

Photochemical generation of carbonate radicals and their reactivity with phenol

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Abstract

The reaction of carbonate radical with phenol in aqueous solution has been investigated in systems in which carbonate radicals were generated by UV irradiation of an aqueous solution of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ (pH 8.0 phosphate buffer). Both steady state and time resolved photolysis experiments were performed. Upon continuous irradiation of complex phenol mixtures, phenol was converted into benzoquinone and dihydroxybenzenes. Benzoquinone was the major by-product in the early stages of the reaction. Laser flash excitation (266 and 355 nm) of the cobalt complex clearly showed the formation of the carbonate radical. When phenol was added to the solution of the complex, a second species was observed which was assigned to the phenoxy radical. The second-order rate constant of reaction between phenol and carbonate radical was found to be equal to $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, in agreement with literature data of $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

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1. Introduction

Hydroxyl radicals are known to be formed in surface waters (photolysis of dissolved organic matter, of nitrate and nitrite ions and Fenton-type reactions) and are also involved when ozonation is used for drinking water production and in the treatment of wastewaters by advanced oxidation processes. The hydroxyl radical is a powerful oxidant. It reacts with most of organic pollutants with high second-order rate constants (10^7 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ depending on the chemical structure of the pollutant) and also with several inorganic compounds [1]. The concentration of hydroxyl radical always results from a balance between the rates of production and consumption. Among ubiquitous scavengers, hydrogenocarbonate and carbonate ions react with hydroxyl radicals with second-order rate constants equal to 8.5×10^6 and $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively [1]. These reactions lead to the formation of the carbonate radical. This latter radical is a strong one-electron oxidant (1.78 V versus SHE at pH 7) [2] has a $\text{p}K_{\text{a}} < 0$ [3,4], and

presents a broad optical absorption in the visible range with $\lambda_{\text{max}} = 600 \text{ nm}$ ($\epsilon_{600 \text{ nm}} = 1850 \text{ M}^{-1} \text{ cm}^{-1}$) [5].

The carbonate radical presents a high and selective reactivity towards other radicals, inorganic as well as organic compounds. Rate constants for reactions involving the radical carbonate are in the range 10^2 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [6]. Carbonate radical may react by electron transfer (aromatic amines, thiols, metals and inorganic anions) or hydrogen transfer (alcohols, primary amines, thiols, phenols). It has been shown that carbonate radicals react more efficiently with phenolate ion; the ratio between $k_{\text{CO}_3^{\bullet-}/\text{phenolate}}$ and $k_{\text{CO}_3^{\bullet-}/\text{phenol}}$ being about 10 [7]. According to Moore et al. [8], carbonate radical reacts with the formation of an intermediate adduct onto the aromatic ring of the phenol anion. The adduct further evolves to phenoxy radical, the spectrum of which has been observed by pulse radiolysis.

Various methods for carbonate radical generation have been investigated. Among them, the initial generation of hydroxyl or sulfate radical further reacting with HCO_3^- or CO_3^{2-} constitutes the most used method. Actually, Mazellier et al. [9] showed the involvement of carbonate radicals during the degradation of carbendazim by $\text{H}_2\text{O}_2/\text{UV}$ in the presence of high amounts of hydrogenocarbonate ions. More recently, Canonica et al. [10] propose the use of ketone triplet excited states acting as elec-

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tron acceptors to generate the carbonate radical assuming this process to occur in the environment.

The photodecomposition of a carbonatoammine complex of Cobalt(III) also leads to the formation of carbonate radical as demonstrated by Cope et al. These authors also showed that the irradiation of the complex leads to an intramolecular photooxydoreduction producing Co^{II} and $\text{CO}_3^{\bullet-}$ with a quantum yield of 0.06 and a photoaquation with a quantum yield $\Phi = 0.1$ [2].

In the present work, carbonate radical was generated by the photolysis of the complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$. This method was selected because it does not involve the formation of intermediate radicals such as hydroxyl radicals. The reactivity between carbonate radicals and phenol has been studied with particular attention to the kinetic aspects and the identification of by-products of the reaction. We focused our attention on the primary step of the reaction (transient species and primary photoproducts). The obtained results allow the validation of the method before to be used with pollutants such as pesticides.

2. Experimental

2.1. Chemicals

Phenol, benzoquinone, catechol, hydroquinone, sodium phosphate salts, 4-methyl-2-pentanone and methanol were commercial products of the purest grade available. All solutions were prepared with purified water (Millipore Milli-Q) and pH measurements were carried out with a Meterlab PHM 210 pH-meter.

The complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ was prepared according to the method described by Basolo and Murmann [11], and further characterized by X-ray diffraction and IR spectroscopy (in KBr pellets).

2.2. Methods and analysis

UV-vis spectra and absorbance measurements were performed on a Secomam single-beam spectrophotometer. Cells of 1 or 5 cm were used.

The irradiation set-up was a batch photoreactor (volume of irradiated solution = 2 L, Internal diameter = 100 mm). The lamp (Heraeus NN 8/15 low pressure mercury lamp) was located at the center of the reactor, in a quartz sleeve (external diameter = 28 mm). The lamp almost exclusively emits at 254 nm according to purchaser's data. The photonic flux at 254 nm was measured with hydrogen peroxide as an actinometer as described by Nicole et al. [12]. Actinometry experiments were performed before each experiment. Typical values equal to $(2.0 \pm 0.4) \times 10^{-6}$ Einstein $\text{L}^{-1} \text{s}^{-1}$ were obtained during the period of the experiments. Hydrogen peroxide concentration was measured according to a method using Ti-complexometry as described by Eisenberg [13].

The concentration of Cobalt(II) was determined by complexometry with NH_4SCN after extraction with methyl isobutyl ketone according to Katakis and Allen [14]. The calibration curve was obtained with Cobalt(II) nitrate hexahydrate.

Laser flash photolysis (LFP) experiments have been performed in the "Laboratoire de Photochimie Moléculaire

et Macromoléculaire" (LPMM-UMR CNRS 6505, Aubière, France). The excitation source was a pulsed nanosecond laser Quanta Ray GCR 130-1 Neodim-YAG (flash time of 9 ns) working at 266 or 355 nm. The detection was achieved with a LKS 60 system from Applied Photophysics. The photonic flux emitted by the laser was evaluated with $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ as an actinometer as described elsewhere [15].

Phenol disappearance and by-products formation were measured with high performance liquid chromatography (HPLC; Waters system equipped with a Waters 996 photodiode array detector). The column was purchased from Interchim (Uptisphere C_{18} , 250 mm \times 3 mm – 5 μm) and the eluant was a mixture (40–60) of methanol–water acidified with acetic acid at a flow rate of 1 mL min^{-1} . The sample volume was 200 μL . The quantification of compounds was performed at 220 nm.

3. Results and discussion

As mentioned above, the excitation of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ leads to two phenomena, an intermolecular photoredox process leading to the formation of $\text{Co}(\text{II})$ and $\text{CO}_3^{\bullet-}$ and a photoaquation reaction [2]. The simultaneous photoaquation process leads to the substitution of CO_3 group by H_2O molecule as a ligand. The UV-vis spectrum of an aqueous solution of the complex in phosphate buffer (pH 8.0) is presented in Fig. 1. A large absorption band is present up to 300 nm and two other bands of weaker intensity can also be detected. The irradiation in this work has been performed within the first absorption band at 254 or 266 nm.

3.1. Formation of carbonate radical

All the experiments were performed in the presence of oxygen, in the presence of phosphate buffer at pH 8.0. The UV-vis spectrum of the complex showed no change in the presence of phosphate salt. Additionally, the complex was stable in the dark in the presence of phosphate at pH 8.0 within the timescale of the experiment.

In a first step, the formation of carbonate radical from the photolysis of the complex synthesized in our laboratory has

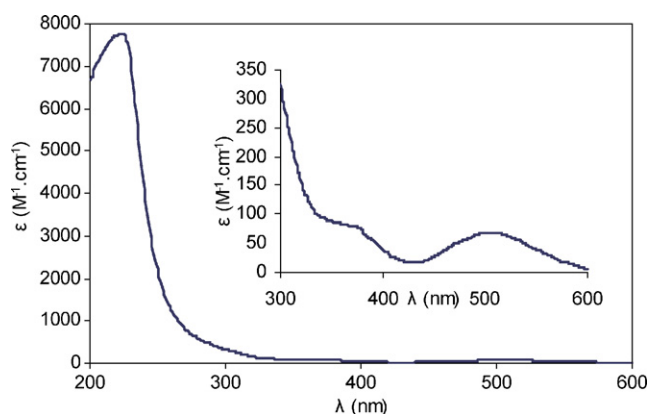


Fig. 1. UV-vis spectrum of an aqueous solution of the complex (400 μM of complex, pH 8.0, phosphate buffer).

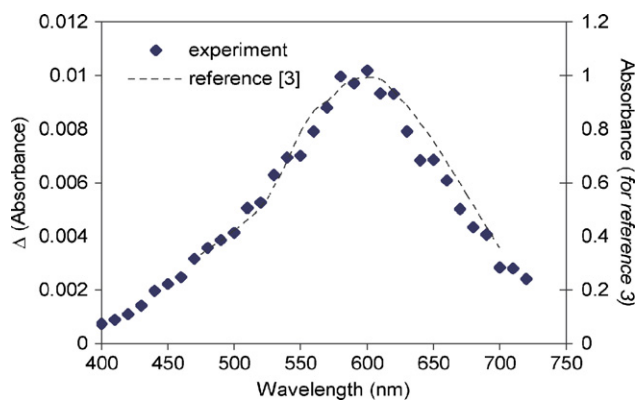
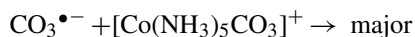
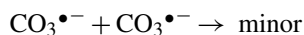


Fig. 2. Spectrum of carbonate radical obtained by LFP ($[\text{Co}(\text{NH}_3)_5\text{CO}_3^+] = 2.0 \text{ mM}$, pH 8.0, phosphate buffer, recorded 400 ns after the laser pulse), compared with reference [3].

been studied. Laser photolysis experiments at 266 nm of a solution containing $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ ($2.0 \times 10^{-3} \text{ M}$) were performed. Following the pulse of the laser, a transient species has been observed, the spectrum of which is shown in Fig. 2. It corresponds unambiguously to that of carbonate radical published elsewhere [3]. The quantum yield of formation of carbonate radical has been determined and found equal to 0.050. It is worth noting that the same spectrum was obtained when the excitation was performed by using the third harmonic of the YAG laser, namely 355 nm.

Simultaneously, steady state irradiation at 254 nm of a buffered solution of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ (pH 8.0; $400 \mu\text{M}$ —total absorbance at 254 nm) leads to the formation of Cobalt(II) with a quantum yield of 0.06 ± 0.01 , which is in quite good agreement with the quantum yield of carbonate radical generated by laser flash photolysis measurements.

According to literature, the carbonate radical may be involved in a second-order recombination reaction and also reacts with the initial complex as follows [6]:



Laser flash photolysis experiments with solutions containing different concentrations of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ (from 0.5 to 5.0 mM, pH 8.0, phosphate buffer) have been performed to determine the second-order rate constant of reaction between carbonate radical and the complex. A value equal to $8.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ has been obtained (data not shown) in complete agreement with literature data [6].

3.2. Reaction of carbonate radical with phenol

In the absence of any irradiation, the mixture complex/phenol is stable. There was no detectable spectral evidence for the existence of ground state interaction between $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ and phenol.

Phenol is known to undergo photolysis upon irradiation at 254 nm [16]. It can be demonstrated that the direct photolysis of phenol (50 or $1 \mu\text{M}$) in the presence of a second absorbing

compound, namely the cobalt complex the absorption of which is total, cannot be higher than 10% by using 0.06 [16] for the phenol direct photolysis quantum yield. This has been checked experimentally.

Under steady state irradiation of a mixture complex/phenol ($400 \mu\text{M}/1.0 \mu\text{M}$, pH 8.0), a fast disappearance of phenol was observed, together with the formation of several by-products. The formation of Co(II) was nearly the same to that obtained with the experiments performed in the absence of phenol.

The use of the complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ leads to an equimolar presence of nitrate ion in the solution. Because nitrate ion is known to generate hydroxyl radical under direct photolysis [17], control experiments were performed with mixtures of phenol (50 or $1 \mu\text{M}$) and nitrate ($400 \mu\text{M}$). In the time scale of our experiments (i.e. less than 20 min of irradiation), the conversion of phenol was less than 15% whereas phenol has completely disappeared in the presence of the complex. Actually, it is largely reported that nitrate ions present a very low molar absorption coefficient at 254 nm (less than $5 \text{ M}^{-1} \text{ cm}^{-1}$) [17].

Moreover, the involvement of hydroxyl radicals in the system was ruled out by experiments performed in the presence of isopropanol ($100 \mu\text{M}$), used as a hydroxyl radical scavenger (literature data: $k(\text{OH}^\bullet + \text{iPrOH}) = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [1] and $k(\text{CO}_3^{\bullet-} + \text{iPrOH}) = 4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ [6]). In these experiments ($[\text{complex}] = 400 \mu\text{M}$, $[\text{phenol}] = 1.0 \mu\text{M}$, $[\text{iPrOH}] = 100 \mu\text{M}$, pH 8.0) we have observed that the presence of isopropanol did not modify the kinetics of phenol disappearance. A complete inhibition of the degradation process should be observed if hydroxyl radical was involved.

3.2.1. Laser flash irradiation

Upon laser flash photolysis of phenol (18 mM)—complex (100 mM) mixture, the formation and disappearance of carbonate radicals were observed and shown in Fig. 3. As previously mentioned, in the absence of phenol, carbonate radicals react with the complex itself. When the pollutant was added, competitive reactions are involved. The rate of carbonate radicals disappearance increased when the concentration of phenol increased. The decay of the signal was shown to obey an apparent first-order kinetic law.

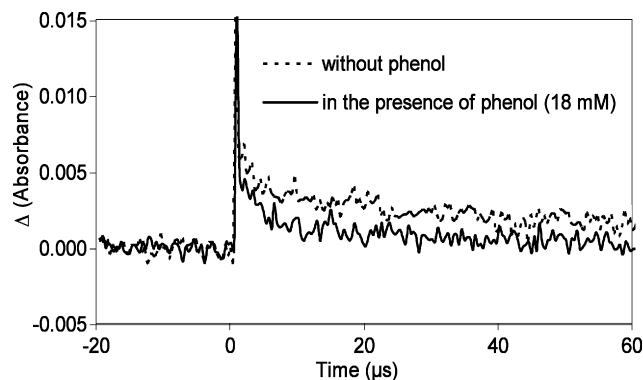


Fig. 3. Signal detected at 600 nm (carbonate radicals) upon 355 nm-excitation of a solution of Cobalt(III) complex (100 mM) in the absence or in the presence of phenol (18 mM).

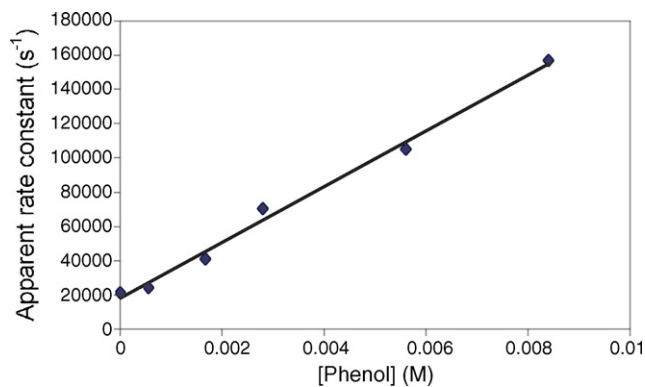


Fig. 4. Apparent first order rate constant of $\text{CO}_3^{\bullet-}$ decay as a function of the initial concentration of Phenol upon 355 nm-laser flash excitation of a mixture of Cobalt(III) complex (2 mM) and phenol (from 0 to 8.4 mM).

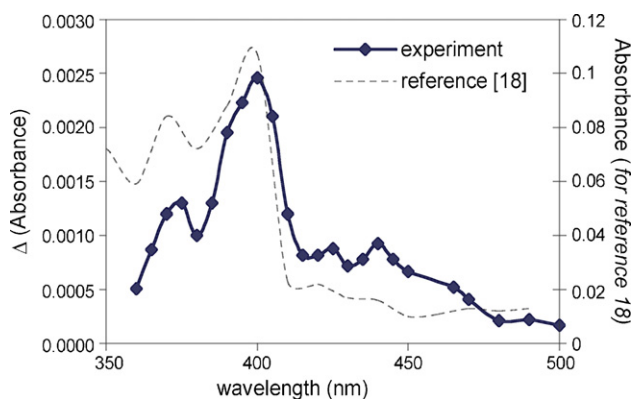


Fig. 5. Spectrum of the phenoxyl radical from 355 nm-excitation of a mixture of Cobalt(III) complex (9 mM) and phenol (20 mM), compared with reference [18].

This result was further confirmed by performing experiments in the presence of increasing concentrations of phenol. The apparent first order rate constant was determined by a fitting program and a plot of k_{obs} as a function of the concentration of phenol in the solution is presented in Fig. 4. A straight line was observed, and the slope which corresponds to the second-order rate constant between phenol and the carbonate radicals was found to be equal to $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This value is quite close to that published in the literature ($2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [8].

During these experiments, the formation of an additional transient species has been observed. The recorded spectrum is presented in Fig. 5 and shows two distinct maxima at 375 and 400 nm. It fitted very well with that of phenoxyl radical published elsewhere [18]. The deformation of the transient absorption spectrum in the shorter wavelength region is owing to the disappearance of the starting complex leading to a decrease of the absorbance.

3.2.2. Continuous irradiation (254 nm)

The degradation of phenol by carbonate radical together with the formation and depletion of primary by-products under continuous irradiation of a mixture ($[\text{Phenol}]_0 = 50 \mu\text{M}$, $[\text{Complex}]_0 = 400 \mu\text{M}$) is reported in Fig. 6. Phenol was transformed into benzoquinone and dihydroxybenzene by carbonate

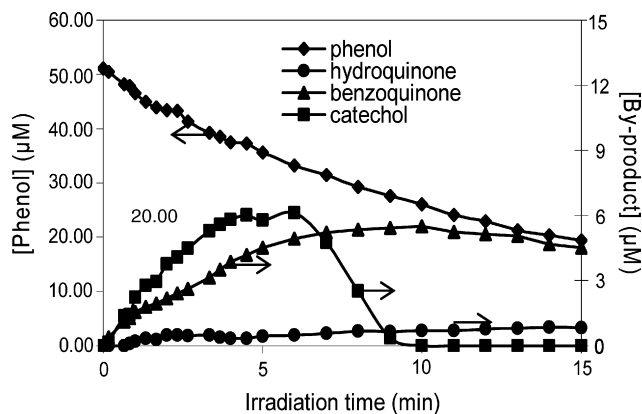


Fig. 6. Degradation of phenol by carbonate radical, formation and depletion of primary by-products (50 μM of phenol, 400 μM of complex, pH 8.0, phosphate buffer).

radicals in the early stage of the irradiation. However, they were further degraded in their turn by the action of carbonate radical. Moreover, the well-known efficient direct photolysis of benzoquinone also contributes to its disappearance [19]. Very small amount of 1,4-dihydroxybenzene (hydroquinone) was detected. This might be due to the partial oxidation of hydroquinone to benzoquinone by Co(III) complex, which has been clearly demonstrated experimentally (data not shown). In the absence of light, catechol is stable in the presence of the complex, this has been experimentally checked. Moreover, neither oxidation nor ground state complexation were detected.

Fig. 7 indicates the relative amount of by-products, obtained by dividing the concentration of the identified by-products by the concentration of phenol disappeared, as a function of the irradiation time. The percentage of the unidentified part is also represented. It was calculated by the following relationship:

$$100 \left(\frac{[\text{phenol}]_{\text{disappeared}} - [\text{benzoquinone}] - [\text{catechol}] - [\text{hydroquinone}]}{[\text{phenol}]_{\text{disappeared}}} \right)$$

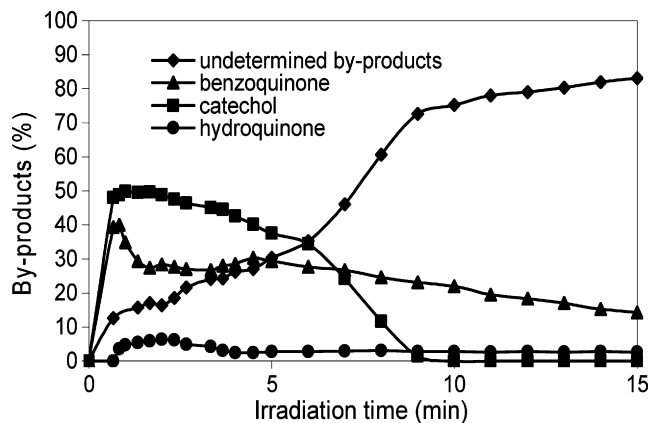


Fig. 7. Relative amount of phenol by-products (50 μM of phenol, 400 μM of complex, pH 8.0, phosphate buffer). The percentage of unidentified by-products is given by the difference between (identified products + phenol remained) and phenol disappeared.

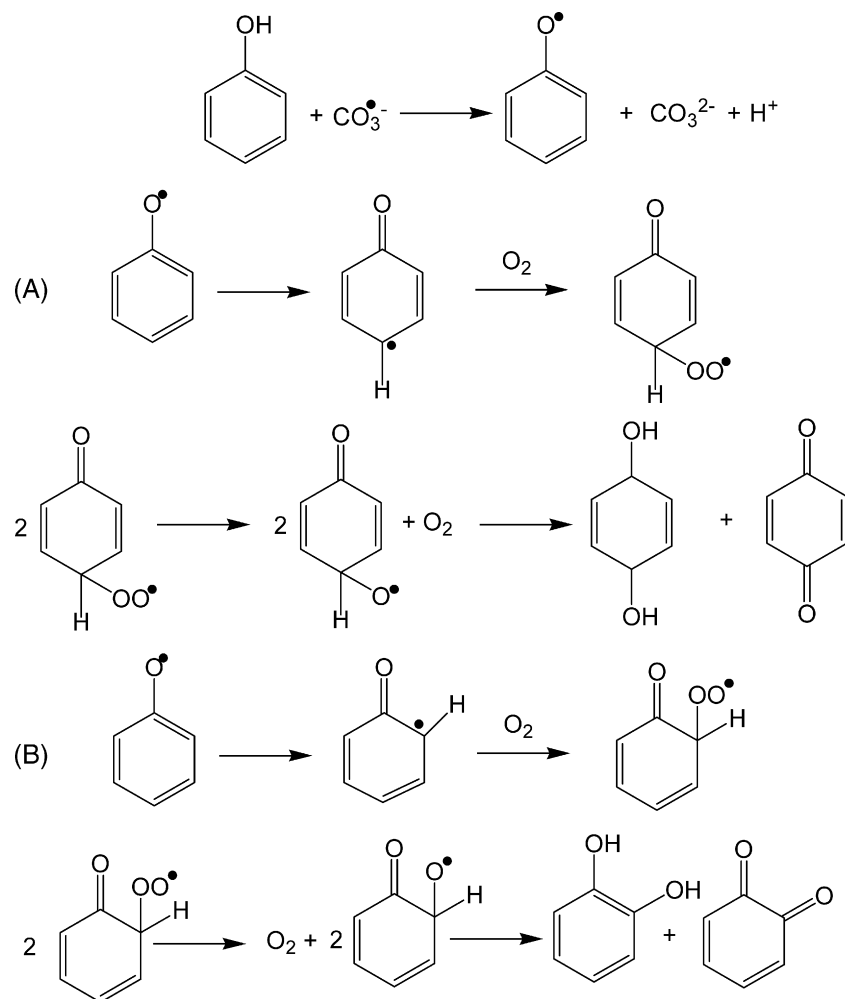


Fig. 8. Proposed reaction pathway for the reaction of the carbonate radical with phenol: path A for *para*-position and path B for *ortho*-position.

As previously mentioned, benzoquinone and catechol represented almost 90% of phenol conversion in the early stages of the experiments. This result is usually obtained during the oxidation of phenol whatever the process employed. For prolonged irradiation, it is worth noting that the relative amount of catechol decreased whereas benzoquinone still accounted for 25% of the phenol degraded. The amount of hydroquinone remained was quite low (<10% whatever the percentage of phenol transformed). It should be noted that the percentage of unidentified products increased markedly for prolonged irradiation times. However, it is well known that the complete oxidation of phenol to CO_2 involves the formation of small size organic acids (not quantified here) [20].

3.2.3. Mechanism

According to all the above results, a degradation pathway of phenol by carbonate radical can be put forward as represented in Fig. 8.

The reaction of the carbonate radical with phenol led to the formation of phenoxyl radical as clearly shown by laser flash irradiation. This may occur by electron transfer or hydrogen abstraction. This has to be put in relation with the reaction of hydroxyl radical with phenol. This reaction may occur

either via hydrogen abstraction from the OH group ($k = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) or via aryl addition ($k = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) resulting in the formation of phenoxyl or dihydroxycyclohexadienyl radical, respectively [21,22]. When phenol reacts with carbonate radical, mainly phenoxyl radical is formed from phenol according to our result.

Then, peroxy radicals can be formed by the reaction of dissolved oxygen with the phenoxyl radical, although the rate constant of oxygen reaction with phenoxyl-type radicals is low [23]. Peroxy radicals are known to evolve to alkoxy radicals and, by disproportionation, further benzoquinone and dihydroxybenzene (the dismutation of hydroquinone to benzoquinone has been observed in the presence of an excess of Cobalt(III): the path A leads to the formation of benzoquinone and hydroquinone, the path B to catechol and an *ortho*-quinone, which is known to be unstable).

4. Conclusions

Irradiation of Cobalt(III) complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ appears to be an efficient means to generate carbonate radical. This method which does not form hydroxyl radical, can be used to study the kinetics and the mechanism of oxidation of organic pol-

lutants by carbonate radical. The reactivity of carbonate radical with phenol has been studied by 254-nm continuous irradiation and classical by-products of oxidation of phenol have been obtained. The second-order rate constant of carbonate radical reaction with phenol has been determined by time resolved UV spectroscopy as being $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Phenoxyl radical was shown as the short live species upon laser flash irradiation. These results allow us to propose a degradation pathway for phenol degradation by carbonate radicals.

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