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RESEARCH NOTE

THE ROLE OF HYDROXYL RADICALS FOR THE DECOMPOSITION OF p-HYDROXY PHENYLACETIC ACID IN AQUEOUS SOLUTIONS

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Abstract—The chemical decomposition of p-hydroxyphenylacetic acid, a priority phenolic pollutant present in wastewaters from some agro-industrial plants, is studied by means of a single photochemical process produced by a polychromatic UV radiation and by hydroxyl radicals generated by the combination of UV radiation plus hydrogen peroxide and by the Fenton's reagent (hydrogen peroxide plus ferrous salts). Batch experiments were conducted to establish the degradation levels obtained and the quantum yields in the single photodecomposition process. An improvement in the decomposition of the phenolic acid in the combined UV/H₂O₂ oxidation is observed, due to the generation of OH radicals, and the contribution of the radical reaction to the global process is determined. In the Fenton's reagent oxidation, the effects of the operating variables (H₂O₂ and Fe²⁺ initial concentrations, pH, type of buffer used) are established and the rate constant for the reaction of p-hydroxyphenylacetic acid with OH radicals is evaluated from a kinetic model, its value being $7.02 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 20°C. © 2001 Elsevier Science Ltd. All rights reserved

Key words—UV radiation, hydroxyl radicals, UV/H₂O₂ combined oxidation, Fenton's reagent, phenolic pollutants, p-hydroxyphenylacetic acid

INTRODUCTION

Wastewaters generated in some agro-industrial plants, like olive oil mills and wine distilleries, present high contaminant levels due to their organic content, mainly phenolic acids and aldehydes. These compounds inhibit to some extent anaerobic digestions (Hamdi, 1992), the most frequent procedure of biodegradation of those effluents. For the transformation of these organic pollutants into more biodegradable residues with low inhibitory potential, several chemical processes which use oxidizing agents such as chlorine, ozone, UV radiation, hydrogen peroxide, etc., have been carried out. And when the decomposition by single oxidants may be difficult because of the low concentrations or the refractory nature of the pollutants present, the advanced oxidation processes (AOPs) (Glaze *et al.*, 1987), which are based on the generation of very reactive and oxidizing radicals like hydroxyl radicals, have been shown to be effective technologies to remove specially toxic and hazardous pollutants from water (Masten and Davis, 1994).

Specifically, photochemical degradations by UV radiation have shown significant technological developments and industrial applications in the treatment of wastewaters in recent years (Yue, 1993), because UV irradiation attacks and decomposes organic molecules by bond cleavage, although usually at very slow rates. Additionally, the presence of hydrogen peroxide increases substantially the rate of the oxidation, due to the generation of hydroxyl radicals, which react with organic compounds with second-order rate constants in the range 10^7 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Buxton *et al.*, 1988; Haag and Yao, 1992). In a similar way, the OH radicals can be formed by the Fenton's reagent, which provides several attractive features for treating organic compounds in wastewaters.

Therefore, due to the great importance of the above-mentioned oxidation methods in the treatment of those types of organic pollutants, a research program was proposed on the kinetics of the decomposition by single UV radiation and by hydroxyl radicals of some of the phenolic acids present in these effluents, with the evaluation of quantum yields for the single photochemical oxidations and rate constants for the reactions among these phenolic compounds and the referred radicals. Thus, in a first stage, p-hydroxyphenylacetic acid was selected in this work as a model compound, because

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Table 1. Experiments conducted in the photochemical process $[B]_0 = 1 \times 10^{-3}$ M

Expt.	System	T ($^{\circ}\text{C}$)	$[\text{H}_2\text{O}_2]_0$ (M)	pH	X_{15} (%)	X_{30} (%)	$k_p \times 10^3 (\text{min}^{-1})$
UV-1	UV	20	—	3	10	18	5.4
UV-2	UV	40	—	3	17	26	8.9
UV-3	UV	20	—	5	24	36	10.9
UV-4	UV	20	—	7	22	33	10.4
UV-5	UV	20	—	9	22	34	10.1
UV-6	UV + H_2O_2	20	1.25×10^{-3}	3	30	69	$k_t \times 10^3$ 19.5
UV-7	UV + H_2O_2	20	2.5×10^{-3}	3	42	78	24.7

it is a major pollutant in wastewaters coming from the wine distillery plants and olive oil extraction processes (Balice *et al.*, 1990). In this work, the hydroxyl radicals were generated by the AOPs constituted by the combinations of UV + H_2O_2 and $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ (Fenton's reagent), and the general objectives were the establishment of the operating variables influence, the report of the degradation levels obtained in each process and the evaluation of the quantum yield in the single photodegradation reaction and the rate constant for the reaction between hydroxyl radicals and p-hydroxyphenylacetic acid.

EXPERIMENTAL SECTION

The reactor used in the single photodecomposition and UV/ H_2O_2 combined degradation experiments always operated in batch mode and consisted basically of a 500 cm^3 cylindrical glass vessel provided with a radiation lamp located in axial position and a quartz sleeve which houses the lamp. This radiation source is a Hanau TQ150 high-pressure mercury vapor lamp which emits a polychromatic radiation in the range from 185 to 436 nm.

The Fenton's reagent reaction experiments were conducted in another 500 cm^3 round-bottom flask with several inlets at the top to allow the introduction of a pH electrode, a thermometer and the reagents. The perfect mixing of these reagents was done by using an agitation system constituted by a variable speed motor. A pH control system was connected to both reactors to keep pH constant at the predetermined value. The initial pH was adjusted by means of a phosphoric acid/phosphate buffer in most cases, although sulfuric acid/sulfate and acetic acid/acetate buffers were also used in some Fenton's reagent oxidation experiments as will be discussed later. During all the experiments, samples were withdrawn from the reactor at regular times for analysis. Potential reactions with OH radicals in the collected samples were quenched by using sodium sulfite, which reacts quickly with hydrogen peroxide.

Analytical grade p-hydroxyphenylacetic acid was used from Sigma. For every experiment conducted, the reactor was filled with 350 cm^3 of p-hydroxyphenylacetic acid aqueous solutions plus the required amounts of hydrogen peroxide in the combined UV/ H_2O_2 process, and ferrous sulfate and hydrogen peroxide in the Fenton's reagent oxidation experiments.

The p-hydroxyphenylacetic acid concentration in the samples was analyzed by HPLC, using a Waters Chromatograph with a 996 Photodiode Array Detector and a Nova-Pak C18 column. The detection was performed at 290 nm and the mobile phase consisted of a mixture of methanol–water–acetic acid (16/79/5% in volume) and with a flow rate

of 1 cm^3/min . The concentration of H_2O_2 in the Fenton's reagent experiments was determined by the peroxidase/DPD method (Bader *et al.*, 1988).

RESULTS AND DISCUSSION

Single UV photolysis

The role of hydroxyl radicals in the decomposition of p-hydroxyphenylacetic acid is clearly demonstrated, in a first stage, with a group of degradation experiments carried out by using alone the polychromatic UV radiation, and by the AOP constituted by the combination of UV radiation and H_2O_2 . Thus, in the single photodecomposition process, the temperature (20 and 40 $^{\circ}\text{C}$) and the pH (3, 5, 7 and 9) were modified. The conversions obtained at two selected reaction times, X_{15} and X_{30} for 15 and 30 min respectively, are summarized in Table 1. These values show a direct influence of the temperature on the process, with increasing conversions, and the subsequent decomposition rates, when the temperature is increased (Expts. UV-1 and UV-2). This result can be expected due to the increase of the quantum yield of a photochemical reaction when this variable is increased. On the other hand, the conversion presents a significant lower value at pH = 3 (Expt. UV-1) and similar values at pH 5, 7 and 9 (Expts. UV-3, UV-4 and UV-5) which indicate no influence of this operating variable on the decomposition process except at low pH. It can be explained by taking into account the higher reactivity of the oxidation reactions for dissociated species than that of non-dissociated species, this aspect being reported by several authors (Shen *et al.*, 1995). In this case, most of the p-hydroxyphenylacetic acid is dissociated at pH = 5 and higher, while at pH = 3 it is scarcely dissociated (p-hydroxyphenylacetic acid $\text{p}K_a = 4.11$).

In a first approach, the kinetic study can be conducted by considering that the photochemical reaction follows a pseudo-first-order kinetics with respect to the p-hydroxyphenylacetic acid concentration, whose rate constant is k_p . According to this, a plot of $\ln [B]_0/[B]$ vs. time must lead to straight lines whose slopes are k_p . After the regression analysis in all the cases, the k_p values depicted in Table 1 are deduced with correlation coefficients greater than 0.99, which validate the goodness of this supposed

kinetics. The observation of these k_p values confirms the trends reported before for the decomposition rate with temperature and pH.

A rigorous kinetic study is performed later for this process with the aim of determining ϕ , the quantum yield of the photoreaction. For this purpose, the reaction model described in a former research (Benitez *et al.*, 1999) is applied to this photochemical decomposition of p-hydroxyphenylacetic acid, leading to the following final equation:

$$[B] = [B]_0 - \frac{\phi}{V} \int_0^t W_{\text{abs}} dt \quad (1)$$

Therefore, according to this equation (1), a plot of the $[B]$ vs. the corresponding term $\int W_{\text{abs}} dt$ must lead to a straight line, whose slope is ϕ/V ; and from this slope the overall quantum yield ϕ of the photoreaction can be deduced.

However, as observed, the evaluation of the above-mentioned integral term requires the determination of the radiation flow rate absorbed by the solution, W_{abs} , at any time of reaction. This determination is made by the procedure described in detail in a previous research (Beltran-Heredia *et al.*, 1996); that is, by means of a radiation source model which describes the distribution of radiant energy within the reactor. In the present case, the Line Source Spherical Emission Model is used (Alfano *et al.*, 1986) whose equations are provided in the mentioned investigation (Beltran-Heredia *et al.*, 1996). Once W_{abs} is known, the integral term $\int W_{\text{abs}} dt$ is calculated for every $[B]$ by fitting the experimental data (W_{abs} , t) to a polynomic expression by least-squares regression analysis and integrating the resultant function. With the integral term evaluated, equation (1) can already be used as described earlier. After regression analysis, the following ϕ values are deduced: 8.4×10^{-3} and 1.4×10^{-2} mol/E for 20 and 40°C, respectively, at pH 3 (Expts. UV-1 and UV-2); while for pH = 5, 7 and 9 at 20°C (Expts. UV-3, UV-4 and UV-5) an average value of 1.7×10^{-2} mol/E is obtained.

Hydroxyl radicals generated by the combination UV + H₂O₂

In the next stage, after the single photodecomposition process was performed, the oxidation of p-hydroxyphenylacetic acid by hydroxyl radicals generated by the combination of UV radiation plus H₂O₂ was studied. In this combined process, the experiments were carried out with different initial concentrations of H₂O₂, according to the values summarized in Table 1. From the conversions obtained at the selected reaction times, two effects can be clearly seen: firstly, the positive influence of the H₂O₂ initial concentration on the process, with increasing conversions when this variable increases (see Expts. UV-6 and UV-7); secondly, the positive influence of the combination UV + H₂O₂ in compar-

ison with the single photodegradation, with significant increases in the conversion in the experiments at similar operating conditions of temperature and pH (see Expts. UV-1 and UV-6). This is a consequence of the enhancement in the decomposition rate of the organic compound produced by the hydroxyl radicals generated in the photolytic decomposition of H₂O₂. A similar evaluation of the pseudo-first-order rate constants as in the single photodecomposition process (represented by k_t in this combined process) leads to the values also showed in Table 1, which confirm the commented enhancements in the decomposition rate due to the presence of the hydroxyl radicals.

Once the radical contribution to the global process is demonstrated, the following step tries to determine in a first approach the value of the pseudo-first-order rate constant corresponding to the radical reaction. Since the reaction mechanisms are complex for the photodegradation of organic compounds, where numerous individual reactions take place and many reaction intermediates are formed and interfere in the process, a rigorous mechanism can not be proposed. However, an approach can be done by assuming that the reaction rate for the global photodecomposition r_T can be considered as the addition of the photochemical r_p and radical r_R reaction rates in the form

$$\begin{aligned} -r_T &= \left[-\frac{d[B]}{dt} \right] = -(r_p + r_R) = (k_p + k_r) [B] \\ &= k_t [B]. \end{aligned} \quad (2)$$

Thus, and according to equation (2), the pseudo-first-order rate constants for the radical reaction k_r can be easily deduced by subtracting the previously determined value of k_p in Expt. UV-1 of Table 1 ($5.4 \times 10^{-3} \text{ min}^{-1}$), from the k_t values of Expts. UV-6 and UV-7 (19.5×10^{-3} and $24.7 \times 10^{-3} \text{ min}^{-1}$, respectively). By doing so, k_r values of 14.1×10^{-3} and $19.3 \times 10^{-3} \text{ min}^{-1}$ for $[H_2O_2]_0 = 1.25 \times 10^{-3}$ and $2.5 \times 10^{-3} \text{ M}$, respectively, are obtained. When these values are compared to those of k_p in Table 1, it is observed that the radical reaction provides a contribution to the total reaction which is significantly higher than that of the individual photochemical reaction.

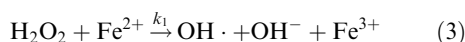
Hydroxyl radicals generated by the combination H₂O₂ + Fe²⁺ (Fenton's reagent)

The hydroxyl radicals are now generated by the Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions. The exact reaction mechanism of the oxidation of organic compounds by this Fenton's reagent is also complex; however, an approximate mechanistic model can be proposed for the global process which takes into account the main reactions. Thus, in this simple mechanism, the initiation step is the generation of OH· by the reaction of hydrogen

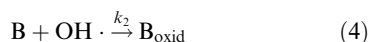
Table 2. Experiments conducted in the Fenton's reagent process pH = 3 T = 20°C

Expt.	[H ₂ O ₂] ₀ (M)	[Fe ²⁺] ₀ (M)	[B] ₀ (M)	X ₅ (%)	X ₃₀ (%)	k _f × 10 ² (min ⁻¹)
F-1	2.5 × 10 ⁻⁴	5 × 10 ⁻⁵	1 × 10 ⁻³	7	16	1.24
F-2	1.25 × 10 ⁻³	5 × 10 ⁻⁵	1 × 10 ⁻³	25	54	4.76
F-3	2.5 × 10 ⁻³	5 × 10 ⁻⁵	1 × 10 ⁻³	37	74	7.87
F-4	5 × 10 ⁻³	5 × 10 ⁻⁵	1 × 10 ⁻³	55	87	12.65
f-5	1.25 × 10 ⁻³	7.5 × 10 ⁻⁵	1 × 10 ⁻³	34	56	7.1
F-6	1.25 × 10 ⁻³	1 × 10 ⁻⁴	1 × 10 ⁻³	39	57	8.09
F-7	1.25 × 10 ⁻³	2 × 10 ⁻⁴	1 × 10 ⁻³	55	59	15.9
F-8	5 × 10 ⁻³	5 × 10 ⁻⁵	2 × 10 ⁻³	35	71	7.16
F-9	5 × 10 ⁻³	5 × 10 ⁻⁵	5 × 10 ⁻³	15	39	2.71

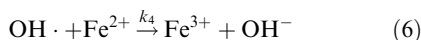
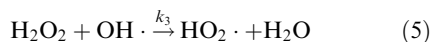
peroxide and ferrous iron (Fe²⁺), according to (Walling and Kato, 1971; Walling, 1975):



Then, these hydroxyl radicals formed react rapidly and nonselectively with most organic compounds, like the p-hydroxyphenylacetic acid, by H-abstraction and addition to C=C unsaturated bonds (Walling, 1975; Buxton *et al.*, 1988), and cause their chemical decomposition:



However, OH radicals may be scavenged by the reaction with the hydrogen peroxide present or with another Fe²⁺ molecule:



Finally, the Fe³⁺ formed can react with H₂O₂ as well as with hydroperoxyl radicals, with regeneration of Fe²⁺.

In this research, several series of experiments of p-hydroxyphenylacetic acid decomposition by Fenton's reagent were conducted by varying the initial concentrations of hydrogen peroxide, ferrous ions and the acid. The values of these operating variables in this group of experiments are summarized in Table 2, which also shows the conversions obtained at two selected times of reaction, 5 and 30 min. It can be seen that the conversion increases with increases in the initial concentrations of H₂O₂ and Fe²⁺, while decreases by increasing the initial concentration of p-hydroxyphenylacetic acid. Similar to the former process, the kinetic study is firstly approached by the evaluation of the pseudo-first order rate constants k_f, with their values also being reported in Table 2.

Another group of decomposition experiments of p-hydroxyphenylacetic acid by Fenton's reagent was performed by varying the pH and the type of buffer used to stabilize the pH, in order to establish the influence of both the operating variables on the oxidation process. Thus, Fig. 1 shows the results of

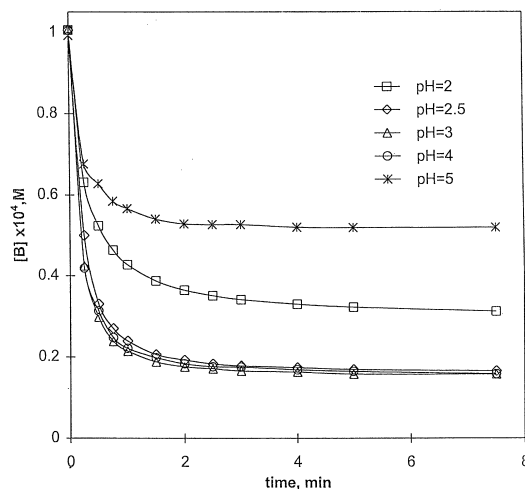


Fig. 1. Fenton's reagent process: influence of the pH on the decomposition of p-hydroxyphenylacetic acid. Experimental conditions: [Fe²⁺]₀ = 5 × 10⁻⁴ M; [H₂O₂]₀ = 5 × 10⁻⁴ M; [B]₀ = 1 × 10⁻⁴ M. Phosphoric acid/phosphate buffer.

the acid concentration evolution with reaction time in experiments where the pH was varied in the range 2–5 and a phosphate buffer was used to adjust the pH. As it is seen, the pH significantly influences the decomposition rate, which progressed at higher rates in the region 2.5–4, with an optimum at pH = 3. Similar results are also reported by several authors (Tang and Huang, 1996; Kwon *et al.*, 1999).

At a pH above 4, the decomposition rate clearly decreases because of the decrease of the free iron species in the solution, probably due to the formation of Fe(II) complexes with the buffer which impede the reaction of Fe²⁺ with H₂O₂ (equation (3)), and also due to the precipitation of ferric oxyhydroxides (Lin and Lo, 1997), which obstruct the reaction of Fe³⁺ with H₂O₂ to regenerate Fe²⁺. Both aspects are favored at higher pH (Zepp *et al.*, 1992), and this precipitation is experimentally confirmed by the presence of turbidity in the samples of experiments carried out at pH = 5. On the other hand, the lower efficiency at pH < 2.5 is due to the formation of the complex species [Fe(II)(H₂O)₆]²⁺ which reacts more slowly with H₂O₂ (equation (3)) than [Fe(II)(OH)(H₂O)₅]⁺, and therefore, produce less amount

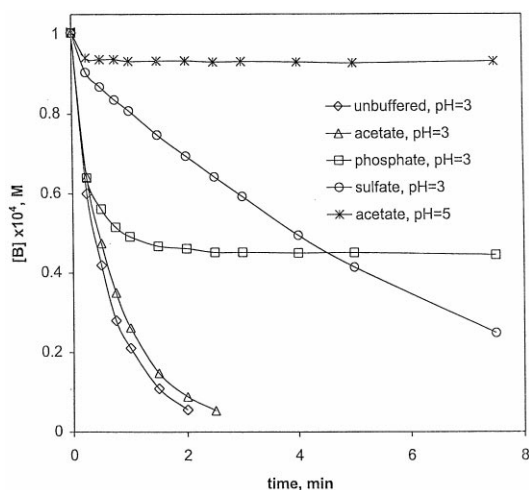


Fig. 2. Fenton's reagent process: influence of the type of buffer used on the decomposition of p-hydroxyphenylacetic acid. Experimental conditions: $[\text{Fe}^{2+}]_0 = 2 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{O}_2]_0 = 5 \times 10^{-4} \text{ M}$; $[\text{B}]_0 = 1 \times 10^{-4} \text{ M}$.

of $\text{OH}\cdot$ (Gallard *et al.*, 1998). In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH (Tang and Huang, 1996), and the reaction of Fe^{3+} with H_2O_2 is inhibited (Pignatello, 1992).

The influence of the type of buffer used to make the pH stable in the p-hydroxyphenylacetic acid decomposition was also investigated in experiments performed at pH=3, the optimum value already deduced. Fig. 2 depicts the results obtained in this group of experiments, with an unbuffered solution and with solutions that were buffered with acetic acid/acetate, phosphoric acid/phosphate and sulfuric acid/sulfate buffers. It can be observed that the best oxidation level was reached in the unbuffered solution (in this experiment, the pH slightly decreased during the reaction from 3 to 2.8), with similar results for the experiment performed with acetic acid buffer. On the other hand, the presence of phosphoric or sulfuric acid buffers decreases the efficiency of the process. As Pignatello (1992) pointed out, it is due to the formation of stable complexes that inhibit the reactivity of Fe^{2+} towards hydrogen peroxide. Finally, in Fig. 2 an experiment with acetic acid buffer at pH=5 was also included. Again, a decrease is observed in the decomposition level in comparison with the experiment at pH=3. This result, in addition to the presence of turbidity in the samples, confirm the effect above discussed for this pH.

In a following step, a more rigorous kinetic study is performed, in this case with the aim to evaluate the more exact rate constant for the reaction between hydroxyl radicals and the p-hydroxyphenylacetic acid (k_2 in equation (4)).

As it is observed, $\text{OH}\cdot$ are generated or consumed in equations (3)–(6). Thus, the concentration profile for these radicals at the initial times of reaction, can

be expressed by the following equation:

$$\frac{d[\text{OH}\cdot]}{dt} = k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}] - k_2[\text{OH}\cdot][\text{B}] - k_3[\text{H}_2\text{O}_2][\text{OH}\cdot] - k_4[\text{OH}\cdot][\text{Fe}^{2+}] \quad (7)$$

By assuming the steady-state condition for the $\text{OH}\cdot$ concentration ($d[\text{OH}\cdot]/dt = 0$), from equation (7) an expression can be deduced for this radical concentration:

$$[\text{OH}\cdot] = \frac{k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_2[\text{B}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{Fe}^{2+}]} \quad (8)$$

On the other hand, the organic compound is decomposed by equation (4), and its degradation rate can be expressed by

$$-\frac{d[\text{B}]}{dt} = k_2[\text{B}][\text{OH}\cdot] \quad (9)$$

Therefore, the introduction of equation (8) into equation (9) leads to

$$-\frac{d[\text{B}]}{dt} = k_2[\text{B}] \frac{k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_2[\text{B}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{Fe}^{2+}]} \quad (10)$$

In this expression, the rate constant k_3 was reported by Walling (1975), its value being $2.85 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, while the constant k_4 for the oxidation of Fe^{2+} (equation (6)) is $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Dorfman and Adams, 1973). Thus, for the evaluation of k_2 , the objective of the present study, equation (10) can be referred to the initial time of reaction and rewritten in the form

$$\frac{[\text{B}]_0 [\text{H}_2\text{O}_2]_0}{(-d[\text{B}]/dt)_0} = \frac{k_4}{k_1 k_2} + [\text{B}]_0 \frac{k_2 + k_3/R}{k_1 k_2 [\text{Fe}^{2+}]_0} \quad (11)$$

where $(-d[\text{B}]/dt)_0$ represents the initial decomposition rate, which is calculated from the experimental data $([\text{B}], t)$, and R is the concentration ratio $[\text{B}]_0/[\text{H}_2\text{O}_2]_0$. Therefore and according to equation (11), a plot of the first term vs. $[\text{B}]_0$ in experiments with a constant concentration of catalyst Fe^{2+} and the same ratio R , must lead to a straight line whose slope is

$$\text{Slope} = \frac{k_2 + k_3/R}{k_1 k_2 [\text{Fe}^{2+}]_0} \quad (12)$$

For the evaluation of this slope, and subsequently the unknown constant k_2 , the group of experiments summarized in Table 3 were carried out (some of them already described in Table 2; that is F-3, F-8 and F-9), where the initial concentrations of p-hydroxyphenylacetic acid and hydrogen peroxide were varied but maintaining constant the ratio R at the values of 0.4 and 1. This Table 3 also includes the experimental values deduced for $(-d[\text{B}]/dt)_0$.

Table 3. Experiments conducted in the Fenton's reagent process for the determination of k_2 $T = 20^\circ\text{C}$ $[\text{Fe}^{2+}] = 5 \times 10^{-5} \text{ M}$

Experiment	R	$[\text{H}_2\text{O}_2]_0$ (M)	$[B]_0$ (M)	$-(d[B]/dt)_0 \times 10^6$ (M s^{-1})
F-10	0.4	1.25×10^{-3}	5×10^{-4}	0.917
F-3	0.4	2.5×10^{-3}	1×10^{-3}	1.62
F-8	0.4	5×10^{-3}	2×10^{-3}	2.82
F-11	0.4	1×10^{-2}	4×10^{-3}	5.18
F-12	1	5×10^{-4}	5×10^{-4}	0.370
F-13	1	1×10^{-3}	1×10^{-3}	0.933
F-14	1	2×10^{-3}	2×10^{-3}	1.25
F-9	1	5×10^{-3}	5×10^{-3}	2.76

The plots mentioned before were made according to equation (11), with the experiments depicted in Table 3 and after regression analysis, the values of 2024.6 and 1912.7 s were obtained for the slopes for $R = 0.4$ and $R = 1$, respectively. With both values and the constant k_3 , the use of equation (12) allows to determine $k_2 = 7.02 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, value for the rate constant of the reaction between $\text{OH}\cdot$ and the *p*-hydroxyphenylacetic acid at 20°C . This value lays in the range of 10^7 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for these rate constants of the reactions of hydroxyl radicals with different organic compounds as it is reported in the literature (Buxton *et al.*, 1988; Haag and Yao, 1992).

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