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Kinetics and Mechanism of Benzene Derivative Degradation with Fenton's Reagent in Aqueous Medium Studied by MIMS

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Membrane introduction mass spectrometry (MIMS) was used to investigate kinetic and mechanistic aspects of the reaction of benzene derivatives with Fenton's reagent (Fe^{2+}/H_2O_2) in water. Under the conditions employed, the reaction rate showed a first-order dependence on the aromatic compound concentration. The order of reactivity observed was $C_6H_5Cl > C_6H_5Br > C_6H_6 > C_6H_5CH_3 > C_6H_5OCH_3 > C_6H_5NO_2 > C_6H_5\text{-}OH$, and, with the exception of $C_6H_5NO_2$, a linear Hammett relationship (log k_X/k_H versus σ_p) was observed. This fact suggests that electronic factors significantly influence reactivity with the Fenton's reagent. Experiments with C_6H_6 and C_6D_6 showed the presence of an isotopic effect of $k_H/k_D = 1.7$, suggesting that cleavage of the benzene C−H bond occurs in the reaction rate controlling step. Mechanistic studies with chlorobenzene showed that mineralization to CO_2 and chloride proceeds via hydroxylation steps producing phenolic, hydroquinonic, and quinonic intermediates.

Introduction

Membrane introduction mass spectrometry (MIMS) is one of the most efficient, simplest, and most sensitive techniques for the analysis of volatile organic compounds in most matrixes such as water, soil, and air. MIMS is based on the selective permeation of an organic compound through a membrane, which acts as the interface between a mass spectrometer and the sample solution (Figure 1). The most common membrane used is silicone rubber (PDMS, poly(dimethylsiloxane)), which owing to its hydrophobic character shows much higher permeability to organic compounds compared to water.[1,2]

The high sensitivity of MIMS allows detection limits on the order of low parts per billion[3] with no need of preconcentration steps. The relative short response time and the possibility of simultaneous analysis of various components and continuous monitoring allow on-line, in-situ,[4] in vivo[5] analysis and kinetic experiments.[6] Kinetic application of the technique has been demonstrated by Lauritsen and Gylling[7] when studying the aerobic degradation of chloroethylenes by the *Methylococcus capsulatus* bacteria. Cooks et al.[8] have performed on-line monitoring of several products of the photolysis of benzyl acetates in water. Recently,[9] it has been demonstrated that MIMS is superior for the analyses of VOCs in water compared to several chromatographic methods with respect to simplicity, detection limits, and linear dynamic range.

The reaction of organic compounds with the Fenton's reagent has been extensively studied in the past few years[10] as one of the most efficient alternatives for the destruction of organic contaminants in effluents. Fenton's system,[11] a mixture of hydrogen peroxide and a ferrous salt, according to the Habber Weiss mechanism generates in situ free hydroxyl radicals by the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

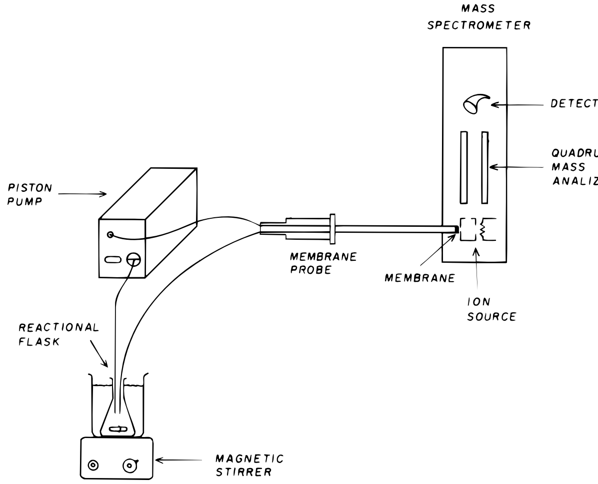

Figure 1. Schematic representation of the MIMS system.

These radicals can hydroxylate aromatic compounds in aqueous solution leading eventually to the complete oxidation, i.e., mineralization, producing CO_2 and H_2O:

$$ArH + H_2O_2 \xrightarrow{Fe^{2+}} ArOH + H_2O \rightarrow\rightarrow CO_2/H_2O \qquad (2)$$

Understanding the mechanism for this oxidation under conditions relevant to waste treatment is essential to formulate an efficient and cost-effective Fenton's process. Scarce information is, however, available on the kinetics and mechanism of these organic reactions. The poor solubility of organic compounds and consequently their low concentrations in water makes product characterization and yield determination difficult. Moreover, to follow the kinetics of such reactions involves frequently complex sample collection, extraction, and off-line analysis by different techniques.

Herein, the MIMS technique is applied to investigate kinetic and mechanistic aspects of the degradation of benzene derivatives (benzene, chlorobenzene, bromobenzene, toluene, methoxybenzene, nitrobenzene, phenol, and hexadeuterated benzene) with Fenton's reagent in aqueous solution. Advantages and the

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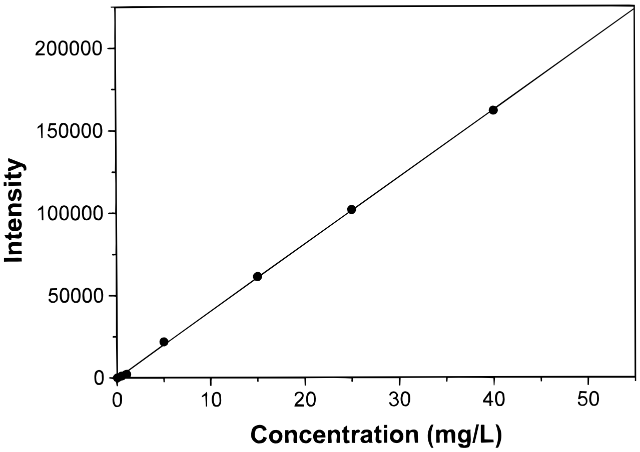


Figure 2. Chlorobenzene MIMS calibration curve.

great potential of MIMS for the study of complex organic reactions taking place in aqueous medium are demonstrated.

Experimental Section

The chemicals were obtained from Aldrich and Merck and were used without further purification. The aqueous solutions of the organic compounds prepared with Millipore MilliQ water were sonicated for 1 h and stirred overnight prior to use.

The experiments were carried out in a HP 5989A II mass spectrometer equipped with a flow-through type membrane probe mounted near the ion source. The details of the probe construction are described elsewhere.[2] A 250 μm silicone membrane (Dow Corning Silastic 500-3) with exposed area of 4 mm^2 was used. Mass spectra were obtained by electron ionization at 70 eV. The most intense fragment in the mass spectrum was used for monitoring each compound [benzene (*m*/*z* 78), chlorobenzene (*m*/*z* 112), bromobenzene (*m*/*z* 156), toluene (*m*/*z* 91), methoxybenzene (*m*/*z* 108), nitrobenzene (*m*/*z* 123), phenol (*m*/*z* 94), and hexadeuterated benzene (*m*/*z* 84)].

In a typical run, the membrane probe was connected to the mass spectrometer as illustrated in Figure 1. Aqueous solution (100 mL at 0.2 mmol/L) of the aromatic compounds had their pH's adjusted to 3 with 0.1 mol/L H_2SO_4 and was pumped (by a piston pump Intralab model 2010) through the membrane probe at 5 mL/ min and returned to the reaction flask. Under stirring and constant temperature kept at 25 ±1 °C by a water recirculating bath, 1 mL of 30% H_2O_2 (8 mmol) and 25 mg of ammoniacal ferrous sulfate (0.1 mmol) were added to the solution. The reaction system was shielded from light using an aluminum foil, and no precaution was taken to remove oxygen from the system. The chloride formed was determined by precipitation with silver and analysis of the silver excess by atomic absorption (Hitachi model Z8200).

Results

Linearity and Reproducibility of the MIMS System. The response linearity and reproducibility of the MIMS system was investigated for each aromatic compound using aqueous solution at different concentrations. A typical response curve is shown in Figure 2 where the ion of *m*/*z* 112 was monitored for aqueous solutions of chlorobenzene. Excellent linearity ($R = 0.999$) and reproducibility were observed over the chlorobenzene concentration range studied. The other benzene derivatives studied showed similar responses. An important factor, especially for the kinetics measurements, is the effect of solution diffusion and membrane permeation on the signal response time of the organic compound in solution. Experiments with solutions of the benzene derivatives studied showed a response time (fall time) of approximately 30 s for the signal intensities to decrease to 60% (where the kinetic measurements were carried out). For low reaction rates, e.g., phenol, nitrobenzene, methoxybenzene, toluene, and benzene, this fall time is negligible, since signal decrease to 60% was observed typically after 20−27 min. In the case of chlorobenzene and bromobenzene, which showed high reaction rates, this effect might introduce an error of up to 20% on the calculated rate constants (*k*). However, this fall time does not affect the order of *k* values nor the Hammett linearity described later.

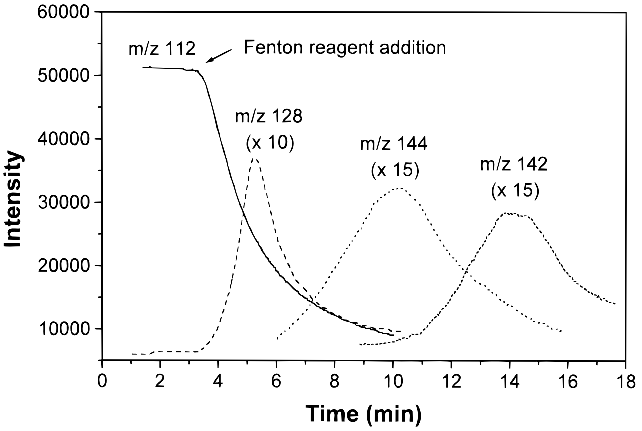
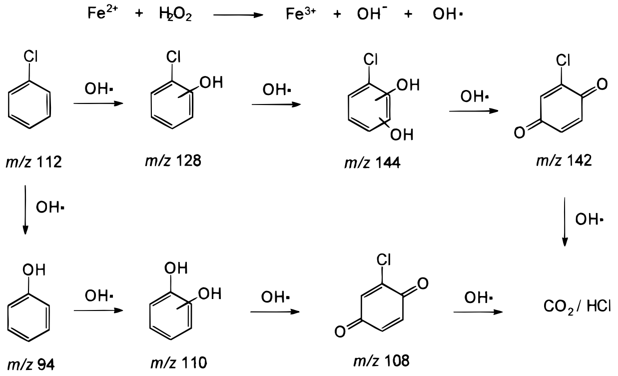


Figure 3. *m*/*z* signals intensities for intermediates during oxidation with Fenton's reagent.

SCHEME 1



Mechanistic Studies of the Oxidation of Chlorobenzene. MIMS was used to monitor intermediates of the chlorobenzene oxidation by the system H_2O_2/Fe^{2+}. These monitored intermediates have been previously identified by GC/MS and HPLC methods.[12] Monitoring of the characteristic ions of possible hydroxylation intermediates is shown in Figure 3. When H_2O_2 is added to the system, the chlorobenzene molecular ion of *m*/*z* 112 immediately decreases with the simultaneous raising of the signal *m*/*z* 128 reaching a maximum and decreasing afterward. These suggest that chlorophenol (ClC_6H_4OH) is formed and further decomposes. As the chlorophenol ion decreases, an ion of *m*/*z* 144 increases, likely the molecular ion (*m*/*z* 144) of the chlorohydroquinone $ClC_6H_3(OH)_2$. Chlorohydroquinone is apparently oxidized further to the respective chloroquinone $ClC_6H_3O_2$, which is identified by its characteristic molecular ion of *m*/*z* 142 (Figure 3 and Scheme 1).[13] No ion of *m*/*z* 156 was observed for $ClC_6H_2(OH)_3$, suggesting that the oxidation to chloroquinone is more favorable compared to further hydroxylation of the ring.

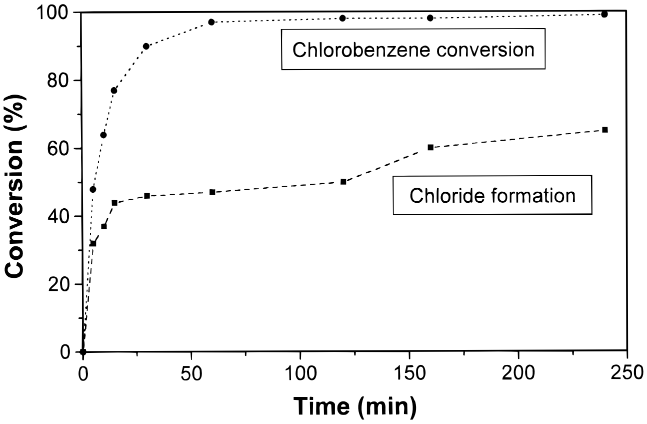


Figure 4. Chlorobenzene conversion and chloride formation during oxidation with Fenton's reagent.

In much minor extension the ion of *m*/*z* 94 characteristic of phenol also appears immediately after the addition of H_2O_2, indicating the occurrence of an *ipso* attack[14] by which the chloro substituent is replaced by an OH group. Like chlorophenol, the phenol is also hydroxylated to hydroquinone and further oxidized to quinone as revealed by the ions of *m*/*z* 110 and 108. Possible degradation pathways are outlined in Scheme 1.

Chloroquinone and quinone are further oxidized to completion leading to mineralization to CO_2 and Cl^-. The chlorobenzene degradation was monitored against chloride formation during the reaction. The results are displayed in Figure 4. Although chlorobenzene is mostly degraded after 50 min, the Cl^- formation reaches only 60% of the expected value after 240 min. Therefore, part of the chlorine must be in solution still in the form of an organic intermediate. The nature of the intermediates between the chloroquinone and CO_2/Cl^- has not been established. Possible reactions following the oxidation of quinones are hydroxylation[15,16] or epoxidation.[17,18] None of the possible intermediates could, however, be detected by the MIMS technique under the experimental conditions. Another reaction alternative for quinones is the oxidation causing rupture of the C_6 ring. Typically these reactions produce C_6 dicarboxylic acids,[19,20] but in some cases the fragmentation to the C_4 maleic acid derivatives occurs.[21,22] These acid intermediates have not been detected, but their formation cannot be ruled out because of their relative high polarity and water solubility that hinders the permeation through the silicone membrane. Low concentration and short lifetime of the acid intermediates may also contribute to weaken the MS signal.

Kinetic Studies of the Reaction with Fenton's Reagent. The reaction of aromatic compounds with Fenton's system involves ring hydroxylation as its initial step. The ferrous salt favors the formation of hydroxyl radicals that attack the aromatic ring.[11]

Figure 5 shows the consumption of chlorobenzene monitored via the ion of *m*/*z* 112. Considering a linear relationship between the chlorobenzene concentration and the ion intensity, a plot of ln I_t/I_0 (I_0 and I_t are the intensities of *m*/*z* 112 at 0 and *t* time, respectively) versus time was obtained. The straight line obtained ($R = 0.998$) indicates that under the conditions employed the reaction is first order with relation to chlorobenzene (Figure 6). For simplicity, it was considered that neither further oxidation steps nor the competitive *ipso* attack affect significantly the initial rate of the first hydroxylation step.

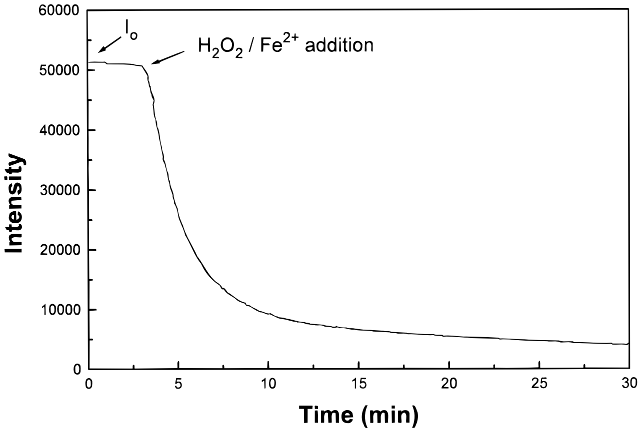


Figure 5. Consumption of chlorobenzene monitored via the ion of *m*/*z* 112.

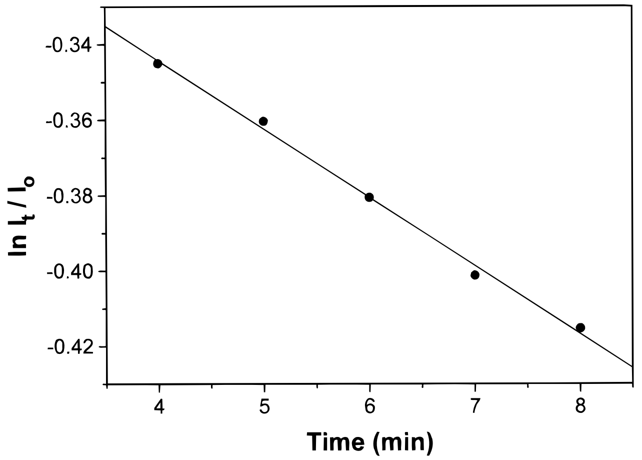


Figure 6. First-order kinetics, ln I_t/I_0 versus time, for the reaction of chlorobenzene with Fenton's system.

TABLE 1: Rate Constants for the Reaction of Aromatic Compounds with Fenton's System ($T = 25$ °C; $[H_2O_2] = 8$ mmol/L; $[Fe^{+2}] = 0.1$ mmol/L; [aromatic] = 0.2 mmol/L)

compound	*k* (min^{-1}) × 10^{-2}	compound	*k* (min^{-1}) × 10^{-2}
chlorobenzene	8.20	methoxybenzene	2.70
bromobenzene	7.40	nitrobenzene	2.60
benzene	5.30	phenol	1.80
toluene	3.10		

The curves (not shown) for the other aromatic compounds were obtained in the same way monitoring in each case characteristic ions (see Experimental Section). All the ln I_t/I_0 versus time plots showed linear behavior. From the slope of each plot, it was possible to calculate the rate constants (*k*). From these rate constants, the following reactivity order is derived: chlorobenzene > bromobenzene > benzene > toluene > methoxybenzene > nitrobenzene > phenol for the hydroxylation of the aromatic compound by Fenton's reagent (Table 1).

The Hammett Parameter. The kinetic data displayed in Table 1 were treated by the Hammet equation[23,24] to investigate the electronic effect of the substituents in the degradation process.

$$\log k_X/k_H = \rho\sigma_X$$

In the Hammett equation, k_X corresponds to the rate constant of the compound bearing the X substituent, k_H is the rate constant of the nonsubstituted compound, σ_X is the substitution constant (Hammett parameter), and ρ is the proportionality factor, which remains constant for a given reaction.

TABLE 2: Log k_X/k_H and the Hammett Parameters (σ_P)[24] for the Benzene Derivatives Compounds

substituent	log k_X/k_H[a]	Hammett parameter (σ_p)
Cl	0.190	0.23
Br	0.145	0.23
H	0.000	0.00
Me	−0.233	−0.17
OMe	−0.293	−0.27
NO_2	−0.309	0.78
OH	−0.469	−0.37

[a] k_X = reaction rate for the substituted aromatic compound and k_H = reaction rate for benzene.

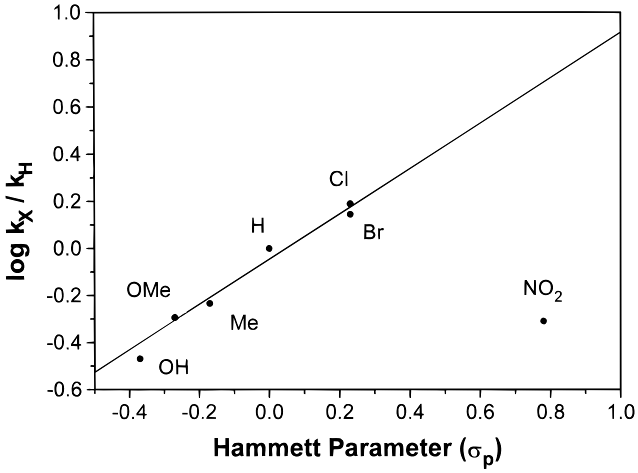


Figure 7. Log k_X/k_H versus the Hammett parameter (σ_p).

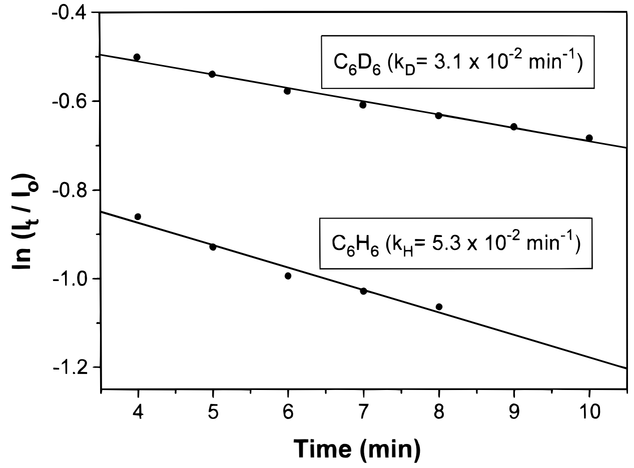


Figure 8. First-order kinetics for the reaction of C_6H_6 and C_6D_6 with Fenton's system.

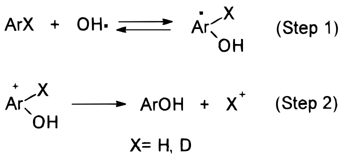
Table 2 shows the calculated values of log k_X/k_H for each compound with the respective values for σ_p. From Figure 7 a good linear correlation between log k_X/k_H and the Hammett parameter (σ_p) can be observed, except for nitrobenzene.

Isotopic Effect. As MIMS employs a mass spectrometer for detection, isotopic effects can also be studied, which is extremely important to clarify reaction mechanisms.[25] Comparing the rate constant for benzene-d_6, C_6D_6 (k_D), and for benzene, C_6H_6 (k_H), a low k_H/k_D ratio of 1.7 was obtained (Figure 8), which suggests that the C−H bond is cleaved in the rate-determining step of the reaction.

Discussion

Reaction Mechanism. According to Habber and Weiss,[26,27] free hydroxyl radicals are the main oxidizing agents formed from Fenton's reagent. The present kinetic studies show that under the reaction conditions employed the rate has a first-order dependence on the concentration of the aromatic compound. This probably occurs owing to the relative high hydroxyl radical concentrations produced by H_2O_2 and Fe^{2+}, which are in much higher proportion compared to the aromatic compounds (H_2O_2:Fe^{2+}:aromatic = 40:5:1).

SCHEME 2



In radical aromatic substitution, both electron-withdrawing and electron-donating substituents increase the reactivity compared to benzene.[28] For example, Summers et al.[29] observed the following reactivity order for the attack by phenyl radicals: $C_6H_5NO_2 > C_6H_5CH_3 > C_6H_5OCH_3 > C_6H_5Cl > C_6H_5Br > C_6H_6$. Edwards and Curci[30] have compiled the reaction rate for several substituted benzene with Fenton's reagent and obtained the following order, $C_6H_5OH > C_6H_6 > C_6H_5OCH_3 > C_6H_5Cl > C_6H_5NO_2 > C_6H_5CH_3$, which shows no clear relationship with the activating/deactivating effects expected for the substituents.

In this work the reaction rate order obtained was $C_6H_5Cl > C_6H_5Br > C_6H_6 > C_6H_5CH_3 > C_6H_5OCH_3 > C_6H_5NO_2 > C_6H_5OH$, which seems to indicate that strong activating groups for electrophilic substitution, such as OH and OCH_3, have a negative effect, whereas deactivating groups, such as Cl and Br, have a positive activating effect for the hydroxylation by Fenton's reagent. Except for $C_6H_5NO_2$, a good linear Hammett (log k_X/k_H versus σ_p) relationship was obtained (Figure 7), suggesting that electronic effects have a significant influence on the reactivity of the aromatic ring toward the Fenton's system.

The reactions with C_6H_6 and C_6D_6 show the operation of a kinetic isotopic effect of $k_H/k_D = 1.7$, indicating that cleavage of the C−H occurs in the rate-limiting step of the reaction. This value, however, seems rather low to explain a process where the rate-limiting step depends exclusively on the C−H rupture. In fact, for SE_1 aromatic electrophilic substitutions or for a simultaneous mechanism (where the C−H bond cleavage releasing H^+ is the rate-limiting step), typical values for k_H/k_D are between 6 and 7.[31] Although the small isotopic effect is not completely understood, the following mechanism is tentatively proposed (Scheme 2).

The isotopic effect will operate if step 2 shows a rate comparable or smaller than step 1 (i.e. $k_2[ArXOH^+] < k_1[ArX][^{\bullet}OH]$). This may occur under the reaction conditions used since there is a large excess of H_2O_2 and Fe^{2+}, which may produce a relatively high concentration of hydroxyl radicals. In this way, if step 1, forming the intermediate $ArXOH^{\bullet}$, is the slow step of the process, the MIMS experiments would show no difference in the consumption of C_6H_6 and C_6D_6 since no C−H bond is broken in this step. Furthermore, it is very reasonable to consider that the rate of formation of both $ArHOH^{\bullet}$ and $ArDOH^{\bullet}$ intermediates is essentially the same.

To explain the small isotopic effect observed, one should consider the reversibility of step 1 and a partition effect. In step 2, the intermediate $ArHOH^+$ should be converted faster to ArOH compared to $ArDOH^+$, considering that the C−H bond is broken in this step. A decrease in the C_6D_6 consumption rate should be observed because the k_2 value for the deuterated intermediate is smaller.

Note that the isotopic studies were carried out monitoring the consumption of C_6H_6 and C_6D_6 (ions of *m*/*z* 78 and 84, respectively) and not the phenol products. The monitoring of these products, C_6H_5OH and C_6D_5OH, for the isotopic study is more complicated since the phenol product is further hydroxylated as soon as it is formed.

Conclusion

MIMS can be used with advantages for the investigation of the hydroxylation of aromatic compounds by Fenton's reagent. The ability to monitor several products simultaneously allows the identification of several reaction intermediates, whereas the continuous monitoring provide detailed information on the kinetics of the reactions involved. This further exemplifies the great potential of MIMS for the study of organic reactions taking place in aqueous medium. In terms of efficiency, sensibility, and simplicity, MIMS is superior to most alternative techniques. This technique might be very interesting for environmental applications such as the study of the organic chemistry in water.

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(13) The signals *m*/*z* 112 and 128, present only in the mass spectra of chlorobenzene and chlorophenol, respectively, do not cause any interference. The signals *m*/*z* 144 and 142 are present in both mass spectra of chlorohydroquinone and chloroquinone. Chlorohydroquinone shows the signal *m*/*z* 142 with relative intensity of 5% causing very low interference on the chloroquinone signal. Chloroquinone shows the signal *m*/*z* 144 with relative intensity of 34%, which might cause some interference on the chlorohydroquinone signal. However, these intermediates are formed and consumed at different times (Figure 3), and any signal interference will not mislead their identification.

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