's electron density, in agreement with the Hammett plot. The oxidation of phenol was found to be second order with respect to phenol and first order with respect to ClO_2 and a possible mechanism is proposed. The phenol/ClO_2 oxidation was found to be pH-dependent since the reaction rate constant increases with increasing pH. The oxidation rate was also significantly enhanced with an increasing methanol ratio in water. The oxidation products, such as benzoquinones, were analysed and confirmed by liquid chromatography and gas chromatography–mass spectrometry. Density functional theory computations at both the B3LYP/6-311+G(d,p) and M06-2X.6-311+G(d,p) levels with the SCRF-PCM solvation model (i.e. with water) further supported the proposed mechanisms in which activation barriers predicted the right reactivity trend as shown by the kinetic experiments.

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Introduction

Phenol and phenolic compounds often appear in wastewaters of chemical, petrochemical, and oil refining industries; for example, monochlorophenols are mainly used as intermediates in dyestuffs and in the manufacture of higher chlorinated phenols;[1,2] 2,4-dichlorophenol (DCP) is used in the synthesis of 2,4-dichlorophenoxyacetic acid.[3] In the trichlorophenol series, 2,4,5-trichlorophenol is employed as an intermediate in the production of the herbicide 2,4,5-trichlorophenoxyacetic acid.[4] Because of their toxicity and poor biodegradability,[5] phenolic wastewaters must be specially treated before being disposed off. Several treatment techniques that have been applied to remove phenolic compounds from wastewaters[5–12] usually involve complicated procedures, showing that they are not economically viable.

Chlorine dioxide has been considered an oxidant for the disinfection of drinking water or wastewater because it produces less objectionable chlorinated organic products such as trichloromethanes, tetrachloromethane, or haloacetic acids;[13] the chlorinated products are generally cancer promoters in humans.[14–16] The unpleasant tastes and odours in water can be completely eliminated by using chlorine dioxide even in small doses.[17] ClO_2 is a highly effective microbiocide at concentrations as low as 0.1 ppm over a wide range of pH, in particular, around (pH 5.0–9.5),[18,19] and its oxidation potential and disinfection strength are not pH dependent,[20] unlike the Fenton oxidant or other photo-catalysts (TiO_2/H_2O_2). Moreover, its preparation requires only low toxic and harmless chemicals.[21] ClO_2 is freely soluble in aqueous solutions where it does not ionise to form a weak acid and also has high selectivity and reactivity with environmentally objectionable waste materials, such as phenols, sulfides, thiosulfates, mercaptans, and amines, and its bacterial disinfection efficiency has been completely analysed.[22]

ClO_2 has been widely used in various industrial processes for the purification of drinking water,[23–26] cyanide removal from industrial wastewater,[27,28] and fouling control in sea water.[29] Furthermore, aqueous ClO_2 has been used to treat wastewater,[30–33] pharmaceutical wastes,[34,35] foodborne microorganisms,[36–38] polycyclic aromatic compounds,[39] phenols,[27,40,41] sulfides/thiosulfides,[42–44] amines,[45] antibiotics,[31,46] and micropollutants[47] or pesticides.[48] Nevertheless, in the literature, there are few reports dealing with phenol oxidation by ClO_2; in addition, no detailed report is found for the analysis of phenol oxidation by means of a combined experimental and computational study. Thus, the present paper deals with the oxidation kinetics of phenols with ClO_2. The rate law was determined along with solvent effects and the influence of pH on the oxidation rate was studied with a possible mechanism. UV-Visible, liquid chromatography (LC), and gas chromatography–mass spectrometry (GC-MS) techniques were used to characterise the oxidation products. To further support our kinetics experiments, we considered the mechanisms shown in Scheme 1 for phenol oxidation and explored them carefully by density functional theory (DFT) computations. Herein, we mainly aimed to predict the rate-limiting step of phenol oxidation while yielding benzoquinone as a final product and to compare the relative reactivity of phenol and chlorophenols with experimental data.

Experimental

ClO_2 Preparation

Chlorine dioxide was prepared by the reaction of sodium chlorite with acetic anhydride in an aqueous solution, as reported elsewhere.[49] Although chlorine dioxide can be produced from acidic solutions of either sodium chlorite[50–52] or sodium chlorate,[53–55] we used sodium chlorite as the starting material. The ClO_2 concentrations were calculated assuming a molar absorptivity coefficient for its aqueous solution at 360 nm of 1225 $cm^{-1}\,M^{-1}$; the absorbance values for the solutions typically varied less than 2.0 % during the experiments. An average ClO_2 concentration was used for the calculation of oxidation rate constants. For all the experiments, ClO_2 was freshly prepared and then used for the experiments.

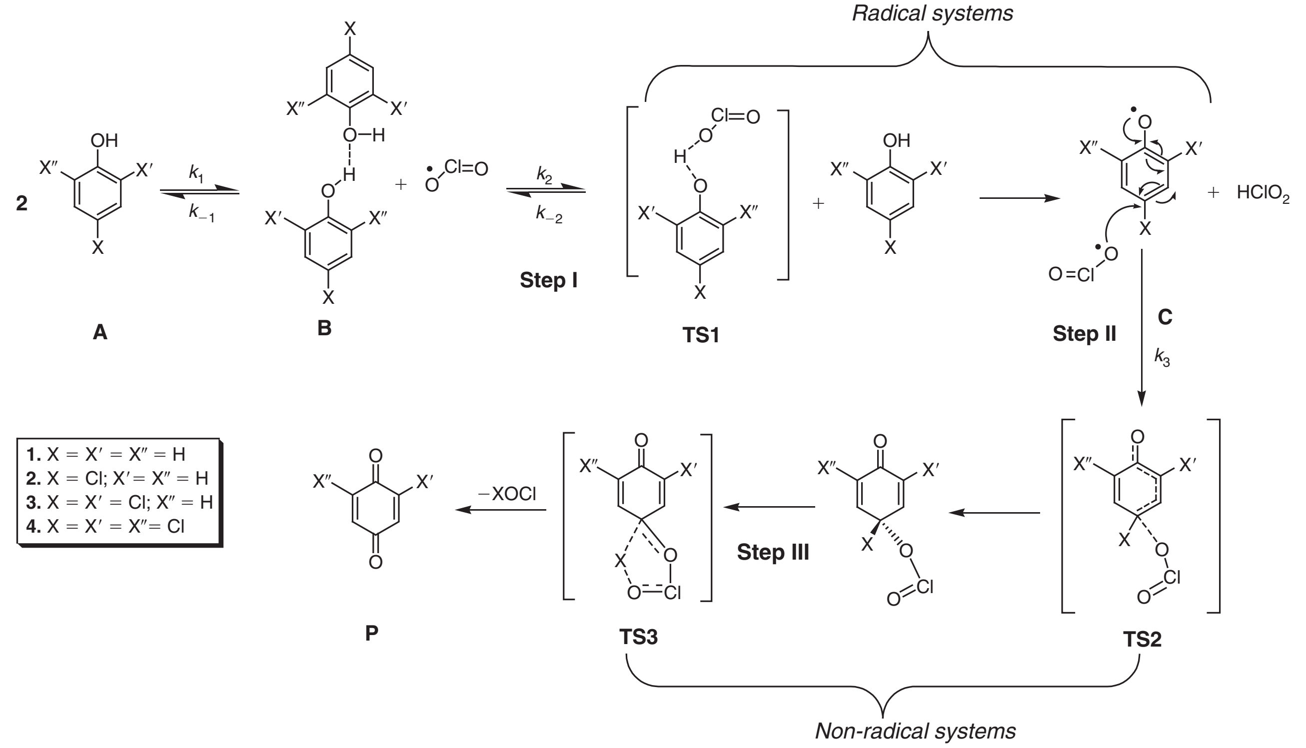
Reaction Kinetics

In a closed vessel (25 mL), phenols (1.0 mM) were oxidised by using chlorine dioxide (3.0 mM). The substrate was prepared in methanol/water (50 : 50) at pH 7.0 for the oxidation. The substrate-to-ClO_2 ratios were 1 : 4, 1 : 6, 1 : 8, and 1 : 10. The pH of the solutions was maintained by phosphate buffer solution (0.025 M) (K_2HPO_4 and KH_2PO_4). Rate constants for the oxidation of all the phenols were determined by plotting the substrate concentrations measured at different intervals against time. Furthermore, the chlorine dioxide decay (blank) in the solvent was examined and was then incorporated in the calculation of the reaction rate.

The phenol concentrations were determined by the colourimetric method; the phenol solution (10 mL) was first mixed with NH_4OH (0.5 N, 0.25 mL) to adjust the pH of the mixture solution to 7.9 ± 0.1 in the phosphate buffer, and 4-aminoantipyrine (0.1 mL) was then added, followed by $K_3[Fe(CN)_6]$ (0.1 mL). The resulting solution mixture was stirred for 15.0 min; the colourless solution turned to red and was then used to measure the concentration of the substrate spectroscopically in the visible region. All the experiments were carried out three times to obtain consistent results.

LC Analysis

HPLC equipment having a Nucleosil C18 column was used in the reversed-phase elution mode to analyse the intermediates formed from the oxidation of phenols, and then a suitable retention time for the intermediates in isocratic conditions was achieved. The appearance of peaks in the chromatogram corresponding to the ionised compounds was better resolved at low pH than at high pH, thus LC was recorded for the phenol solution at a low pH (pH 3.5). The phosphate buffer (0.01 mol L^{-1}) in CH_3CN/MeOH (80 : 20, v/v) was used to maintain the pH of the



Scheme 1. Phenol oxidations of mono-, di-, and trichlorophenols with a chlorine dioxide radical illustrates three different pathways (I–III) which also have be used for density functional theory (B3LYP/6-311+G**) computations.

solution. For the pH adjustment of the solution, phosphoric acid was employed. Furthermore, although a wide range of mobile phases, such as acetonitrile, THF, and methanol, was studied, it was found that an appropriate selectivity was suitable when the mobile phase was CH_3CN/MeOH (80 : 20) at a flow rate of 0.5 mL min^{-1} in the phosphate buffer (0.01 mol L^{-1}). The solutions were filtered through a 0.45 μm nylon filter unit before LC analysis.

GC-MS Analysis

GC/MS was used to analyse the formation of products from the phenol oxidation. GC with a capillary column (30 m, 0.25 mm internal diameter) having 0.5 μm film thickness Rtx-5ms (5.0 % phenyl–95 % dimethylarylenesiloxane) was employed. For the column, the oven temperature was programmed as follows: 100°C for 1.0 min, heated to 160°C at 30°C min^{-1}, and then heated at 15°C min^{-1} to 210°C; finally the temperature was set at 270°C by heating at 3.5°C min^{-1}. After injecting the sample (0.5 μL), a delay time of 150 s was set to avoid the solvent peak in the GC. A splitless mode was used for the injection with the purge valve closed for 3.0 min. In the column, the flow rate of helium was 1.0 mL min^{-1}. The sample solution, after ClO_2 (2.5 mM) oxidation with phenol (10.0 mM) in methanol/water (70 : 30) at pH 7.0, was filtered through a 0.45 μm nylon filter unit before the GC-MS injection. The sample was separated into individual components using a temperature-controlled gas chromatogram and then the mass spectrum for each GC component was obtained.

Table 1. The phenol oxidation data (substrate/ClO_2, 1 : 4)
See text for data definitions

Compounds	$\Sigma\sigma$	k [M^{-1} s^{-1}]	ln k	ΔG [kJ mol^{-1}]
Phenol	0	0.083	−2.488	6.066
4-Chlorophenol	0.23	0.067	−2.703	6.588
2,4-Dichlorophenol	0.46	0.05	−2.995	7.301
2,4,6-Trichlorophenol	0.69	0.041	−3.194	7.785

Results and Discussion

Oxidation of Phenols and their Kinetic Studies

Because of experimental considerations, kinetic studies were carried out at 3.0 mM of ClO_2 under excess ClO_2 to phenol (4 : 1, 6 : 1, 8 : 1, 10 : 1). The concentrations of phenol were determined as a function of time. A plot of [phenol]$^{-1}$ *v.* time yielded a straight line, and a similar behaviour was observed for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorephenol (Table 1) so that the reaction is of second order with respect to phenol with a pseudo reaction rate constant given by this slope. The value of this rate constant in turn is directly proportional to the concentration of ClO_2 (Fig. 1), yielding an overall reaction rate second order with respect to phenol and first order with respect to ClO_2. The concentration of phenol as a function of time was determined by UV-vis spectroscopy. In order to determine the concentration of the phenols in the visible region of the spectra, a colourimetric reaction between the different phenols and 4-aminoantipyrine was carried out to prepare their coloured derivatives which absorb in the visible region. The absorption of the phenols was measured at different times at 510 nm (Table 1). The degradation by ClO_2 of phenol is greater than for the chlorophenols, where the chlorine at the *para*-or/and *ortho*-position hinders the oxidation rate (see Table 1).

Proposal of Mechanism and the Reaction Rate Law

For the oxidation of different phenols, we propose that the ClO_2 radical reacts with the substrate to produce a ClO_2^- ion or $HClO_2$, and a phenoxyl radical which then reacts with another ClO_2 radical to form an adduct that consequently loses HOCl. Two equivalents of ClO_2 are consumed in the reaction to yield the product. Under neutral (pH 7) or alkaline conditions, the adduct is not seen by HPLC or GC because of a rapid pH-dependent hydrolysis.

It was observed that the increase of chlorite ion concentration in the reaction mixture reduces the reaction rate, and it shows that $k_{-1} > k_2$ (Scheme 1, step II). A plot of $1/k$ *v.* [ClO_2^-] is shown in Fig. 2 (inset) and yields good linearity, as expected.

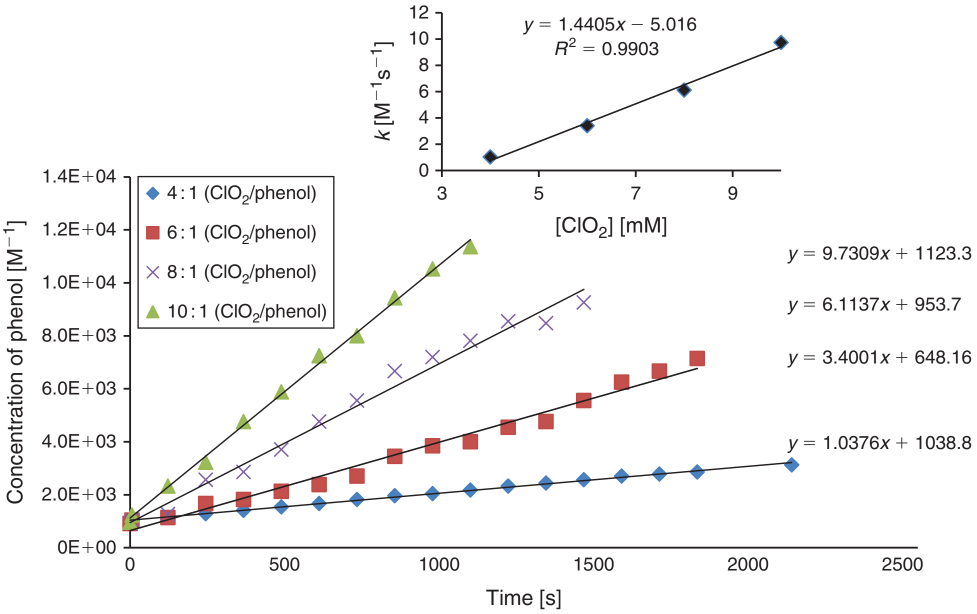


Fig. 1. Phenol oxidation at different concentrations of ClO_2.

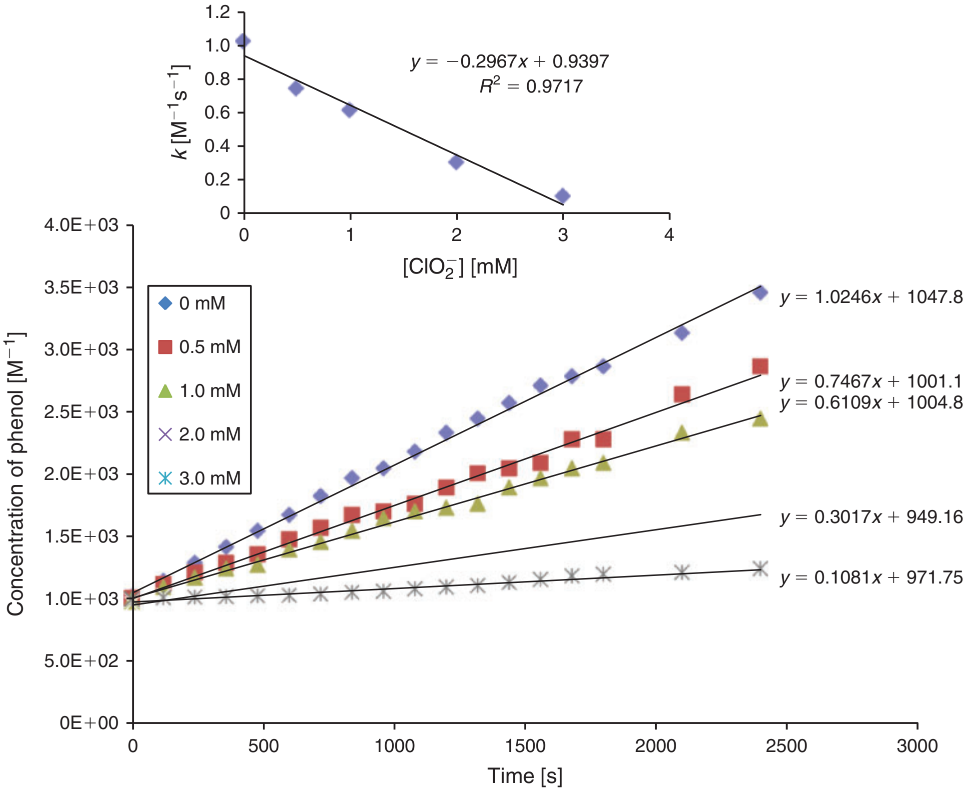


Fig. 2. Effect of chlorite ion on the phenol oxidation by ClO_2 (substrate/ClO_2, 1 : 4).

Phenol forms a short lived dimer held together by hydrogen bonding, which is then stepwise oxidised by ClO_2:

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$B + ClO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

$$C + ClO_2 \xrightarrow{k_3} P \tag{1}$$

where A is phenol, B is the dimer of phenol, and P are the oxidation products. Applying the steady-state approximation to [B] yields

$$[B] = \frac{k_1[A]^2 + k_{-2}[C]}{k_{-1} + k_2[ClO_2]} \tag{2}$$

and then also to [C], substituting the above value for [B], yields

$$[C] = \frac{k_1 k_2 [A]^2 \times [ClO_2]}{k_{-1}k_{-2} + k_{-2}k_3[ClO_2] + k_2 k_3 [ClO_2]^2} \tag{3}$$

Thus $\frac{d[P]}{dt} = k_3[C] \times [ClO_2]$. Substituting the above value of [C] and further assuming that 1) the second reaction is irreversible, $k_{-2} = 0$, once the dimer has decomposed by reacting with ClO_2 it cannot be reformed by the reverse reaction, the result is

$$\frac{d[P]}{dt} = \frac{k_1 k_2 k_3 [A]^2 [ClO_2]}{k_{-1}k_3 + k_2 k_3 [ClO_2]} \tag{4}$$

Finally, 2) if $k_{-1} >> k_2$ it is much more likely for the dimer to break apart than to react with ClO_2, the result is the observed kinetics:

$$\frac{d[P]}{dt} = k[A]^2[ClO_2]; k = \frac{k_1 k_2}{k_{-1}} \tag{5}$$

Confirmatory evidence for the mechanism are: 1) the reaction rate was observed to decrease with an increment in temperature; this unusual observation, is presumably because the complex B dissociates more readily and so is shorted lived and then unlikely to react with ClO_2, 2) the reaction rate also decreases with decreasing pH, apparently because in acidic solution the phenols form analogues of hydronium ions which are then blocked from forming the complex (phenol dimer) by hydrogen bonding.

Studies of pH versus k

The effect of increasing the solvent medium pH from 4.0 to 10.0 causes k to increase, yielding a linear relationship between log k and pH (Fig. 3). This is consistent with the previous reports that the rate constant for organic degradation by ClO_2 is significantly pH dependent if the organic compound is ionisable.[56–59] Phenol is easily ionisable in aqueous solution, thus the increase of rate constant with pH was observed as expected. It is known that as the solution pH increases, the oxidation reduction potential of ClO_2 increases while the hydrogen bond between the oxygen and water molecules is weakened.

Solvent Effect on k

The oxidation rate constant of phenol by ClO_2 in methanol–water media was found to increase considerably with

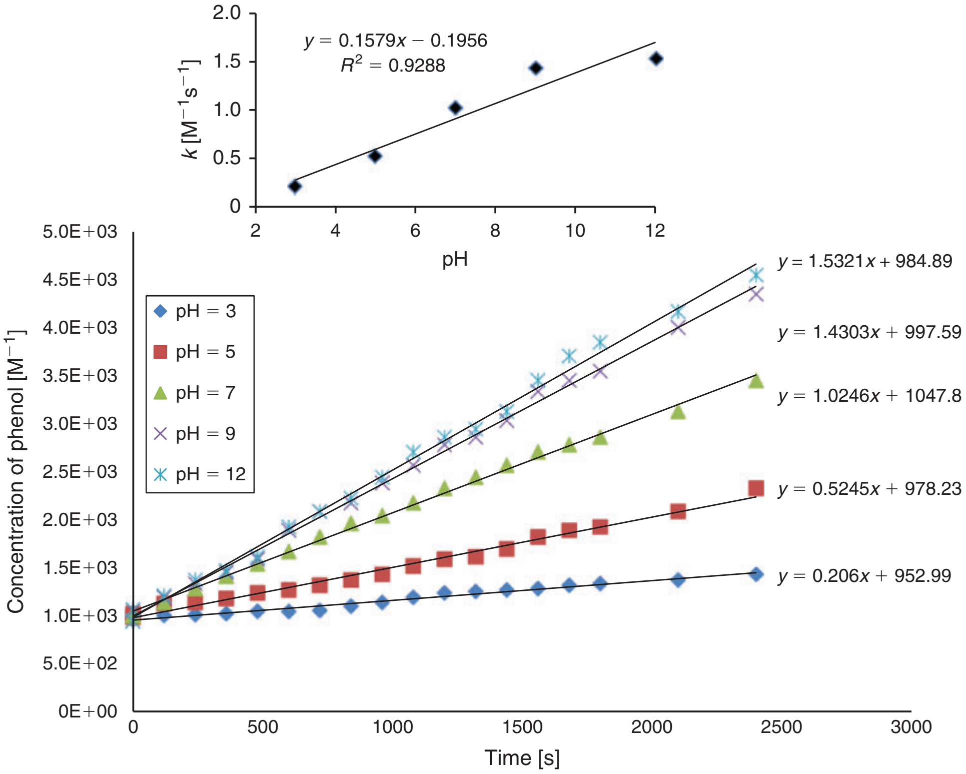


Fig. 3. pH effect on phenol oxidation by ClO_2 (substrate/ClO_2, 1 : 4).

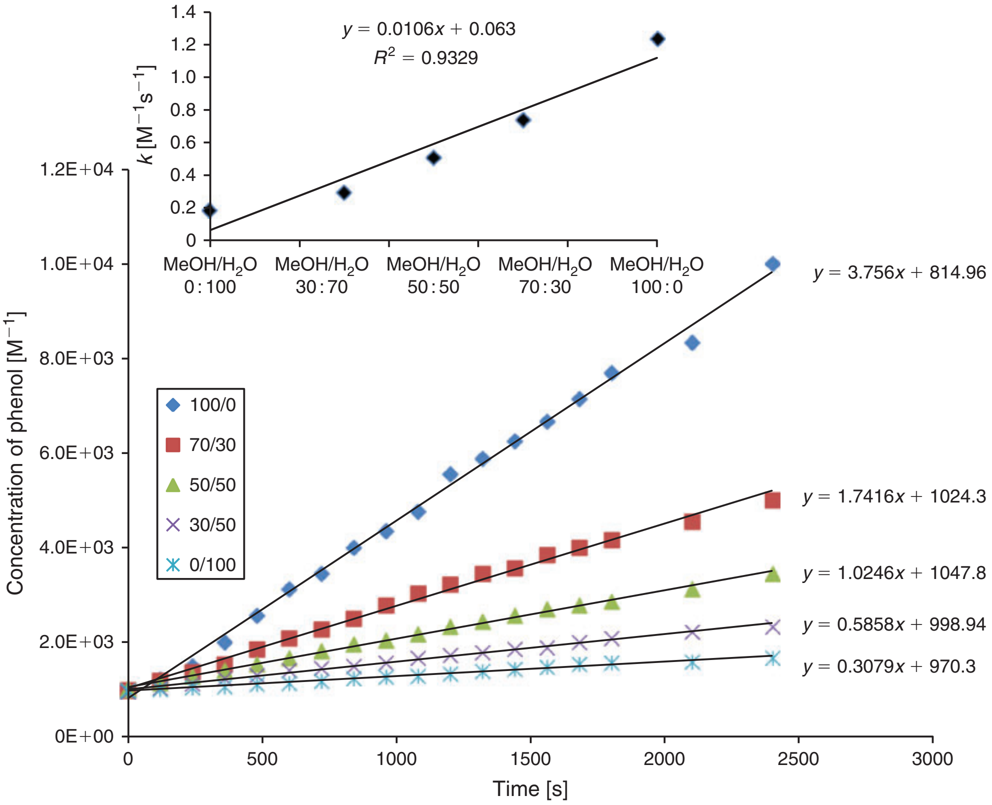


Fig. 4. Solvent effect on the phenol oxidation (substrate/ClO_2, 1 : 4).

methanol content, being maximum in pure methanol, implying that the rate constant decreases with increasing polarity of the medium (Fig. 4). When the water ratio increases so does the hydrogen-bond formation of phenol with the more polar water molecule thus shielding the O–H bond of phenol, so that its reaction rate is retarded, meaning that the formation of hydrogen bonds plays a substantial role in the reactivity of phenol.

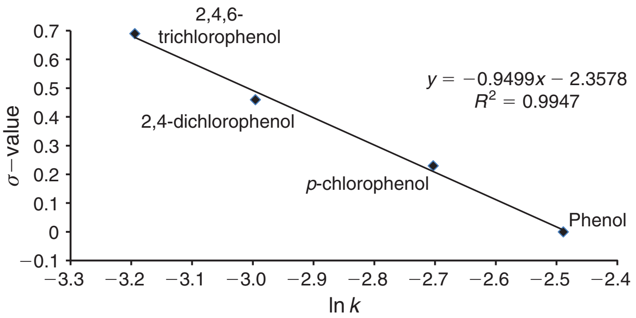


Fig. 5. Hammett plot: Correlation between substituent constant (σ) *v.* ln k for the different phenols (substrate/ClO_2, 1 : 4).

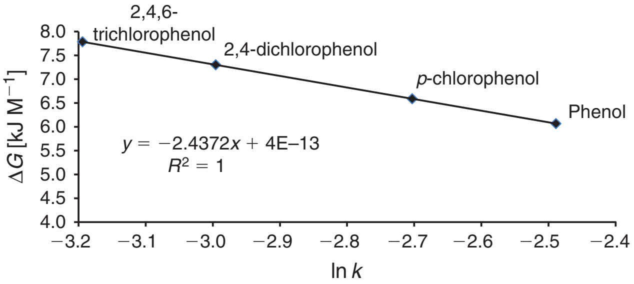


Fig. 6. Gibb's free energy plot for different phenol oxidation (substrate/ClO_2, 1 : 4).

Hammett Plot for Phenols/ClO_2 Oxidation

The Hammett plot, which describes the linear free-energy relationship among reaction rates, was used to develop quantitative relationships between structure and activity.

$$\ln k = \ln k_0 + \rho\sigma \tag{6}$$

$$\rho = \ln(k_{\text{phenol}}/k_x) \sum \sigma \tag{7}$$

For the compounds, the observed rate constants were applied in the Hammett equation and a good correlation was found between log k and substituent σ values (Fig. 5), i.e. the electron-donating or electron-withdrawing groups altered the aryl alcohol oxidation. Thus, a higher reaction rate for phenol and a lower rate for 2,4,6-trichlorophenol were observed. Furthermore, for the Hammett plot, the correlation reaction constant value (ρ) was -0.9499, where the sign of the slope indicates whether a reaction rate is accelerated or suppressed by electron-donating or electron-withdrawing substituents. In the present study, a negative slope ($\rho = -0.9499$) is observed, which indicates that there is a positive charge at the reaction centre in the transition state of the rate-limiting step, confirming that the rate of the reaction is suppressed by electron-withdrawing substituents; in contrast, the introduction of electron-releasing substituents at the *para*-position of the aryl structure enhances the electron density on the reaction centre and increases the reactivity. In addition, the magnitude of ρ is a measure of the susceptibility of the reaction to the electronic characteristics of the substituent. Moreover, the reaction constant was correlated with Gibbs free energy data (Fig. 6).

In addition, for the degradation rate of phenols, the free energy data were obtained by applying the following equation, $\Delta G^0 = -RT \ln k$, in order to relate the free energy data with the oxidation rate (Table 1) and it is seen that the reaction rate increases with decreasing Gibbs free energy. It was found that a more negative value resulted for phenol than for the other compounds, because of the greater rate constant for its reaction with ClO_2. The introduction of electron-withdrawing groups such as Cl in the aromatic phenol structure decreases the electron density in the ring, thus retarding the attack of the electron deficient ClO_2 radical on the phenol; in particular, the abstraction of H from phenol by ClO_2 turns out to be harder, yielding a lower rate constant for 2,4,6-trichlorophenol than for the other compounds.

On the other hand, since there is no electron-withdrawing group in the phenolic ring which can enhance its reactivity upon oxidation due to high electron density from the aromatic ring influenced by the ring-current, the phenol ring can be oxidised with great ease, especially by hydrogen abstraction from OH by ClO_2. Therefore, one can identify the relative reactivity of phenol with the electron accepting groups. The impact of chloro-substitution of phenols on the rate of reaction can be justified from the inductive effect due to the σ-acceptor behaviour of chlorine, although there is a resonance effect driven by the chlorine lone-pair (π-donor). Consequently, we can anticipate that several chloro-groups coincide with a decrease in the reactivity. Our experiments thus clearly show the following trend in reaction rate for these oxidations: phenol $>$ 4-chlorophenol $>$ 2,4-dichlorophenol $>$ 2,4,6-trichlorophenol.

LC and GC-MS Studies

The phenol oxidation was analysed by LC and GC methods. The LC results indicate that the peak height of phenol decreases with the increase of new signals at retention time (R_t) 7.35 and 5.32 min; in addition, the new signals were grown at the expense of the reduction of the phenol peak (R_T 9.40 min). The signals at R_T 9.40 and 9.22 min match the retention time of phenol and hydroquinone (HQ), respectively. In addition, an attempt to characterise this product using IR spectroscopy indicates the presence of a C=O group.

In the GC chromatogram (Supplementary Material, Fig. S1), the prominent peaks were at R_T 3.39, 8.96, and 10.49 min and these were selected for analysis by MS. The first two signals corresponded to the R_T of phenol (phenoxide ion) and benzoquinone, respectively. The corresponding molecular masses were m/z 92.9 (phenoxide ion) and 107 (benzoquinone), and their fragmentation patterns coincide with that of phenoxide and benzoquinone, respectively (see Supplementary Material), confirming the formation of benzoquinone as a major product of the phenol oxidation by ClO_2 oxidation. The possibility of chlorination by HOCl cannot be ruled out by the coupling of different free radicals.[60–62]

The mechanism (see Scheme 1) indicates that two equivalents of ClO_2 are consumed in the reaction and step II is the rate determining step in the ClO_2 consumption. Due to the one-electron acceptor characteristic of chlorine dioxide, the expected reaction mechanism could involve a radical formation (Scheme 1). As for the reactions of ClO_2 with phenols,[63,64] the formation of an unstable intermediate can be expected that will later be converted into hydroquinone and hypochlorous acid. In acidic solutions ($<$ pH 4), there is another key reaction in which chlorite is 'recycled' into the ClO_2 pool by the disproportionation of its acid form. In the oxidation, the approximate number of electron equivalents per ClO_2 is 5, as compared with 2 in the peroxide-based oxidations.

Table 2. The activation free energies (kinetics, $\Delta G^{\neq}$) and reaction enthalpy (thermodynamics, ΔH_r) in kcal mol^{-1}, calculated at the SCRF-PCM-B3LYP/6-311+G(d,p) level (in water) for a series of different phenol/ClO$_2$ oxidations producing 1,4-benzoquinone derivatives (see Scheme 1) in comparison with the barriers calculated at the SCRF-M06-2X/6-311++G(d,p) level

Compound	B3LYP/6-311+G(d,p) level					
	I		II		III	
	$\Delta G^{\neq}$	ΔH_r	$\Delta G^{\neq}$	ΔH_r	$\Delta G^{\neq}$	ΔH_r
Phenol (**1**)	6.08	−12.94	22.51	−7.47	2.05	−95.33
4-Chlorophenol (**2**)	5.58	−13.45	24.24	−4.15	6.96	−47.77
2,4-Dichlorophenol (**3**)	8.47	−11.78	26.76	−3.04	7.52	−48.29
2,4,6-Trichlorophenol (**4**)	10.10	−12.68	27.02	−1.42	7.75	−49.09

Compound	M06-2X/6-311+G(d,p) level		
	$\Delta G^{\neq}$	$\Delta G^{\neq}$	$\Delta G^{\neq}$
Phenol (**1**)	7.02	16.32	2.52
4-Chlorophenol (**2**)	8.55	18.28	8.85
2,4-Dichlorophenol (**3**)	11.45	21.68	10.93
2,4,6-Trichlorophenol(**4**)	14.81	23.74	13.69

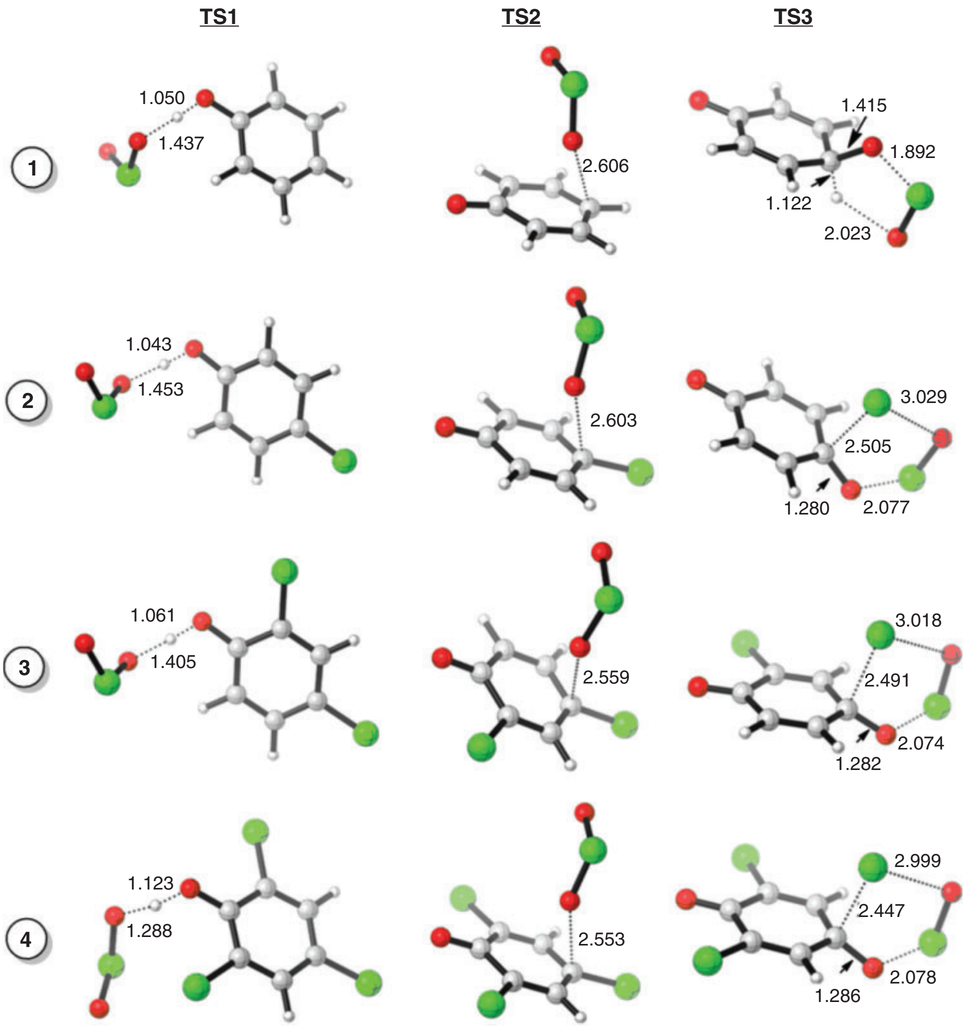


Fig. 7. Optimised transition state geometries (**TS1**, **TS2**, and **TS3**) for the three successive steps of phenol oxidations by ClO$_2$ (Scheme 1) computed at the SCRF-PCM-B3LYP/6-311+G(d,p) level along with some selected bond distances (Å). Compounds: phenol (**1**), 4-chlorophenol (**2**), 2,4-dichlorophenol (**3**), and 2,4,6-trichlorophenol (**4**).

Computational Analysis

Herein, the progress of phenol/ClO_2 oxidation for four different reactions has been analysed based on the proposed mechanism in Scheme 1 using DFT computations.[65–67] All stationary point geometries in the mechanism were optimised by using the B3LYP functional[68–71] with the 6-311+G(d,p) basis set[72] as implemented in the *Gaussian09* package.[73] In order to attain more authentic structures and energies, we re-optimised all gas-phase geometries at the SCRF-B3LYP/6-311+G(d,p) level using the PCM model where water was used as a solvent. The unrestricted B3LYP calculations were carried out wherever radical systems (step I) were involved in the mechanism. As far as the relative reactivity trend is concerned, the performance of UB3LYP/6-311+G(d,p) is acceptable for radical reactions (I and II) as shown by recent studies[74–79] but at the same time some of the studies on radicals have shown the weakness of this DFT method.[80–83] In view of this and to further assist our B3LYP analysis, we also performed the computation at the SCRF-M06-2X/6-311+G(d,p) level[84–86] since this new generation DFT method has been proven to be as accurate as high level theories[80–82] for radical systems. Although the absolute quantities of activation free energies show some variation between these two DFTs, the relative trends in the barriers (Table 2) are quite remarkable. In addition, to test the reliability of both DFT methods, we carried out a set of higher level calculations for the formation of a phenoxide radical from phenol and ClO_2 (i.e. step I) at both CCSD(T)/6-31+G(d,p) and CBS-QB3 levels on B3LYP/6-311+G(d,p) geometries (see Table S3 in the Supplementary Material). The activation barrier for this pathway at the B3LYP level was in reasonable agreement with the higher level barrier but it was quite comparable with the M06-2X barrier. Therefore, one can consider either B3LYP or M06-2X quantities while discussing the kinetic aspect of the reactions. Frequency calculations confirmed that equilibrium geometries were found to have all real frequencies whereas transition state (TS) geometries had only one imaginary frequency (see Supplementary Material).

The frontier molecular orbitals (FMOs) calculated at the DFT level reveal that the energy gap between the HOMO and LUMO decreases (see Supplementary Material) from phenol (**1**) to 4-chlorophenol (**2**) to 2,4-dichlorophenol (**3**) to 2,4,6-trichlorophenol (**4**) i.e. as the number of chloro-substituents increases. In view of this, the reactivity of phenol towards oxidation should increase with the increase in the number of chloro groups. This qualitative analysis clearly indicates the reactivity order as expected, but the quantitative energies obtained from the reaction profile geometries in comparison with experimental data will provide more conclusive remarks for phenol/ClO_2 oxidations.

The oxidation of phenols **1**–**4** by ClO_2 proceeds by three successive steps (Scheme 1) and these mechanisms were analysed by concerted TSs at the B3LYP/6-311+G(d,p) level (see Supplementary Material for M06-2X/6-311+G(d,p) geometries). Computations clearly illustrate the nature of these TSs (Fig. 7) by formed and cleaved bonds in these pathways as follows: (I) The addition of phenol to ClO_2 involves a hydrogen abstraction in which a weakening of the O–H bond (1.04–1.12 Å) due to bond cleavage along with the formation of a H···O bond (1.40–1.45 Å) in **TS1s** leads to the formation of a phenoxide radical. (II) The formation of a cyclohexadienone derivative occurs upon further addition of ClO_2 to a phenoxide radical. Herein, a new O···C bond (2.5 – 2.6 Å) occurring between ClO_2 and the *para*-carbon of phenol is seen to be formed faster but it disrupts the π-delocalization of the benzene ring; thus the energy of the TSs (**TS2s**) should be higher than the expected value. A gradual decrease in the C···O distance while going from **1** to **4** reflects the lateness of the TS in the series of reactions and this would provide a subsequent increase in the activation barrier. (III) The benzophenones have been

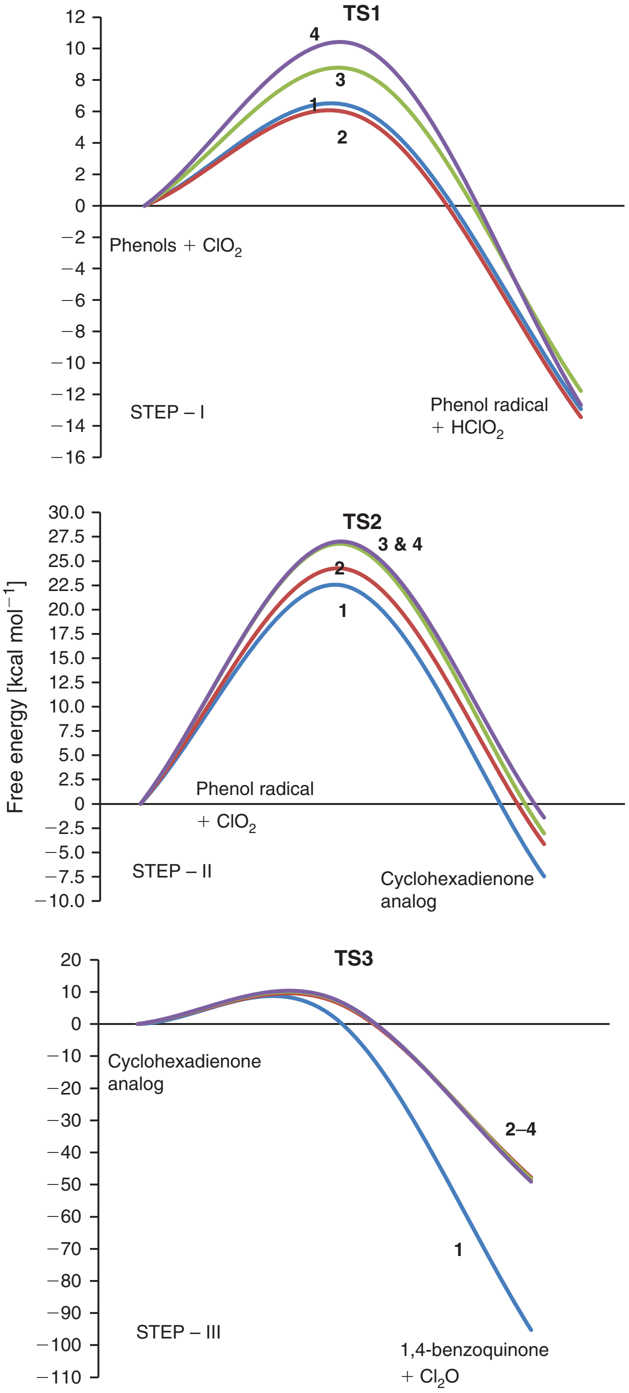


Fig. 8. The potential energy diagram (kinetic and thermodynamic energies) for a series of different phenol/ClO_2 reactions (phenol (**1**), 4-chlorophenol (**2**), 2,4-dichlorophenol (**3**), and 2,4,6-trichlorophenol (**4**)) forming 1,4-benzoquinone derivatives (Scheme 1) obtained from SCRF-PCM-B3LYP/6-311+G(d,p) computations. See Table 1 for a clear trend in the reaction barriers and energies.

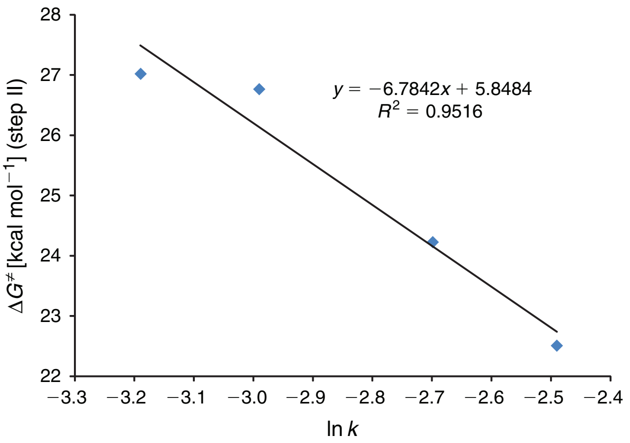


Fig. 9. A correlation of ln *k* (experimental) with the predicted activation energies (B3LYP/6-311+G**) of the rate-limiting step obtained for the oxidation of phenol and chlorophenols by ClO_2.

formed from cylohexadienone derivatives by via TS3s where carbonyl group (C=O) formation occurs to a lesser extent (Fig. 8) in chloro-derivatives compared with the typical system as revealed by the C=O distance (~1.42 *v.* ~1.28 Å) and this is an indication of a slower reaction of all the chlorophenols.

The progress of the oxidation of phenol and the chlorophenols with ClO_2 has been analysed by three consecutive reaction energy pathways (Fig. 8) based on the proposed mechanisms. It is to be noted that the difference in activation barriers between the B3LYP and M06-2X levels is found to be roughly 1–4 kcal mol^{-1} throughout the reaction paths, but we have shown below only B3LYP data for further discussion. Computations indicate that the first step of the reaction starting from phenol to form a phenoxide radical proceeds much faster than the second step that yields a cyclohexadienone analogue as shown by the activation free energies in Table 2 and Fig. 2, whereas the third pathway which forms 'benzophenone' is found to be the fastest one. In particular, the formation of cyclohexadienones occurs by a loss of aromaticity in the phenol ring which leads to a significantly high barrier (22–27 kcal mol^{-1}). It is also to be noted that the hydrogen abstraction process (I) is only slightly slower than the benzophenone formation (III) because the activation free energies are found to be 6–10 and 2–7 kcal mol^{-1}, respectively. Reaction enthalpies in Table 2 (see also Fig. 8) reveal that the phenoxide radical formation is quite exothermic as shown by enthalpy of reactions of approx. −12 to −13 kcal mol^{-1} in all four reactions but such exothermicity drops off (≈ -1 to -7 kcal mol^{-1}) while forming the cyclohexedienone/*p*-benzoquinone derivatives by dearomatisation as occurs in the kinetic pathway. Concurrently, the formation of benzophenone in step III shows a relatively much higher exothermicity (−48 to −95 kcal mol^{-1}) due to a strong π-conjugation in the product. Thus, DFT computations predict that the final step of our mechanism is much more favourable kinetically as well as thermodynamically and the formation of cyclohexedienone/*p*-benzoquinone (step II), illustrating a very high barrier, could be the rate-limiting step (Table 2 and Fig. 8). Interestingly, both kinetic and thermodynamic energies shown in the reaction pathways are in good accordance with the Hammond's postulate because the reaction with greater exothermicity arises from a lower barrier although the ultimate product provides an unusually high exothermic energy.

Moreover, the effect of chloro substituents on phenol upon oxidation by chlorine dioxide can be understood from the calculated activation free energies shown in Table 2 and Fig. 8. Herein, as the number of chloro groups increases from phenol to 4-chlorophenol to 2,4-dichlorophenol to 2,4,6-trichlorophenol (**1**–**4**), the activation barrier found in all three pathways increases in this order. Remarkably, our DFT prediction (Table 2) indicates the same trend in the reactivity of these phenols as we have shown by kinetics experiments (Table 1), although a trend in the exothermicity of these reactions is slightly random. Computations again prove that the σ-accepting ability of the chloro group actually decreases the reactivity of phenol towards the oxidation process. The main emphasis of this study can be demonstrated from a correlation between ln *k* values and predicted activation free energies (~98 %) in Fig. 9, which exhibits an excellent agreement between computed and experimental quantities. Thus, our combined DFT and experimental study provides strong evidence to support the proposed mechanism and relative reactivity trend in phenol and chlorophenols for the oxidation reaction by ClO_2.

Summary and Conclusion

Chlorine dioxide has been shown to be an effective oxidant for the degradation of phenols. Among the studied compounds, phenol exhibits a greater oxidation rate constant than the other compounds, agreeing with the Hammett plot (log *k v.* σ). In contrast, for 2,4,6-trichlorophenol, a lower reaction rate was observed because of the electron withdrawing chlorine groups at the *para* and *ortho*-positions, thus producing a more positive Δ*G* value than the other compounds. The phenol/ClO_2 oxidation is found to be of second order with respect to phenol and first order with respect to ClO_2, in agreement with our proposed mechanism for the oxidation. Furthermore, the oxidation of phenol by ClO_2 is pH dependent since the reaction rate constant increases with increasing pH. The oxidation rate is also considerably enhanced with the increasing methanol ratio in the water medium. In the oxidation products analysed by LC and GC/MS, glycine and benzoquinone are found to be the major products. Predictions based on DFT computations (B3LYP/6-311+G(d,p)) provided strong support for the proposed mechanisms because the reactivity trend shown by kinetics is in excellent agreement with the predicted activation barriers.

Supplementary Material

Supplementary Material containing the experimental and theoretical data can be found on the Journal's website.

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