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# KINETICS OF THE REACTION BETWEEN OZONE AND PHENOLIC ACIDS PRESENT IN AGRO-INDUSTRIAL WASTEWATERS

JESUS BELTRAN-HEREDIA[1]*, JOAQUIN TORREGROSA[1],
JOAQUIN R. DOMINGUEZ[1], JOSE A. PERES[2]

[1] Departamento de Ingenieria Quimica y Energetica, Universidad de Extremadura, 06071 Badajoz, Spain
[2] Departamento de Quimica, Universidad de Tras os Montes e Alto Douro, 5001 Vila Real, Portugal

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**Abstract**—The kinetics of the ozonation of three phenolic acids is investigated from ozone absorption experiments in a semi-continuous reactor. After the evaluation of stoichiometric ratios for the individual reactions between ozone and each phenolic acid, the oxidation of *p*-hydroxybenzoic acid by ozone is performed in a first stage. The influence of the operating variables on the degradation process is established, and the application of a mass transfer with chemical reaction model based on the film theory leads to the determination of the reaction orders and kinetic rate constants. The experimental absorption rates obtained agree well with those calculated theoretically. In the second stage, a mixture of ferulic acid (4-hydroxy-3-methoxycinnamic acid), *β*-resorcylic acid (2,4-dihydroxybenzoic acid) and *p*-hydroxybenzoic acid is ozonated under different experimental conditions. The kinetic study is performed by means of a competitive method that takes *p*-hydroxybenzoic acid as reference compound. The application of this model allows to determine the kinetic rate constants for each compound, which are correlated as a function of pH and temperature. The results obtained support that the kinetic regime of absorption is fast and pseudo-first order with respect to ozone, a condition required by the competitive method used. © 2001 Elsevier Science Ltd. All rights reserved

*Key words*—Ozonation, kinetics, phenolic acids, film theory, kinetic rate constants

## NOMENCLATURE

| | |
|---|---|
| $a$ | specific interfacial area, $m^{-1}$ |
| $C_A^*$ | equilibrium ozone concentration, $mol\,L^{-1}$ |
| $C_B$ | *p*-hydroxybenzoic acid concentration, $mol\,L^{-1}$ |
| $D_A$ | ozone diffusivity in liquid phase, $m^2\,s^{-1}$ |
| $D_B$ | phenolic acid diffusivity in liquid phase, $m^2\,s^{-1}$ |
| $E$ | enhancement factor |
| $E_a$ | activation energy, $kJ\,mol^{-1}$ |
| $E_i$ | instantaneous enhancement factor |
| $F_g$ | volumetric gas flow, $L\,h^{-1}$ |
| Ha | Hatta number |
| $k$ | kinetic rate constant for the ozone-*p*-hydroxybenzoic acid reaction, $L\,mol\,acid^{-1}\,s^{-1}$ |
| $k'$ | parameter defined in equation (9) |
| $k_i$ | kinetic rate constant for the ozone–acid *i* reaction, $L\,mol\,acid^{-1}\,s^{-1}$ |
| $k_L$ | liquid-phase mass transfer coefficient, $m\,s^{-1}$ |
| $k_La$ | volumetric mass transfer coefficient in liquid phase, $s^{-1}$ |
| $k_0$ | preexponential factor, $L\,mol\,acid^{-1}\,s^{-1}$ |
| $k_R$ | kinetic rate constant for the ozone–reference acid reaction, $L\,mol\,acid^{-1}\,s^{-1}$ |
| $m$ | reaction order for ozone |
| $[M_i]$ | acid *i* concentration in the mixture, $mol\,acid\,L^{-1}$ |
| $[M_R]$ | reference acid concentration in the mixture, $mol\,acid\,L^{-1}$ |
| $n$ | reaction order for *p*-hydroxybenzoic acid |
| $n_i$ | inlet ozone concentration in the gas stream, $mol\,L^{-1}$ |
| $n_0$ | outlet ozone concentration in the gas stream, $mol\,L^{-1}$ |
| $N_Aa$ | gas absorption rate of ozone in liquid phase, $mol\,L^{-1}\,s^{-1}$ |
| $[O_3]$ | ozone concentration in the solution, $mol\,L^{-1}$ |
| $p$ | exponent of the $[OH^-]$ |
| $pO_3$ | ozone partial pressure, kPa |
| $T$ | temperature, K or °C |
| $t$ | reaction time, min |
| $V$ | liquid volume in the reactor, L |
| $X$ | phenolic acid conversion, % |
| $z$ | stoichiometric ratio for the ozone–acid reaction, $mol\ O_3\,mol\,acid^{-1}$ |

## INTRODUCTION

Organic substances are usually present in water supplies and wastewaters, and constitute harmful pollutants which must be degraded in purification and treatment plants. Among them, phenolic compounds, and especially acids, are abundantly present in some wastewaters from agro-industrial plants, as those coming from distillery (Benitez *et al.*, 1999a) or olive oil mills (Benitez *et al.*, 1999b), and they incorporate to these effluents a significant contaminant load because of their high toxicity, refractory character and high stability in aqueous medium.

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*Author to whom all correspondence should be addressed. Tel.: +34-24-289385; fax: +34-24-271304; e-mail: jbelther@unex.es

Several chemical processes are carried out with effectiveness for the reduction of that organic matter, by using oxidizing agents like chlorine and chloroderivatives, and more recently, ozone, UV radiation, hydrogen peroxide, etc. The objective of these oxidations is the transformation of the organic pollutants into harmless and low-biodegradable substances.

Ozonation is one of the methods that gives better results in the degradation of these species and reduces to a great extent the problem. In general, it is often preferred over chlorination for the removal of organic pollutants present in waters due to its higher oxidation potential than that of chlorine. In addition, chlorination has been linked to the formation of organohalogen in general, and trihalomethanes in particular such as chloroform, bromo dichloromethane, chloro dibromomethane and bromoform, etc., while ozonation does not leave by-products that need to be removed (Rice, 1980).

Due to its interest, the role of ozonation and its related oxidation processes in treating several organic substances, which are frequently present in industrial effluents and wastewaters, has been examined by different authors (Rice, 1980; Gurol and Nekouinaini, 1984; Glaze *et al.*, 1987; Reynolds *et al.*, 1989; Masten and Davies, 1994). However, most of these works paid little attention to the interaction of gas–liquid mass transfer with chemical reaction, and there are only a few kinetic data about those processes.

Therefore, a research program was designed on the kinetic study of the degradation by ozone of some phenolic acids which are present as pollutants in the above-mentioned wastewaters from agro-industrial plants. In this research program, the main objectives are the evaluation of the stoichiometric ratios, the settlement of the general influence of the operating variables, the investigation of kinetic regime of ozone absorption and the determination of the kinetic parameters (reaction orders and rate constants) for the reaction between ozone and each acid. The resulting kinetic parameters will be of great interest for the successful design and operation of ozonation reactors in wastewater treatment plants.

## KINETIC MODEL

According to the film theory (Danckwerts, 1970; Charpentier, 1981), in a general process in which a gas is absorbed into a liquid following an irreversible $m,n$-order reaction with the liquid solute, the gas absorption rate can be expressed by the equation

$$N_A a = k_L a C_A^* E \qquad (1)$$

where $E$ is the enhancement factor.

In addition, in a process like the present ozonation reaction, where no free dissolved ozone was detected in the liquid solution, this absorption rate can also be expressed as a function of the phenolic acid disappearance rate:

$$N_A a = z\left(-\frac{\mathrm{d}C_B}{\mathrm{d}t}\right) \qquad (2)$$

The absence of ozone in liquid solution suggests that all the ozone reacts in the diffusion film and none diffuses unreacted into the liquid bulk. This is a common situation for many ozone–organic reactions (Yao and Haag, 1991; Hoigné and Bader, 1983a, b), and according to the film theory, these types of reactions take place in the fast kinetic regime.

Moreover, inside the fast regime, there is a particular situation when the reaction can be considered to be of pseudo-$m$ order with respect to the gas being dissolved. For this case, the film theory proposes that $E=$ Ha, Ha being the Hatta number which indicates the relative importance of the chemical reaction compared to the mass transfer, and is defined in the form

$$\mathrm{Ha} = \frac{1}{k_L}\sqrt{\frac{2}{m+1}\, k D_A C_A^{*m-1} C_B^n} \qquad (3)$$

This pseudo-$m$-order regime of absorption is accomplished when the following criterion is fullfilled:

$$3 < \mathrm{Ha} < E_i/2 \qquad (4)$$

where $E_i$ is the instantaneous enhancement factor, which can be evaluated by the equation provided by the film theory:

$$E_i = 1 + \frac{D_B}{D_A}\frac{zC_B}{C_A^*} \qquad (5)$$

In the present ozonation process, the fast and pseudo-$m$-order kinetic regime is initially assumed, but later it must be proved by determining the parameters Ha and $E_i$ and verifying the condition given by equation (4). With the condition $E=$ Ha and equations (1), (2) and (3), it must be written

$$-\frac{\mathrm{d}C_B}{\mathrm{d}t} = \frac{aC_A^*}{z}\sqrt{\frac{2kD_A C_A^{*m-1} C_B^n}{m+1}} \qquad (6)$$

Supposing initially a reaction of first order with respect to the acid, $n = 1$, rearranging and integrating equation (6) with the initial condition

$$t = 0; \quad C_B = C_{B0} \qquad (7)$$

we obtain

$$\sqrt{C_{B0}} - \sqrt{C_B} = k't \qquad (8)$$

with $k'$ being equal to

$$k' = \frac{aC_A^*}{2z}\sqrt{\frac{2kD_A C_A^{*m-1}}{m+1}} \qquad (9)$$

According to equation (8), a plot of the first term vs. time should lead to a straight line whose slope is $k'$, and from equation (9) the kinetic rate constant $k$ can be deduced.

When an ozonation process of a mixture of solutes takes place as in the present situation, the evaluation of the kinetic constants for the several organic compounds which are ozonated simultaneously can be conducted by the kinetic model proposed by Gurol and Nekouinaini (1984), and based on the presence of a reference compound having a known rate constant.

In effect, the direct reaction between an organic compound M and ozone can be represented by the general expression

$$\mathrm{M} + z\mathrm{O}_3 \rightarrow \text{products} \tag{10}$$

where $z$ is the stoichiometric ratio.

According to the literature, a second-order kinetics for the reactions between ozone and organic compounds can be assumed. Thus, as several authors pointed out (Gurol and Nekouinaini, 1984; Yao and Haag, 1991; Hoigné and Bader, 1983a, b; Xiong and Graham, 1992), the second-order reaction is the common situation in the ozonation of different organic substances, and especially in the case of phenolic derivatives.

Therefore, if it can be assumed that the reaction is first order with respect to both, ozone and the organic compound M, the rate expressions of disappearance for every acid $i$ and the reference acid $R$ will be

$$-\frac{\mathrm{d}[\mathrm{M}_i]}{\mathrm{d}t} = \frac{k_i}{z_i}[\mathrm{O}_3][\mathrm{M}_i] \tag{11}$$

$$-\frac{\mathrm{d}[\mathrm{M}_R]}{\mathrm{d}t} = \frac{k_R}{z_R}[\mathrm{O}_3][\mathrm{M}_R] \tag{12}$$

where $k_i$ and $k_R$ are the kinetic rate constants for the direct degradation reaction by ozone of $\mathrm{M}_i$ and $\mathrm{M}_R$ respectively.

By dividing both equations, and integrating between $t = 0$ and $t$, we obtain

$$\ln\frac{[\mathrm{M}_i]_0}{[\mathrm{M}_i]_t} = \frac{k_i z_R}{k_R z_i}\ln\frac{[\mathrm{M}_R]_0}{[\mathrm{M}_R]_t} \tag{13}$$

Thus, a plot of ln $([\mathrm{M}_i]_0/[\mathrm{M}_i]_t)$ against ln $([\mathrm{M}_R]_0/[M_R]_t)$ yields a straight line whose slope is the ratio of kinetic rate constants. As $k_R$, $z_i$ and $z_R$ are known, $k_i$ can be determined for each compound.

This dynamic approach and equation (13) are applicable for situations in which the concentration of the organic compounds remains virtually undepleted in the liquid film. According to the film theory (Danckwerts, 1970; Charpentier, 1981) two absorption regimes satisfy this condition: the very slow or diffusional kinetic regime with reaction taking place in the bulk liquid, and the fast and pseudo-first-order regime with reaction occurring in the liquid film. The film theory proposes that those situations are possible when the following criteria are fulfilled:

- for very slow regime: $\mathrm{Ha} < 0.02$;
- for fast and pseudo-first-order regime: the previously mentioned equation (4).

Once the direct kinetic rate constants are obtained, the kinetic regime of ozone absorption must be definitively established in order to confirm if the previous condition required by this competitive method is fulfilled (equation (4)). For this purpose, it is necessary to evaluate the Hatta number and the instantaneous enhancement factor. However, in the present case in which the reaction medium is constituted by a mixture of solutes which are simultaneously ozonated, instead of equations (3) and (5) for Ha and $E_\mathrm{i}$ in a simple reaction, they must be calculated according to Onda *et al.* (1970) by the expressions

$$\mathrm{Ha} = \frac{1}{k_\mathrm{L}}\sqrt{D_A \sum (k_i[\mathrm{M}_i])} \tag{14}$$

$$E_\mathrm{i} = 1 + \frac{\sum (D_{Bi} z_i [\mathrm{M}_i])}{D_A C_A^*} \tag{15}$$

which take into account the contributions of the stoichiometric ratios and rate constants of each individual ozone–phenolic acid reaction.

## MATERIALS AND METHODS

The experiments were performed in a semi-continuous agitated glass reactor submerged in a thermostatic bath to keep the temperature at the desired value within ±0.5°C. The reactor had five inlets at the top for stirring, sampling, bubbling the gas feed, venting and measuring the temperature.

Ozone was produced from an oxygen stream in an ozone generator, and the ozone–oxygen mixture could be sent to the reactor or to a flask to analyze the ozone in the gas; this concentration was determined iodometrically (Kolthoff and Belcher, 1957), while its concentration in the aqueous solution was measured colorimetrically by the indigo method (Bader and Hoigné, 1981).

For every experiment conducted, the reactor was filled with 350 $\mathrm{cm}^3$ of buffered aqueous solution. It was previously prepared by adding the amount of orthophosphoric acid and sodium hydroxide needed to obtain the desired pH and the ionic strength was always 0.1 M.

In the single ozonation experiments *p*-hydroxybenzoic acid was dissolved in these buffered solutions with an initial concentration of 100 ppm. In a similar way, in the ozonation experiments of the acid mixtures, amounts of ferulic acid, $\beta$-resorcylic acid and *p*-hydroxybenzoic acid were dissolved in the same volume of 350 $\mathrm{cm}^3$ of buffered solutions to obtain an initial concentration of 100 ppm of each acid.

During the experiments, samples were taken out periodically to determine the remaining phenolic acid concentration in the solution. The samples were analyzed by HPLC, using a Waters Chromatograph with a Photodiode Array Detector mod. 996 and a 15 cm Nova-Pak C18 column. As mobile phase a mixture of methanol and water was used (20 : 80 v/v), with a flow rate of 1 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ and the detection was performed at 280 nm.

Several parameters are later needed in the kinetic study: the liquid mass transfer coefficient, the interfacial area, the diffusivities of ozone and the diffusivities of the different acids in water, and the equilibrium ozone concentration. Values of the liquid mass transfer coefficient $k_L$ and the interfacial area were determined by the chemical method described in a previous work (Benitez *et al.*, 1991); diffusivities of ozone in water $D_A$ were obtained from Matrozov *et al.* (1976), and diffusivities of the acids in aqueous solution $D_B$ were evaluated by means of the Wilke–Chang equation (Reid *et al.*, 1977); and the equilibrium ozone concentrations $C_A^*$ were calculated from data of Henry's law constants as a function of pH and temperature provided by Sotelo *et al.* (1989). The specific interfacial area was found to be constant at $62\,\mathrm{m}^{-1}$, and the values for the remaining parameters under different experimental conditions are compiled in Table 1 (except $C_A^*$, which is shown in Table 2).

## RESULTS AND DISCUSSION

### *Stoichiometric ratios*

The stoichiometric ratio of the individual ozone–phenolic acid reactions must be evaluated for the later kinetic study of these ozonation processes. For its determination, experiments were previously carried out under homogeneous conditions, by mixing separately aqueous solutions of ozone and each acid of known concentration. The ozone solution was prepared by bubbling an ozone–oxygen stream into high-purity water until it was saturated. In order to avoid as much as possible, the interferences of reactions between ozone and subproducts, the phenolic acid initial concentrations were higher than that of ozone between one and seven times. It ensured that ozone is consumed exclusively by its reaction with the acid immediately.

The concentrations of ozone and acid in the initial aqueous solution, and the remaining acid concentration in the final solution were measured by means of the following equation:

$$z = \frac{[O_3]_0}{C_{B0} - C_B} \tag{16}$$

The homogeneous experiments performed by mixing separately aqueous solutions of ozone and each acid lead to stoichiometric ratios of 0.5 (for ferulic acid) and 1.5 (for *p*-hydroxybenzoic acid and *β*-resorcylic acid) moles of ozone consumed per mole of acid reacted. In Fig. 1 it can be observed that $z$ takes a high value and decreases, as the initial phenolic/ozone ratio increases until it reaches a constant value. This effect can be explained by the presence of other competitive reactions when phenolic acid concentration is low compared to that of ozone: in this case, some intermediate products that consume ozone are formed, resulting in a higher value of $z$. But when the phenolic acid concentration is increased, it consumes all ozone and a constant value is reached that corresponds to the reaction studied.

### *Ozonation of p-hydroxybenzoic acid*

The ozonation of *p*-hydroxybenzoic acid was carried out in the semi-continuous tank reactor described in the Experimental Section, in experiments where the gas flow rate and the initial concentration of *p*-hydroxybenzoic acid were kept constant at 40 L $\mathrm{h}^{-1}$ (at room conditions) and $7.24 \times 10^{-4}\,\mathrm{mol\,L}^{-1}$, respectively. The studied temperatures were 10, 20, 30 and 40°C; the pH values were 2, 5, 7 and 9, and the ozone partial pressure ranged from 0.09 to 0.38 kPa. Table 2 presents the values taken for these variables in a group of experiments, and as a measure

Table 1. Mass transfer coefficients and diffusivities values

| $T$(°C) | $k_L$ ($\times 10^5\,\mathrm{m\,s}^{-1}$) | $D_A$ ($\times 10^{10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) | $D_{B\mathrm{FER}}$ ($\times 10^{10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) | $D_{B\mathrm{RES}}$ ($\times 10^{10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) | $D_{B\mathrm{PHB}}$ ($\times 10^{10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) |
|---|---|---|---|---|---|
| 10 | 10.4 | 9.25 | 4.38 | 5.43 | 5.60 |
| 20 | 12.3 | 12.49 | 5.91 | 7.33 | 7.56 |
| 30 | 17.9 | 16.22 | 7.68 | 9.53 | 9.82 |
| 40 | 23.2 | 20.47 | 9.70 | 12.03 | 12.40 |

Table 2. Ozonation experiments of *p*-hydroxybenzoic acid

| | | | | | $X$ (%) | |
|---|---|---|---|---|---|---|
| Expt. | $T$ (°C) | pH | $pO_3$ (kPa) | $C_A^*$ ($\times 10^5\,\mathrm{mol\,L}^{-1}$) | 5 min | 15 min |
| O-1 | 10 | 5 | 0.32 | 3.84 | 30 | 65 |
| O-2 | 20 | 5 | 0.32 | 2.97 | 37 | 77 |
| O-3 | 30 | 5 | 0.36 | 2.70 | 39 | 86 |
| O-4 | 40 | 5 | 0.38 | 2.25 | 52 | 93 |
| O-5 | 20 | 2 | 0.36 | 3.74 | 7 | 23 |
| O-6 | 20 | 7 | 0.34 | 3.05 | 60 | 98 |
| O-7 | 20 | 9 | 0.38 | 3.27 | 75 | 100 |
| O-8 | 20 | 5 | 0.22 | 2.07 | 26 | 64 |
| O-9 | 20 | 5 | 0.09 | 0.89 | 12 | 30 |

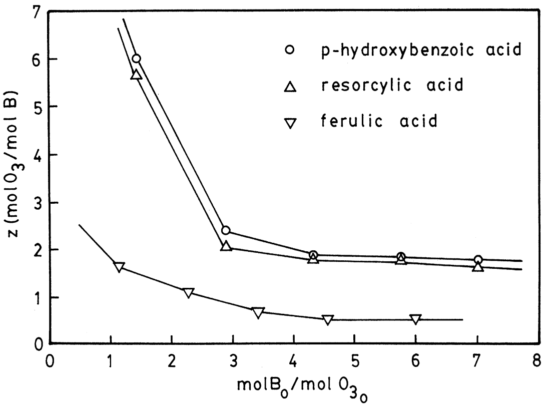

Fig. 1. Determination of the stoichiometric ratios for the ozone–phenolic acid reactions.

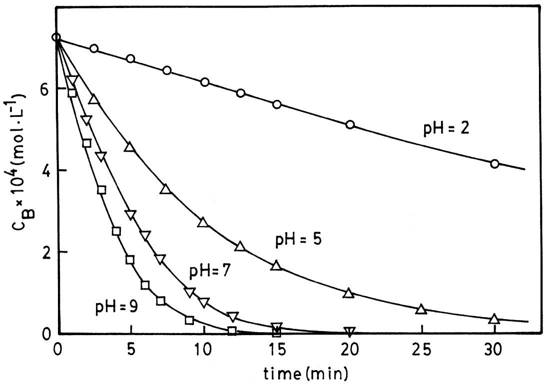

Fig. 2. pH influence on the *p*-hydroxybenzoic acid degradation. Experiments O-2, O-5, O-6 and O-7.

of the degree of oxidation reached, the conversion of *p*-hydroxybenzoic acid $X$ at 5 and 15 min of reaction is also shown. Fig. 2 presents the concentration evolution with time at various pH values (experiments O-2, O-5, O-6 and O-7): at a given time, an increase of conversion can be seen when this variable increases because the rate constant also increases with pH (Yao and Haag, 1991).

Regarding the influence of the temperature on a general ozonation process, two opposite effects must be considered: when temperature increases the reaction rate constant also increases, but the equilibrium ozone concentration decreases. For the *p*-hydroxybenzoic acid degradation a positive effect on the degradation is obtained when the temperature increased (see experiments O-1, O-2, O-3 and O-4). So in this case, it can be concluded that the raise in the rate constant dominates over the diminution of the equilibrium concentration.

Table 2 shows that the increase of ozone partial pressure leads to a rise in the conversion of *p*-hydroxybenzoic acid as could be also expected: the disappearance rate of the organic substance augments with the increment of the ozone absorption rate. This rate is proportional to the ozone solubility

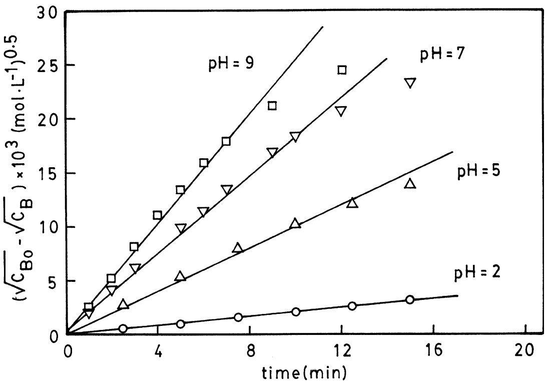

Fig. 3. Determination of the $k'$ constants. Experiments O-2, O-5, O-6 and O-7.

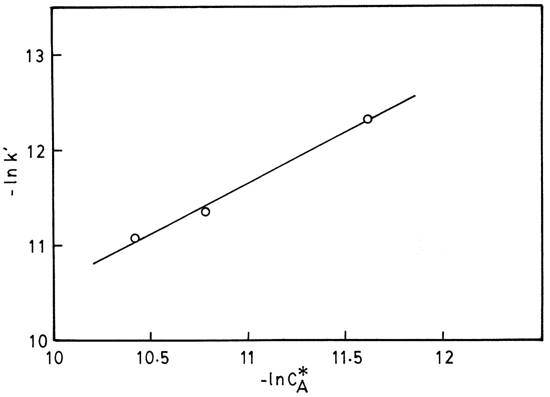

Fig. 4. Determination of the $m$ order with respect to ozone. Experiments O-2, O-8 and O-9.

$C_A{}^*$ as has been shown in equation (1); solubility increases with the ozone partial pressure (Sotelo *et al.*, 1989).

For the determination of ozonation kinetics, according to equation (8), a plot of the first term vs. time should lead to a straight line whose slope is $k'$. Thus, Fig. 3 shows as an example, this plot corresponding to the experiments conducted modifying the pH. As can be observed, points lie on straight lines, corroborating equation (8), and the supposed $n = 1$ order.

Table 3 shows the $k'$ values obtained from least-square regresion analysis for all the experiments of Table 2. It can be observed that these slopes $k'$ always increase with the increase of any experimental variable studied. This is due to the fact that $k'$ depends on the ozone solubility $C_A^*$ (which at the same time is affected by the ozone partial pressure, temperature and pH), and the pseudo-rate constant $k$.

Equation (9) allows to determine the reaction order $m$ for ozone. Thus, a plot of ln $k'$ vs. ln $C_A^*$ for the experiments conducted at the same pH and temperature (experiments O-2, O-8 and O-9) should yield a straight line with a slope of $(m+1)/2$. Fig. 4

shows the mentioned plot and by least-square regression analysis a slope of 1.058 is deduced. So, an $m = 1$ order of reaction with respect to ozone can be proposed.

With this value and rearranging equation (9), the $k$ constant can be deduced:

$$k = \frac{4k'^2 z^2}{a^2 C_A^{*2}} \tag{17}$$

The kinetic rate constants were evaluated for every experiment conducted and are depicted in Table 3. As they are affected by the temperature and pH, these constants can be correlated by a modified Arrhenius expression in the form

$$k = k_0 \exp(-E_a/RT)[\mathrm{OH}^-]^p \tag{18}$$

A multiple regression analysis of the $k$ values vs. temperature and $[\mathrm{OH}^-]$ was followed leading to: $k_0 = 3.56 \times 10^{15}$ L mol acid$^{-1}$ s$^{-1}$, $E_a = 40.49$ kJ mol$^{-1}$ and $p = 0.31$.

In order to verify the fast and pseudo-first-order absorption kinetic regime supposed previously, the Hatta number and the instantaneous enhancement factor must be calculated. Thus, from equations (3) and (9), the Hatta numbers are deduced by the expression

$$\mathrm{Ha} = \frac{2zk'}{aC_A^*} \frac{\sqrt{C_B}}{k_L} \tag{19}$$

and the instantaneous enhancement factor $E_i$ is calculated by equation (5). Table 3 also shows both the Ha and $E_i$ values obtained for all the experiments at the initial time, when it can be assumed that ozone only reacts with *p*-hydroxybenzoic acid. It can be observed that condition (4) is fullfilled or practically fullfilled in all the experiments, corroborating that the absorption-reaction process is fast and pseudo-first order with respect to ozone.

### *Ozonation of the mixture of phenolic acids*

In a second stage, ozonation experiments of mixtures of the three phenolic acids selected were conducted varying the temperature (10–40°C) and pH (2–9). Table 4 specifies the values of those variables in a set of experiments with the corresponding $C_A^*$ values after application of Henry's law constants from Sotelo *et al.* (1989), while the initial acids concentrations were 100 ppm or: $5.15 \times 10^{-4}$ mol L$^{-1}$ for ferulic acid, $6.49 \times 10^{-4}$ mol L$^{-1}$ for *β*-resorcylic acid and $7.24 \times 10^{-4}$ mol L$^{-1}$ for *p*-hydroxybenzoic acid.

In a similar way as in the single ozonation of *p*-hydroxybenzoic acid, temperature and pH have a positive effect on the degradation. Thus, Table 5 shows the results obtained for the conversion in those experiments at a selected time of 10 min taken as an example: it can be seen that for any of the acids, the increase of the temperature (experiments C-3, C-2, C-1 and C-4) and pH (experiments C-6, C-2, C-5 and C-7) leads to an increase of acid conversion, and subsequently, in the oxidation rate. It can be explained taking into account that the oxidation rate increases when the reaction rate contants augment (which occurs with the increase of the temperature and pH).

Finally, in order to establish the different oxidation rates among the studied acids in the ozonation process, Fig. 5 shows the degradation curves in experiment C-7 as an example the following sequence of degradations where can be observed:

*p*-hydroxybenzoic acid < *β*-resorcylic acid

< ferulic acid

Table 3. Kinetic rate constants, Hatta numbers and instantaneous enhancement factors in the ozonation of *p*-hydroxybenzoic acid

| Expt. | $k'$ ($\times 10^5$ mol$^{0.5}$ L$^{-0.5}$ s$^{-1}$) | $k$ ($\times 10^{-4}$ L mol$^{-1}$ s$^{-1}$) | Ha | $E_i$ |
|---|---|---|---|---|
| O-1 | 1.23 | 26.8 | 4.08 | 18.1 |
| O-2 | 1.56 | 53.3 | 5.63 | 23.1 |
| O-3 | 1.89 | 73.4 | 5.20 | 25.4 |
| O-4 | 2.25 | 118 | 5.68 | 30.3 |
| O-5 | 0.37 | 1.84 | 1.05 | 18.6 |
| O-6 | 2.93 | 179 | 10.3 | 22.6 |
| O-7 | 4.06 | 299 | 13.3 | 21.1 |
| O-8 | 1.17 | 62.1 | 6.08 | 32.7 |
| O-9 | 0.45 | 48.5 | 5.37 | 74.4 |

Table 4. Ozonation experiments of the phenolic acids mixture

| Expt. | $T$ (°C) | pH | pO$_3$ (kPa) | $C_A^*$ ($\times 10^5$ mol L$^{-1}$) | $N_A a_{\mathrm{exp}}$ ($\times 10^7$ mol L$^{-1}$ s$^{-1}$) | $E_{\mathrm{exp}}$ |
|---|---|---|---|---|---|---|
| C-1 | 30 | 5 | 0.33 | 2.45 | 10.70 | 4.02 |
| C-2 | 20 | 5 | 0.33 | 3.11 | 10.78 | 4.61 |
| C-3 | 10 | 5 | 0.35 | 4.26 | 19.00 | 7.03 |
| C-4 | 40 | 5 | 0.31 | 1.84 | 10.86 | 4.16 |
| C-5 | 20 | 7 | 0.33 | 2.95 | 16.12 | 7.27 |
| C-6 | 20 | 2 | 0.35 | 3.59 | 7.287 | 2.70 |
| C-7 | 20 | 9 | 0.33 | 2.79 | 64.51 | 30.7 |

Table 5. Conversions, kinetic rate constants, Hatta numbers and instantaneous enhancement factors in the ozonation of the phenolic acids mixture

| Expt. | $X_{FER}$ (%) | $X_{RES}$ (%) | $X_{PHB}$ (%) | $k_{FER}$ ($\times 10^{-4}$ L mol acid$^{-1}$ s$^{-1}$) | $k_{RES}$ ($\times 10^{-4}$ L mol acid$^{-1}$ s$^{-1}$) | Ha | $E_i$ |
|---|---|---|---|---|---|---|---|
| C-1 | 78 | 28 | 17 | 182 | 131 | 10.8 | 56.2 |
| C-2 | 76 | 26 | 13 | 160 | 109 | 12.6 | 44.5 |
| C-3 | 79 | 30 | 24 | 53 | 35 | 7.75 | 32.6 |
| C-4 | 80 | 37 | 34 | 184 | 133 | 10.1 | 74.0 |
| C-5 | 70 | 51 | 42 | 190 | 264 | 18.1 | 45.8 |
| C-6 | 79 | 6 | 4 | 26 | 3.4 | 3.75 | 38.9 |
| C-7 | 83 | 68 | 53 | 226 | 447 | 22.7 | 49.3 |

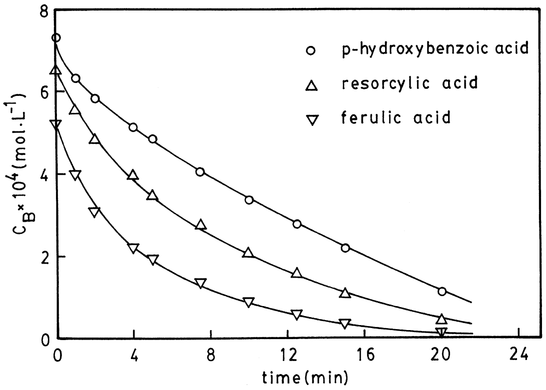

Fig. 5. Comparison of the ozonation rates for the phenolic acids studied. Experiment C-2.

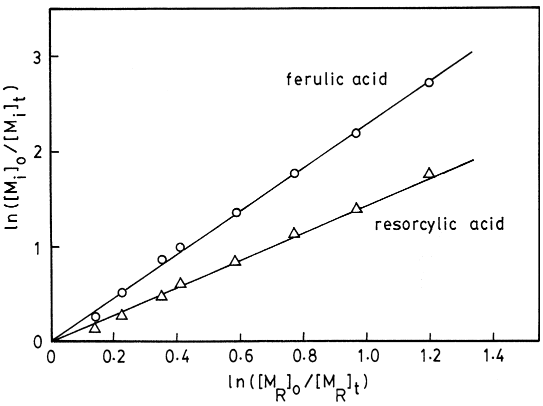

Fig. 6. Determination of the ratio $k_i z_R / k_R z_i$ for the phenolic acids studied. Experiment C-6.

In the present system, an approach to its kinetic regime of ozonation can be made from the experimental results, in order to determine if one of the two mentioned kinetic regimes of reaction takes place. Thus, as in this process no ozone dissolved is detected in the liquid phase, the gas absorption rate can be determined from the ozone absorbed and reacted, by the expression

$$N_A a = \frac{(n_i - n_0)F_g}{V} \tag{20}$$

where $n_i$ and $n_0$ are the inlet and outlet concentrations of ozone in the gas stream, the difference between both being the ozone absorbed and reacted in the liquid phase; $F_g$ is the volumetric gas flow rate (40 L h$^{-1}$ at room conditions in these experiments), and $V$ is the liquid volume (350 cm$^3$).

On the other hand, as was previously established, according to the film theory, the gas absorption rate is also given by equation (1). So, from both equations (1) and (20), the experimental $E$ can be calculated by

$$E_{exp} = \frac{(n_i - n_0)F_g}{k_L a C_A^* V} \tag{21}$$

Table 4 also shows the values obtained at initial time of reaction as example for $N_A a$ and $E_{exp}$ by using equations (20) and (21), respectively: as can be seen, the $E_{exp}$ values are always higher than 1, and according to the film theory (Danckwerts, 1970) it suggests that the kinetic regime of the general ozonation process is fast and the reactions mainly take place in the liquid film. This conclusion partially satisfies condition (4) of fast reaction regime.

In addition, it can be expected that the kinetic regime in this reaction system is also of pseudo-first order, although this requirement will be confirmed later with more accuracy by determining the Ha number for each experiment when the rate constants will be known. The film theory proposes that the pseudo-first-order reaction takes place when the concentration of reactant M in the liquid bulk is much greater than $C_A^*$, and the reaction does not cause any significant depletion of component M through the liquid film. This is the situation that probably occurs in the present system due to the fact that the initial concentration of each acid is about 25 times higher than $C_A^*$ (depicted in Table 4).

So, with the fast regime of pseudo-first order assumed, the evaluation of the $k_i$ constants for the direct reaction between ozone and each phenolic acid can be performed by using equation (13). For this objective, *p*-hydroxybenzoic acid is taken as reference compound.

Thus, according to equation (13), Fig. 6 shows the plot of ln $([M_i]_0/[M_i]_t)$ against $\ln([M_R]_0/[M_R]_t)$ corresponding to the experiment C-7 as an example. As can be seen, experimental points lie satisfactorily around straight lines confirming the goodness of the model used. Similar plots were obtained for the rest of the experiments.

Table 6. Values obtained for $k_0$, $E_a$ and $p$

| | $k_0$ ($\times 10^{-12}$ L mol$^{-1}$ s$^{-1}$) | $E_a$ (kJ mol$^{-1}$) | $p$ |
|---|---|---|---|
| Ferulic acid | 9.92 | 32.77 | 0.13 |
| $\beta$-Resorcylic acid | 2305 | 38.96 | 0.30 |

After least-square regression analysis, the slopes were obtained in all cases, and with the corresponding $k_R$ values (depicted in Table 3), the $k_i$ were deduced for the phenolic acids. Table 5 depicts the values found for every experimental series. Later, by assuming that these kinetic rate constants are functions of temperature and pH, general expressions like equation (18) can be proposed for each acid which correlate the $k_i$ values. A multiple regression analysis is performed and Table 6 shows the values determined for $k_0$, $E_a$, and $p$ for ferulic acid and $\beta$-resorcylic acid.

Table 5 reports the values deduced for Ha and $E_i$ with equations (14) and (15) in the experimental series of Table 4 at the initial times of the ozonation process, when it is assumed that ozone only reacts with the initial acids, and its reaction with the intermediates products formed is nearly negligible. As can be observed, the condition for fast kinetic regime of pseudo-first order as equation (4) establishes is satisfied in all the experiments, corroborating the previously assumed kinetic regime of absorption and the goodness of the model used.

## CONCLUSIONS

The homogeneous experiments performed by mixing separately aqueous solutions of ozone and each acid lead to stoichiometric ratios of 0.5 (for ferulic acid) and 1.5 (for $p$-hydroxybenzoic acid and $\beta$-resorcylic acid) mol of ozone consumed per mol of acid reacted.

In the ozonation of $p$-hydroxybenzoic acid, the operating variables (temperature, pH and ozone partial pressure) have a positive effect on the oxidation process (see Table 2). The application of a model based on the film theory that combines mass transfer with chemical reaction allows to determine the kinetic reaction parameters. Thus, an overall second order is deduced and the kinetic rate constants are evaluated and correlated by the Arrhenius-type expressions:

$$k = 3.56 \times 10^{15} \exp(-4871/T)\,[\mathrm{OH}^-]^{0.31}$$

$$\mathrm{L\ mol\ acid^{-1}\ s^{-1}}$$

From the results obtained in the simultaneous ozonation of mixtures of ferulic acid, $\beta$-resorcylic acid and $p$-hydroxybenzoic acid, a direct influence of the operating conditions is also found. An approach to the regime of absorption is made by determining the reaction factors which suggest that the global process takes place in the fast and pseudo-first-order kinetic regime. The use of a competitive model, which takes $p$-hydroxybenzoic acid as reference compound, leads to the evaluation of the kinetic rate constants for each acid in every experiment. With these constants, the experimental Hatta numbers and the instantaneous enhancement factors are calculated and confirm the previously supposed kinetic regime of the reaction.

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