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Theoretical and experimental interpretations of phenol oxidation by the hydroxyl radical

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ABSTRACT

Phenol oxidation by ·OH radicals produced by the Fenton reaction was studied and the oxidation process was monitored by the UV–visible, ^{13}C NMR and LC techniques. The results show that benzoquinone is formed. In the NMR and LC experiments, since the peaks corresponding to isomers *ortho* and *para*- benzoquinones are unresolved, DFT was used to determine the branching ratios of the isomers formation that coincides with their ΔG values (*ortho* > *para* > *meta*): 72% for *ortho*, 23% for *para* and 5.0% for *meta*. Furthermore, the energy profile of the ·OH attack at *ortho* is quite similar to that at the *para* position while the *meta* position attack is less favored by 2.0 kcal/mol.

1. Introduction

Hydroxyl radical, based oxidation of organic components in wastewaters is a growing technique particularly the Fenton reaction, which produces OH radicals at low cost and is suitable at room temperature [2–4]; furthermore, it does not produce toxic by-products. The generation of the OH radical by the Fenton reaction is as follows [1]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (k = 63\ M^{-1}\ s^{-1}) \qquad (1)$$

The mechanism of the Fenton reaction with organic substrates can roughly be divided into two groups: (1) A pathway based on the involvement of the hydroxyl radicals and (2) another mechanism based on the participation of the ferryl ion (FeO^{2+}), a highly reactive iron-oxo complex species. Although the aqua oxoiron(IV) species is believed to be an alternative to the OH radical in oxidation chemistry, the ferryl intermediate does not form in the reaction between Fe^{2+} and H_2O_2 in aqueous solution [5] while in the Fenton reaction, the generation of the aqueous hydroxyl radical is well established [6,7] and the mechanism of OH radical production is now well understood [8–15]. Moreover, it has been proven that the Fenton reaction with $(CH_3)_2SO$ under air-free conditions yields ethane, methylsulfinic acid and small amounts of methane and dimethyl sulfone; these products are known to be derived from ·OH radicals [5,16]. Consequently, in the Fenton reaction, ·OH is produced and not the ferryl ion species.

In phenol oxidation chemistry, it has been reported that the formation of benzoquinone is a prominent intermediate [17–43], but that formation process is still not completely resolved; for example, it is possible that the H-abstraction from phenolic OH during the reaction can form benzoquinone; however, its formation is ineffective since this pathway produces only a small amount (5.0%) [43]. Hence, the production of benzoquinone from phenol oxidation by attacking the OH radical at the phenol ring is still a topic of study; the present paper deals with the benzoquinone isomers generated from phenol oxidation. Although the detection of benzoquinone in the phenol oxidation by NMR and LC techniques is successful, these methods are unable to resolve the *ortho*, *para*, and *meta*-benzoquinone isomers; thus DFT was used to calculate the branching ratios of these isomers and to propose a possible mechanism for the oxidation.

2. Experimental studies

2.1. Chemicals and solvents

All chemicals used in the experiment were purchased from Sigma–Aldrich: Phenol, hydrogen peroxide solution (30 wt.%), ferrous sulfate, ferric sulfate, sodium hydroxide solution, sulfuric acid were used without further purification.

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2.2. Oxidation of phenol by the Fenton method

A phenol solution (1.0 mM) was prepared in water: methanol (80:20%) as the medium and it was treated with the Fenton reaction at pH 3.5. The pH of the solution was adjusted by H_2SO_4 or NaOH. After mixing the phenol with iron(II) solutions, H_2O_2 was added to initiate the reaction, the proportion of Fe(II): H_2O_2 being 1:5. The concentration of phenol was monitored spectrophotometrically at 500–510 nm by observing the absorbance decrease in a double beam UV/vis/NIR spectrophotometer (Perkin Elmer, Lambda-900). To the substrate solution, 4-aminoantipyrine was added in order to see the phenol peak in the visible region. The oxidation process was also analyzed by Liquid Chromatography (LC, Varian, pump model 9012) coupled with a diode array as a detector by using an analytical column C18, and the data acquisition was carried out through Start Varian software. The solutions were filtered through a 0.45 μm nylon filter unit before injection into the LC. The formation of intermediates was also studied by ^{13}C NMR (Varian Gemini, 300 MHz) by using TMS as an internal standard. All the experiments were carried out three times at room temperature for consistency of results.

2.3. Computational procedure

Electronic structural calculations were performed with a Gaussian03 program [44]. Unrestricted DFT methods were used to calculate the energies of the radicals. All geometries of the reactants, products and stationary points were fully optimized at the B3LYP/6-31G (d,p) level of theory, and in all cases, the character of the stationary points was confirmed by analyzing the frequency calculations: only positive eigenvalues for minima and one negative eigenvalue (imaginary frequency) for transition states were employed. It was verified that the motion along the reaction coordinate corresponds to the expected transition vector. In addition, in order to avoid the problem of the basis set superposition error and to minimize the basis set truncation error, the energy profiles for the addition of ·OH to phenol were recalculated using the complete basis set extrapolation CBS-QB3 approach [45]. Another important feature of the CBS-QB3 methodology is that it also corrects for spin contamination (proportional to <S2>). Therefore, the CBS-QB3 method was selected for radical additions to unsaturated hydrocarbons because these kinds of transition states suffer from spin contamination. In the CBS-QB3 calculations, the solvent effects were introduced by using the IEF-PCM model with radii = uahf. To compute $\Delta G^{\neq}$ values, the reference state was changed from 1.0 atm, as calculated from the Gaussian program outputs, to 1.0 M and the solvent cage effects were included according to the corrections proposed by Okuno [46], taking into account the free volume theory [47]. These corrections are in good agreement with those independently obtained by Ardura et al. [48] and other authors [49].

3. Results and discussion

Phenol oxidation was performed by the Fenton reagent, which was monitored by a UV–visible spectrophotometer, ^{13}C NMR, and LC. After analyzing the results, it was found that the phenol concentration had considerably decreased because of the oxidation (Fig. 1); for example, the initial concentration (1.0×10^{-3} M) of phenol was reduced to 1.5×10^{-5} M within 40 min of the reaction, indicating that the OH radical, which is produced by the Fenton reagent, effectively oxidizes phenol. Moreover, it was observed in the reaction process that there was a lag period at the initial time (20 min), meaning that at the initial stage, the reaction declines rapidly by the consumption of [Fe(II)] through the Fenton reaction (Eq. (1)). The reaction then was recovered through the reduction of the Fe(III) by hydroquinones (HQ) to Fe(II); this is because the regeneration of Fe(II) through the reduction of Fe(III) ion by H_2O_2 is much slower than that by hydroquinones [17]. Therefore, if the total iron concentration $[Fe]_T$ is equal to the initial concentration of $[Fe(III)]_I$, the lag phase is a slow rate-limiting reduction (Eq. (2)), where Fe(III) is reduced to Fe(II) by 1,4-or 1,2-HQ to sustain the Fenton reaction (Eq. (1)) for the production of OH radicals. Thus the regeneration of Fe(II) transforms the lag phase to the reaction progress phase.

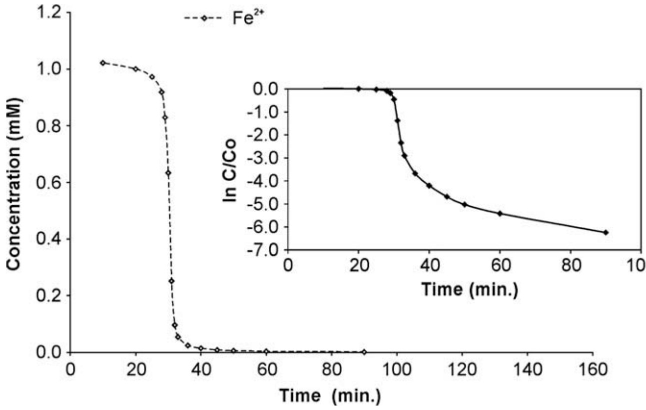

Fig. 1. Oxidation of phenol by the Fenton reaction.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (k = 1.0 \times 10^{-2}\ M^{-1}\ s^{-1}) \qquad (2)$$

$$Fe^{3+} + \text{hydroquinones} \rightarrow Fe^{2+} \quad (k = 4.4 \times 10^{2}\ M^{-1}\ s^{-1}) \qquad (3)$$

3.1. ^{13}C NMR and LC evidences of phenol oxidation

The oxidation of phenol by the Fenton reaction was analyzed by ^{13}C NMR at different time intervals. The results (Fig. 2) indicate that a considerable change in the spectra occurred after the addition of the Fenton reagent to the phenol solution and that the change was mainly due to phenol oxidation to benzoquinone. For example, in the spectra (Fig. 2a), four signals corresponding to four different carbons of phenol appeared; the peak at 158.0 ppm is assigned to carbon attached to OH and the remaining signals of 117.0, 132.3 and 122.2 ppm correspond to the carbons at *ortho*, *meta* and *para* positions to OH, respectively; however, following the Fenton reagent addition to the phenolic solution, after 60 min (Fig. 2b), new signals developed at 189.0 and 176.0 ppm corresponding to carbons (—C═O) of hydroquinone (HQ), and carboxylic acid, respectively, the signals at 108. 5 and 102.5 ppm being due to C═C of HQ. Finally, all signals presented in the region (100–180 ppm) (Fig. 2c) disappeared except the signals (174.0 and 102 ppm) corresponding to —C═O and C═C of HQ; this confirms the formation of HQ from phenol by the OH radical. However, the peaks corresponding to the hydroquinone isomers, such as *meta*, *ortho* and *para* products are not resolved by the ^{13}C NMR.

In addition, the LC technique was employed to analyze the intermediates of phenol oxidation at the reversed-phase elution mode by a Nucleosil C18 column; this was applied under isocratic conditions to achieve a suitable retention time for the intermediates. It is generally known that a low pH is necessary for the ionized compounds to yield highly resolved peaks in the liquid chromatogram. In the present experiment, the phosphate buffer (0.01 mol L^{-1}) in CH_3CN: MeOH (80:20 v/v) was used to maintain a low pH of the phenol solution (pH 3.5) and phosphoric acid was used to adjust the pHs. Furthermore, a wide range of mobile phases such as acetonitrile, THF and methanol was studied; it