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Authors
Yang, Xuejing
Duan, Yanghua
Wang, Jinling
et al.

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The Impact of Peroxymonocarbonate (HCO₄⁻) on the Transformation of Organic Contaminants during Hydrogen Peroxide (H₂O₂) *in situ* Chemical Oxidation (ISCO)

Xuejing Yang[a,b], **Yanghua Duan**[a], **Jinling Wang**[b,c], **Hualin Wang**[b,c], **Honglai Liu**[c], **David L. Sedlak**[a,*]

[a]Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, CA 94720-1716, USA

[b]National Engineering Laboratory for Industrial Wastewater Treatment, East China University of Science and Technology, Shanghai, 200237, China

[c]State Key Laboratory of Chemical Engineering, East China University of Science and Technology (ECUST), Shanghai 200237, China

Abstract

Under the conditions employed when in situ chemical oxidation is used for contaminant remediation, high concentrations of H_2O_2 (e.g., up to ~10 M) are typically present. Using ^{13}C NMR, we show that in carbonate-rich systems, these high concentrations of H_2O_2 result in a reaction with HCO_3^- to produce peroxymonocarbonate (HCO_4^-). After formation, HCO_4^- reacts with phenol to produce di- and tri-hydroxyl phenols. HCO_4^- reacts with substituted phenols in a manner consistent with its electrophilic character. Exchanging an electron-donating substituent in the *para* position of a phenolic compound with an electron-withdrawing group decreased the reaction rate. Results of this study indicate that HCO_4^- is a potentially important but previously unrecognized oxidative species generated during H_2O_2 *in situ* Chemical Oxidation (ISCO) that selectively reacts with electron-rich organic compounds. Under conditions in which HO· formation is inefficient (e.g., relatively high concentration of HCO_3^-, low total Fe and Mn concentrations), the fraction of the phenolic compounds that are transformed by HCO_4^- could be similar to or greater than the fraction transformed by HO·. It may be possible to adjust treatment conditions to enhance the formation of HCO_4^- as a means of accelerating rates of contaminant removal.

Graphical Abstract
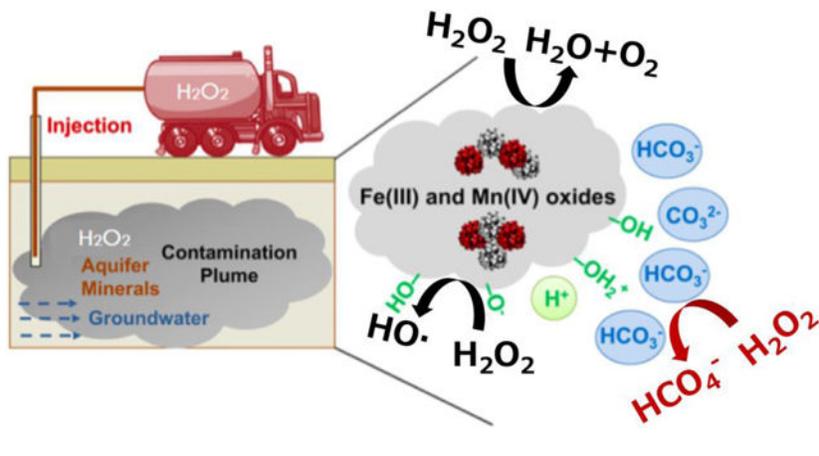
INTRODUCTION

Over the past three decades, ISCO has emerged as a cost-effective remediation technology for contaminated soil and groundwater due to its rapid implementation and ability to treat a variety of contaminants.[1–4] Currently, H_2O_2 is one of the most widely applied oxidants used for ISCO. When H_2O_2 is introduced to the subsurface, it reacts with dissolved and surface-associated iron ($\equiv Fe^{II}$ or $\equiv Fe^{III}$) to produce reactive oxygen species, including hydroxyl radical (HO·) and hydroperoxyl radical (HOO·):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO \cdot + HO^- \qquad \text{(eq.1)}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO \cdot + H^+ \qquad \text{(eq.2)}$$

$$\equiv Fe^{II} + H_2O_2 \rightarrow \ \equiv Fe^{III} + HO \cdot + HO^- \qquad \text{(eq.3)}$$

$$\equiv Fe^{III} + H_2O_2 \rightarrow \ \equiv Fe^{II} + HOO \cdot H^+ \qquad \text{(eq.4)}$$

$$2\, H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{(eq.5)}$$
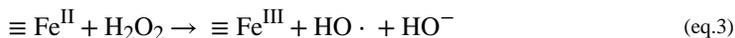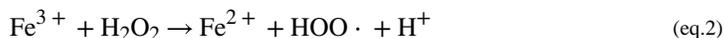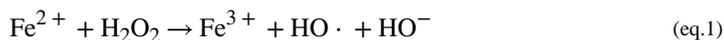
In parallel with these reactions, H_2O_2 reacts with iron and manganese species in a process that results in the production of H_2O and O_2 without the formation of reactive oxygen species (eq. 5). Measurement of the stoichiometry efficiency (E, the number of moles of organic compound oxidized per mole of H_2O_2 lost, eq. 6) under conditions in which the concentrations of the organic contamination are high enough to capture all of the HO· produced indicate that non-radical reactions (i.e., eq. 5) typically account for over 99% of the H_2O_2 loss[5–8]. In other words, H_2O_2 ISCO is inherently inefficient because a two-electron transfer mechanism predominates rather than radical chain reactions that produce HO·[9].

$$E = \frac{\Delta[\text{Organic Compound}]}{\Delta[H_2O_2]} \times 100\% \qquad \text{(eq.6)}$$

As a result of ineffecient nature of the process, relatively high concentrations of H_2O_2 (i.e., 1–10 M) are typically encountered near the injection well.[1, 10, 11] Under these conditions, reactions that are usually considered to be unimportant under more dilute conditions may contribute to the oxidation of contaminants. In particular, peroxymonocarbonate ion (HCO_4^-), a substitution product formed when H_2O_2 reacts with bicarbonate (HCO_3^-), can be formed (eq. 7):[12, 13]

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O \quad K = 0.32 \pm 0.02 M^{-1} \qquad \text{(eq.7)}$$
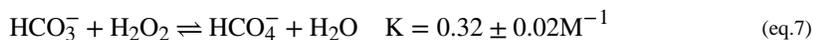
Percarbonate has been detected during the production of alkali-metal peroxocarbonate salts[12, 14] and in enzymatic reactions.[15] It also has been evaluated as a potential oxidant for organic contaminants when contaminated groundwater from carbonate-rich formations undergoes pump-and-treat remediation.[16–18] However, its role in contaminant transformation during ISCO has not been considered previously. HCO_4^- is a selective electrophile that reacts with electron-rich compounds, such as organosulfides,[13, 19] amines[20] and alkenes.[21] To assess the potential of HCO_3^- to contribute to contaminant removal during H_2O_2 ISCO, we studied the formation of HCO_4^- and its reaction with substituted phenols under conditions typically encountered during remediation.

MATERIALS AND METHODS

Materials and Chemicals.

All experiments were performed with water purified by a Milli-Q system. $NaHCO_3$, $NaOH$, NaH_2PO_4, Na_2HPO_4, H_3BO_3, $Na_2B_4O_7$ and other inorganic chemicals were obtained from Sigma-Aldrich at ACS reagent purity. Stock solutions of phenol (50 mM) and H_2O_2 (10 M), standardized by $KMnO_4$ titration[22], were stored at 5 °C. ^{13}C enriched $NaHCO_3$ used for NMR analysis was purchased from Cambridge Isotope Laboratories Inc. 5,5-dimethyl-1-pyrroline N-oxide (DMPO, ESR grade) from Sigma Aldrich was used as a spin trap. The color indicator for H_2O_2 measurement, $TiOSO_4$ (15% wt) solution, was purchased from Fluka.

Kinetics Experiments.

In most experiments, reactions were initiated by mixing equal volumes of a phenol solution and a buffered H_2O_2-containing solution in a 2-mL borosilicate glass auto-sampler vial at room temperature. Typically, the initial phenol concentrations ranged from 0.5 to 5.0 mM. $NaHCO_3$ was used both as the buffer and as a reactant at concentrations ranging from 10 to 1000 mM. To initiate the reaction, an aliquot of H_2O_2 was carefully added to the glass vial by pipette to a final volume of 2 mL. The auto-sampler vial was immediately capped after H_2O_2 addition. There was no headspace or noticeable bubble formation before the experiment. After manual shaking for 30 s, samples were injected into the HPLC at time intervals of 5 or 15 min for determination of phenol concentrations. For the measurement of

H$_2$O$_2$, a separate set of vials was prepared and sampled in parallel. Three replicate measurements were conducted for each treatment. The reaction rate constant of pseudo first order for phenol conversion was calculated as follows:

$$k_{obs} = -\frac{\ln([PhOH]/[PhOH]_0)}{t}$$

(eq. 8)

Analytical Methods.

For the measurement of phenol, 10 or 25 μL aliquots were injected with an Agilent® 1260 Infinity auto-sampler in an Agilent 1200 series HPLC system equipped with a C18 column (300 × 3mm, 4μM; Phenomenex, Aschaffenburg, Germany). Phenols were detected by UV absorbance at 271 nm. Acetonitrile (40%) and 10 mM formic acid (60%) were used as the mobile phase at a flow rate of 1 mL/min. For substituted phenols, the flow rate was reduced to 0.6 mL/min and a gradient program was employed as described previously.[23] The concentration of H$_2$O$_2$ was determined with the TiOSO$_4$ colorimetric method[24] using a UV-vis spectrophotometer (Shimadzu UV-2600). The pH of the solution was measured with a Mettler Toledor 230 pH meter with an InLab® Flex Micro electrode. The existence of ring opening products was identified by analysis on a Waters UHPLC-MS Acquity autopurification system, which equipped with a XBridge C18 column (3.5μm, 4.6 ×100 mm), with the mass spectrometer operated in the full scan mode of a range of a m/z of 84 to 248. The gaseous products in headspace were measured by gas chromatography (HP 7890; Agilent Technologies) with an HP-Plot Q (15 m × 0.53 mm × 40 μm), a Plot Molesieve 5A column (30 m × 0.53 mm × 50 μm) and a TCD detector.

Electron Paramagnetic Resonance (EPR).

Experiments to assess the presence of free radical species, including hydroxyl radical (HO·) and carbonate radical (CO$_3^{2-}$·) were conducted with DMPO as a spin trap.[25] A Bruker EMX-8/2.7C spectrometer was operated at X-field with a center field at 3511.520 G and a sweep width of 200 G. The microwave frequency was 9.873 GHz and the power was 2.016 mW. The sweep time of the signal channel was 41.9 s with a 3.56×10^4 gain at the receiver. Before each experiment, the sample solution was freshly prepared with H$_2$O$_2$ (0.25 M) and bicarbonate (10–1,000 mM). After stirring for 30 s, 1 mL aliquots were mixed with 1 mL DMPO (10 mg/L) immediately. The obtained solution was transferred into a 100 μL capillary tube, which was then fixed in the resonant cavity of the spectrometer. The experiment was performed at room temperature.

^{13}C Labeling Nuclear Magnetic Resonance (NMR).

^{13}C NMR spectra were measured on a Bruker Advanced 400 MHz instrument. Solutions were prepared as described for the kinetics study with the addition of 10% D$_2$O. The stock solutions of phenol and H$_2$O$_2$ employed were the same as those used for the kinetic measurements section and ^{13}C enriched NaHCO$_3$ (1000 mM) was prepared with 10% D$_2$O in MilliQ water as the buffer solution. The solution was continuously mixed by a vortex mixer for 5 min before injecting it into the NMR tube for signal collection at room temperature. Spectra were obtained with a dI=8 s and 32 times of acquisitions. The

concentrations of H_2O_2 and HCO_3^- varied from 0.25 M to 5 M and 50 mM to 1000 mM, respectively. When the concentration of HCO_3^- was lower than 50 mM, the signal: noise ratio of the spectra was too low for the detection of peaks.

RESULTS AND DISCUSSION

Effect of $NaHCO_3$ concentration on phenol transformation during H_2O_2-ISCO.

The HCO_3^- concentration in groundwater undergoing ISCO depends upon the geochemistry of the aquifer. The concentration of HCO_3^- in groundwater typically ranges from 0.1 to 10 mM.[26] If a carbonate-containing aquifer is subjected to acidification (e.g., through release of acidic contaminants or chemical reactions that produce acid) or if biological processes produce CO_2 as a product of metabolism processes, higher concentrations can occur.

To assess the potential importance of HCO_4^- to phenol transformation, 250 mM H_2O_2 was added to a 10 mM HCO_3^- solution at pH 8.4. Under these conditions, approximately 20% of phenol disappeared after 90 minutes, whereas 40% loss was observed over the same period when the initial HCO_3^- was increased to 100 mM (Figure 1). Little if any phenol loss was observed in borate buffer, phosphate buffer or solutions without buffer.

The loss of phenol was accompanied by the appearance of new peaks at retention times around 5.6 min, 6.5 min and 8.7 min that can be assigned to 1,2,4-benzenetriol, hydroquinone and 1,4-benzoquinone, respectively (Figure S1~S3). The formation of polyhydroxylated benzene derivatives, including hydroquinone and 1,4-benzoquinone, has been reported for advanced oxidation processes, such as Fenton`s reagent,[27] UV-H_2O_2[28, 29] and electro-Fenton processes.[30, 31] In the HCO_4^- system, no catechol was detected. Instead, 1,2,4-benzenetriol was the predominant product. These observations suggest that a different mechanism than the sequential oxidation reaction observed for oxidants like HO· may be involved. For example, the Elb oxidation mechanism, which has been studied for the oxidation of phenols also produces 1,2,4-benzenetriol as a primary product.[32, 33] In the HCO_4^- system, a ring cleavage product with a m/z of 158, which may correspond to a compound like 2-hydroxy muconic acid or maleylacetate was detected (Figure S4). Further research is needed to definitively identify the compound.

HCO_4^- detection by NMR.

To identity the oxidant species, NMR spectra were collected with varying concentrations of H_2O_2 and constant concentrations of ^{13}C-enriched $NaHCO_3$ (Figure S5). An additional peak was detected between 158.2 and 158.5 ppm as $NaHCO_3$ increases that can be assigned to HCO_4^-.[13, 34–36] As the concentration of H_2O_2 increased from 0.25 to 5.0 M, the relative peak height of ($[HCO_4^-]/[HCO_3^-]$) increased from 0.05 to 0.49.

After the addition of H_2O_2 to the $NaHCO_3$ solution, bubbles were observed within 2 min. The gaseous products were collected and analyzed by gas chromatography. O_2 was the major product, suggesting that HCO_4^- may decompose (eq. 9) or react with H_2O_2 (eq. 10).[13, 35]

$$2\,HCO_4^- \rightarrow 2\,HCO_3^- + O_2 \qquad\qquad \text{(eq. 9)}$$

$$HCO_4^- + H_2O_2 \rightarrow HCO_3^- + H_2O + O_2 \qquad\qquad \text{(eq.10)}$$
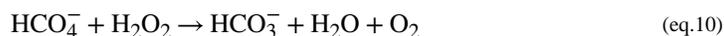
The addition of phenol inhibited the formation of bubbles. For instance, bubbles were observed only after 15 min in the presence of 0.5 mM phenol. The decrease in bubble formation can be explained by the consumption of HCO_4^- by phenol, which occurs in competition with reactions 8 and 9.

Involvement of Hydroxyl Radical (HO·).

The potential involvement of free radicals in phenol transformation was tested by electro paramagnetic resonance (EPR). As a control, a 250 mM H_2O_2 solution was irradiated with ultraviolet light (254 nm) in the absence of HCO_3^- to generate the HO·. A standard EPR signal of the DMPO-HO· adduct was clearly observed with an intensity ratio of 1:2:2:1 (Fig. S6). Due to the scavenging of HO·, no EPR signal was detected with the addition of 10 mM NaHCO₃. No obvious EPR signal could be detected in the H_2O_2-HCO_3^- system at HCO_3^- concentrations ranging from 10 mM to 1000 mM even after 30 minutes. This suggests that phenol transformation in this system occurs via a non-radical pathway.

Effect of NaHCO₃ on Phenol Transformation.

The transformation of phenol was measured at different NaHCO₃ concentrations with initial concentration of phenol of 0.5 mM and an initial H_2O_2 concentration of 250 mM. Under these conditions, the rate of phenol disappearance increased in proportion to the NaHCO₃ concentration (Figure 2a and Figure S7). Measurement of H_2O_2 indicate that less than 5% of the H_2O_2 disappeared during the 120 min experiments even at the highest NaHCO₃ concentration (i.e., the final concentration of H_2O_2 was 240 mM).

Effect of H_2O_2 on Phenol Transformation.

The rate of phenol transformation also was measured at varying H_2O_2 concentrations, at an initial phenol concentration of 0.5 mM and an initial HCO_3^- concentration of 1000 mM. The rate of phenol loss approximately doubled as $[H_2O_2]_0$ increased from 50 to 200 mM. Above 200 mM of H_2O_2, only a small increase (21.2%) in phenol removal rate was observed at a concentration of H_2O_2 of 1000 mM (Figure 2b and Figure S8). The diminishing effect of H_2O_2 at higher concentration may be attributable to increased loss of HCO_4^- through a reaction with H_2O_2 (e.g., eq. 9). We also observed a decrease in the measured initial concentration of phenol at higher initial H_2O_2 concentrations, which may have been due to the formation of HCO_4^- and its reaction with phenol in the approximately 30 s period prior to collection of the first sample.

Effect of Initial Phenol Concentration.

Rates of phenol decomposition were also measured at intial phenol concentrations ranging from 0.1 to 2.5 mM (Figure S9a and S9b). Rates of phenol loss significantly increased as

[Phenol]$_0$ increased in a proportional manner from 2.0×10^{-3} mM·min^{-1} at 0.1 to 1.1×10^{-2} mM·min^{-1} at 0.5 mM. Above 0.5 mM, the rate of phenol transformation was constant (Figure 2c). The observations suggest that some of the HCO$_4^-$ is lost to reactions with H$_2$O$_2$ or decompose at phenol concentration below 0.5 mM (eq. 9 and 10). Above 0.5 mM phenol, HCO$_4^-$ preferentially reacted with phenol.

The effects of varying initial concentrations of reagents are consistent with Scheme 1. As indicated by the NMR results, low concentrations of HCO$_4^-$ ($10^{-2}\sim10^{-5}$mM) are produced when H$_2$O$_2$ and HCO$_3^-$are present. As expected, increasing [HCO$_3^-$]$_0$ increased the concentration of HCO$_4^-$ by shifting the equilibrium toward the right. Increasing [H$_2$O$_2$]$_0$ also shifted the equilibrium to the right but it also increased the rate of conversion of HCO$_4^-$ into O$_2$ and HCO$_3^-$. The loss of H$_2$O$_2$ through reactions with HCO$_4^-$ was less importance when the initial phenol concentration was above 0.5 mM.

Reactivity of HCO$_4^-$ towards Other Substituted Phenols

To assess the reactivity of HCO$_4^-$ towards various phenolic compounds, six phenolic compounds were studied at concentration of 0.5 mM in the presence of 250 mM H$_2$O$_2$ and 1000 mM NaHCO$_3$ in the pH range of 8.2~8.8 (Figure 2d). Changing the *para* substituent on the aromatic ring from an electron-donating group, such as -OH, to an electron-withdrawing group, such as –NO$_2$, decreased the reaction rate. The strong rate acceleration observed for electron-donating substituents is consistent with electrophilic attack of HCO$_4^-$ to the phenolate species. Further research is needed to assess the mechanism of the reaction, the products and the potential role of the phenolate species in the reactions.

Comparisons on the performance with other ISCO techniques.

To assess the importance of HCO$_4^-$ to the transformation of other compounds in the H$_2$O$_2$-ISCO process, we predicted the rate of transformation of the organic contaminants through the HCO$_4^-$-initiated transformation reaction. We fitted the data of phenol disappear vs. time as a pseudo first-order process to facilitate comparisons with reported values for other treatment processes.[37–40] The observed reaction rate constant in our system at 10 mM NaHCO$_3$ was $(3.20\pm0.23)\times10^{-3}$ min^{-1}, which is over four times higher than rates of phenol loss observed when goethite was used to activate H$_2$O$_2$ in borate buffer at the same pH (i.e., pH 8.4±0.2).[7] The HCO$_4^-$ reactions were also faster than other heterogeneous Fenton systems[7, 41, 42] indicating that this process could be a relevant for understanding the efficacy of H$_2$O$_2$- ISCO.

Environmental Implications.

When H$_2$O$_2$ is used for ISCO, high concentrations of the oxidant can persist for several days in the area undergoing treatment. Under many circumstances, most of the H$_2$O$_2$ decomposes by reactions catalyzed by Fe and Mn associated with mineral surfaces. Organic contaminants, including phenolic compounds, are oxidized as the H$_2$O$_2$ decomposes because a small fraction (i.e., <1%) of the H$_2$O$_2$ produces HO· during the catalytic decomposition process. During the period when H$_2$O$_2$ is present, a small fraction will react with HCO$_3^-$ to form HCO$_4^-$, which can also transform electron-rich contaminants, such as phenolic

compounds and possibly chlorinated ethenes. In aquifers that contain carbonate minerals, HCO_4^--mediated transformation of phenolic compounds can occur at rates similar to those attributable to HO· produced from H_2O_2. For example, if magnesite ($MgCO_{3(s)}$) is in equilibrium with groundwater at pH 7, the HCO_3^- concentration will be approximately 8 mM (see supporting information). Under these conditions, extrapolation of the data in Figures S7 and 2d indicate that approximately 10–20% loss of phenol and 30–50% loss of the anisole (i.e., a more reactive contaminant) would be expected through peroxymonocarbonate reactions during the first two hours of ISCO treatment.

Most of the groundwater contaminants that are the targets for ISCO treatment (e.g., benzene, petroleum hydrocarbons) react with peroxymonocarbonate at relatively slow rates. It is unlikely that peroxymonocarbonate reactions alone would ever be a preferred option for ISCO treatment because they are relatively slow. If compounds that react with HCO_4^- were the target of a remediation project, it might be possible to increase the rates of the reactions by amending the H_2O_2 with relatively high concentrations of HCO_3^- (e.g., 100–1000 mM) prior to injection. These elevated concentrations of HCO_3^- would scavenge HO· produced during H_2O_2 decomposition and could clog aquifer pores if sufficient quantities of divalent cations (e.g., Ca^{2+}, Mg^{2+}) were present. Additional research is needed to assess the potential for enhancing HCO_4^--mediated reactions during ISCO treatment or exploiting this process for other treatment methods.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGEMENTS

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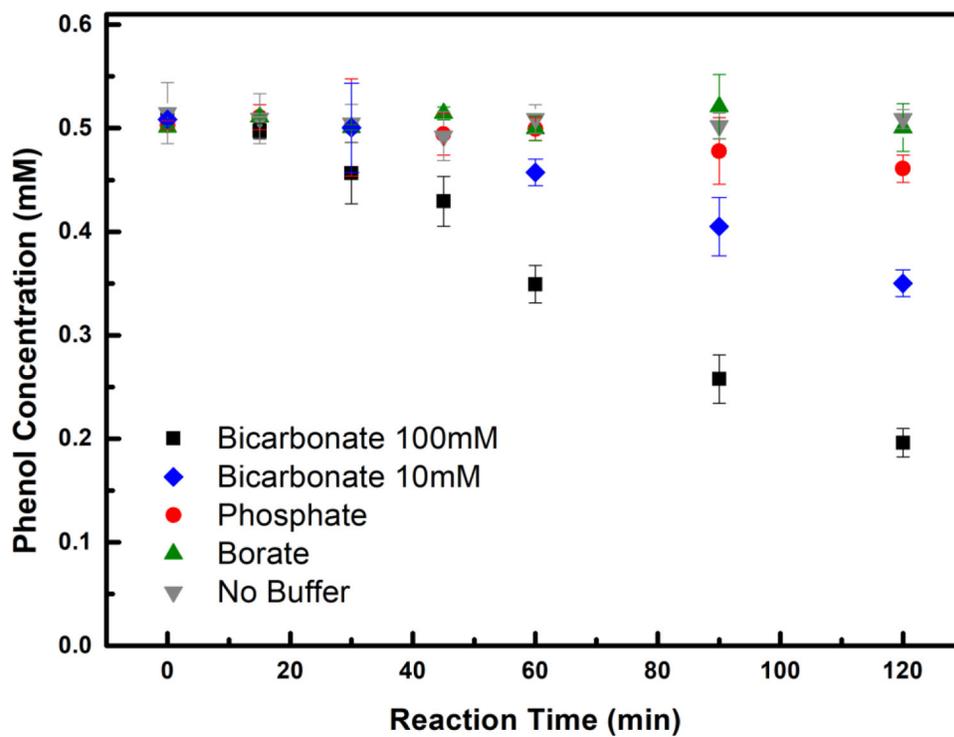
Figure 1.
Phenol transformation in various buffer, bicarbonate of 100 mM (■), bicarbonate of 10 mM (◆), phosphate of 10 mM (●), borate of 10 mM (▲) and no buffer (▼). Experimental conditions: $[H_2O_2]_0 = 250$ mM, $[phenol]_0 = 0.5$ mM, pH= 8.4 ±0.2
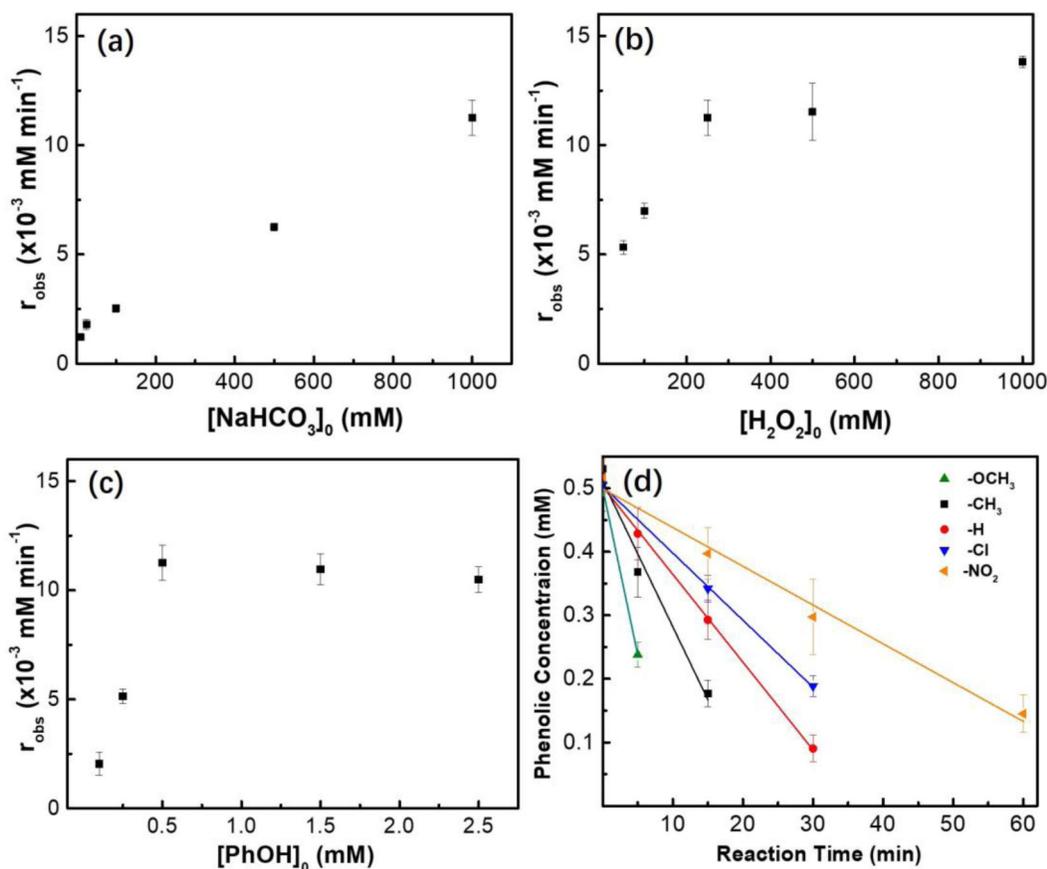
Figure 2.
(a) Dependence of initial rate of phenol loss (r_{obs}) on the initial concentration of NaHCO$_3$, Conditions: [Phenol]$_0$=0.5 mM, [H$_2$O$_2$]$_0$=250 mM, [NaHCO$_3$]$_0$ 10–1000 mM, pH pH= (8.4–8.7) ±0.2**; (b)** Dependence of initial rate of phenol loss (r_{obs}) on the initial concentration of H$_2$O$_2$. Conditions: [Phenol]$_0$=0.5 mM, [NaHCO$_3$]$_0$= 1000 mM, [H$_2$O$_2$]$_0$=50–1000 mM. pH=(8.4–8.7) ±0.2; **(c)** Dependence of reaction rate on the initial concentration of phenol. Conditions: [NaHCO$_3$]$_0$=1000 mM, [H$_2$O$_2$]$_0$=250 mM, [phenol]$_0$=0.1–2.5 mM, pH=(8.4–8.7) ±0.2; **(d)** Disappearance of various substituted phenolic compounds by HCO$_4^-$. Conditions: [H$_2$O$_2$]$_0$ =250mM, [HCO$_3^-$]$_0$ =1000mM, [Phenolic]= 0.5 mM, pH=(8.4–8.7) ±0.2
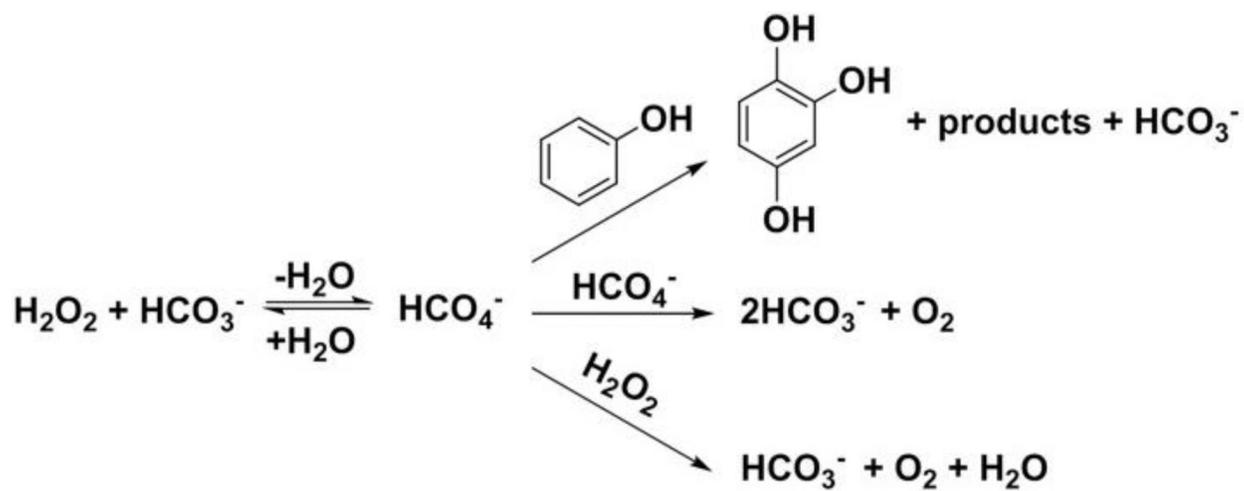
Scheme 1.
Plausible Reaction pathway under varying concentration of reagents