

Rate constants for the reactions of ozone with chlorophenols in aqueous solutions

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Abstract

The oxidation by ozone of several chlorophenols (CPs): 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, tetrachlorocatechol (3,4,5,6-tetrachloro-2-hydroxy phenol) and 4-chloroguaiacol (4-chloro-2-methoxy phenol), is studied in order to provide values of the overall rate constant for the reaction between ozone and these chlorophenols. Single ozonation experiments of 4-chlorophenol were conducted in an homogeneous system, and ozonation reactions of CP mixtures were performed in a heterogeneous system, leading to the evaluation of the overall ozonation rate constants in acidic aqueous solutions. These second order rate constants increase several order of magnitude with the pH as does the degree of deprotonation of the dissolved compounds (i.e. from 10^3 to 10^9 l/(mol s) for different CPs). The specific rate constants for the ozonation of the non-dissociated and dissociated forms of the studied CPs are also determined and reported. The values obtained allow calculation of the overall rate constants and prediction of the reactivities of the several CPs at different operating conditions in the whole range of pH. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorophenols constitute a group of organic substances that are introduced into the environment as a result of several man-made activities, such as wood preservatives, waste incineration, uncontrolled used of pesticides, fungicides and herbicides, etc., as well as by-products formed during bleaching of pulp with chlorine and in chlorination of drinking water for disinfection [1]. Because of their numerous origins, they can be found in industrial

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wastewaters, soils and surface waters, particularly in the vicinity of production plants and wood-preserving facilities. They have obtained notoriety as hazardous substances, because most of them are toxic and only partially biodegradable, and present long persistence in the environment. As they constitute a threat to human health and produce a public concern, several of them have been listed among the 65 priority pollutants by the US EPA [2]. Therefore, it is highly recommended to develop effective methods for their removal from waters where they are present.

Among these water purification procedures, several chemical processes which use oxidising agents such as ozone, UV radiation, hydrogen peroxide, etc., have been carried out with success [3]. Generally, the results of those treatments are less toxic final products and a global reduction of the organic matter. For situations where the degradation by single oxidants may be difficult, because the organics are present at low concentrations or they are specially refractory to the oxidants, the more effective advanced oxidation processes (AOPs) have also been extensively used [4]. These AOPs are based on the generation of very reactive and oxidising radicals with great destruction power, mainly hydroxyl radicals [5].

Inside the first group of the chemical purification processes above mentioned by means of single oxidants, ozonation is one of the methods that gives better results in the oxidation of refractory contaminants. In general, it is often preferred over chlorination for the removal of organic pollutants present in waters and wastewaters such as these CPs, due to its higher oxidation potential than that of chlorine, and because of the nature of the by-products formed, which are more biodegradable [6].

Most of the studies concerning the ozonation of CPs are focused on the evaluation of the degradation levels obtained for these pollutants or the identification of some reaction by-products generated with the proposition of reaction mechanisms. And in some cases, approximate kinetic rate constants for the destruction of CPs by ozone are provided [7,8]. However, for the successful design and operation of ozone reactors in water treatment plants, the kinetic equations and the values of rate constants for the ozonation reactions in aqueous solutions are needed, and only a few studies about the specific decomposition kinetics of these CPs in water with the evaluation of the rate constants are available in the literature.

With these considerations in mind, a research program was designed on the oxidation by ozone of several common chlorophenols: 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), tetrachlorocatechol (TeCC) and 4-chloroguaiacol (4-CGC). The main objectives were to obtain and report values of the rate constants for the direct reaction between ozone and each chlorophenol. For this purpose, in a first stage single ozonation experiments of 4-CP were conducted in a homogeneous system, and the overall rate constants were evaluated for this reaction by varying the pH in acidic conditions. Later, in a second stage, heterogeneous ozonation reactions of CPs mixtures were carried out in order to determine the mentioned overall rate constants for the ozonation of each CP by using a competitive kinetic model described by Gurol and Nekouinaini [9]. Finally, because of the reaction rate of ozonation of acidic substances such as these CPs, is often regulated by the fraction of deprotonated species present, the specific ozonation rate constants of the non-dissociated and dissociated species of the studied CPs are also calculated and reported.

2. Materials and methods

The CPs used were obtained from Sigma with a purity of 99% and were used without further purification. Ozone was produced from a bottled oxygen stream in a laboratory ozone generator (Yemar, mod. HPA). The water for solutions was obtained from a Millipore Milli-Q water system. All the solutions were buffered, adjusting the pH at the selected value by adding orthophosphoric acid and di-potassium hydrogen phosphate, so that the total ionic strength in the final solution was always 0.05 M.

Previous ozonation experiments were carried out under homogeneous conditions in order to obtain the stoichiometric ratio for the direct reaction between ozone and each CP. They were conducted by mixing aqueous buffered solutions of known concentrations of both, ozone and the CP, being the latter around 10 times higher to assure the total consumption of ozone practically at an instantaneous rate by the CP and not by the intermediate products formed. The ozone solutions were prepared by delivering the ozone–oxygen mixture through a sintered glass disperser to high purity water in a 500 ml glass flask, until it was saturated (final concentrations of dissolved ozone around $(8-9) \times 10^{-4}$ M). At the end of the experiment, the final concentration of the CP was analysed in the reacting medium and the stoichiometric ratio was determined as will be stated in Section 3.1.

The reactions between ozone and 4-CP were carried out in a homogeneous system at 20°C. A stock ozone solution was prepared as discussed above. As these reactions are very fast, several 25 ml thermostated bottles were used as reactors, and each one contained the 4-CP solution with the appropriate buffer and *tert*-butanol 0.01 M to scavenge OH radicals. Then, volumes of the stock ozone solutions were fed to each bottle and at different time intervals, the reaction inside each bottle was stopped by fast addition of Indigo Reagent, allowing to measure the dissolved ozone concentration remaining in the aqueous phase. The amounts mixed of both solutions were necessary to obtain the desired values for the initial concentrations of ozone and 4-CP in every experiment. Again, the 4-CP initial concentration was around 10 times higher than that of ozone, which assured that ozone is consumed exclusively by its reaction with 4-CP, and avoided as much as possible the interferences of reactions between ozone and by-products. Moreover, as the decrease in the concentration of the 4-CP is not significant, it allowed obtaining conditions of pseudo first-order kinetics.

On the other hand, the experiments of the reactions between ozone and the rest of CPs were carried out in heterogeneous conditions, in a 500 ml semi-continuous glass reactor, introduced in a thermostatic bath in order to maintain the constant temperature of 20°C. Solutions of mixtures of two dissolved CPs (also containing *tert*-butanol 0.01 M) and buffered at the desired pH were fed to the reactor, and the ozone–oxygen gas mixture from the ozone generator was introduced continuously into the reactor through a porous plate. Once the process had started, several samples were taken out periodically to analyse the CPs concentrations, and the results were used as will be described in Section 3.3.

The CPs concentrations in the samples were analysed by HPLC by using a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Nova-Pak C18 Column. The detection was made at the maximum wavelength of absorption of each CP (all of them in the range 280–300 nm), with a 1 ml/min mobile phase constituted by methanol–water–acetic acid. The ozone concentration in the gas phase was measured iodometrically by bubbling

the gas in a potassium iodide solution. The dissolved ozone concentration in the aqueous solution samples was determined by the potassium indigo trisulfonate method [10].

3. Results and discussion

3.1. Stoichiometric ratios

The stoichiometric ratios of the individual reactions ozone-CPs must be evaluated for the later kinetic study of these ozonation processes. For their determinations, previous experiments in homogeneous conditions were performed as described above. The concentrations of ozone and CPs in the initial aqueous solutions and the remaining CPs concentrations in the final solutions were measured. By means of the following equation:

$$z = \frac{[\text{O}_3]_0}{[\text{CP}]_0 - [\text{CP}]} \quad (1)$$

the experimental stoichiometric ratios z were evaluated for every experiment conducted. The results obtained showed that, regardless of the CP considered, this ratio remained around 2 mol of ozone consumed per mol of each CP reacted.

3.2. Homogeneous ozonation of 4-CP

In this first stage, the homogeneous degradation by ozone of 4-CP was studied at 20°C, by mixing solutions of known concentrations of ozone and 4-CP, according to the procedure described in the Section 2. The initial experimental conditions varied in those experiments were the initial concentration of 4-CP (1×10^{-4} , 3×10^{-4} and 4×10^{-4} M), the initial concentration of ozone (10 times lower than that of the organic; that is: 1×10^{-5} , 3×10^{-5} and 4×10^{-5} M, respectively) and the pH (2, 2.5 and 3). This acidic range of pH was selected in order to minimise the ozone decomposition into hydroxyl radicals, which is favoured at higher pH as will be stated later. With this approach, the CPs were only degraded by a direct molecular ozone attack.

The ozone concentration in the solution was analysed through the experiments, and the influence observed of the operating variables was as follows. Fig. 1 shows the increase of the ozone conversion as a function of the reaction time in experiments conducted by varying the initial 4-CP concentration, at pH=2 taken as example. As can be seen, there is a positive influence of the initial 4-CP concentration on the conversion, and therefore, an increase on the disappearance rate of ozone when this variable is increased. Similar results are obtained at higher pHs.

Regarding to the pH influence, Fig. 2 shows the experimental results obtained for the decay of the ozone concentration with reaction time during the 4-CP ozonation (with an initial 4-CP concentration of 4×10^{-4} M) at the three experimental pHs of work (2, 2.5 and 3). It is clearly seen the larger ozone concentration decay, and subsequently the increase in the ozone disappearance rate, when the pH is increased.

Initially, this positive influence of the pH in the reaction rate could be attributed to the presence of reactive radicals. At it is well known, ozone reacts with the organic matter

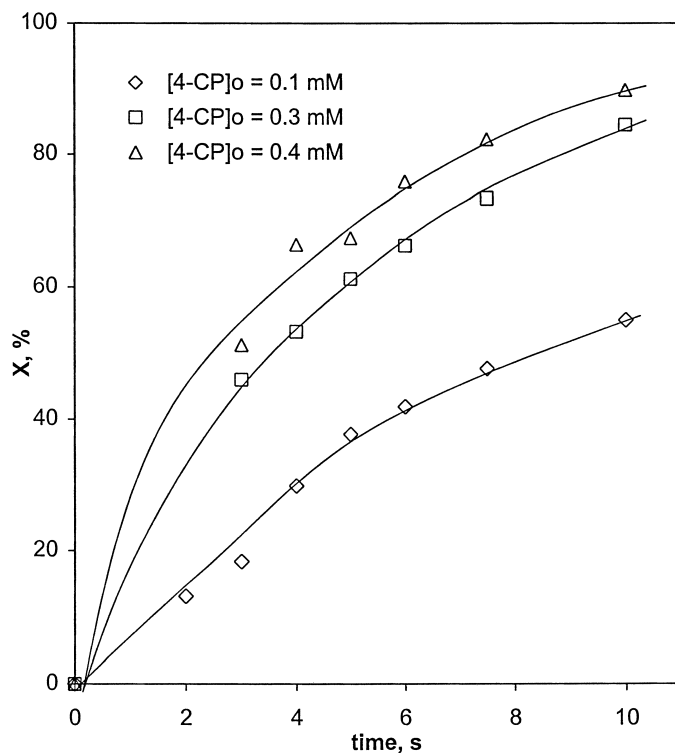


Fig. 1. Influence of the 4-CP initial concentration on the conversion of ozone at pH=2.

in water via two pathways [11,12]: by a direct attack to the solute of molecular ozone, or through a variety of derived oxygen radicals which can act as secondary oxidants. In the first pathway, this direct attack is followed by an electrophilic aromatic substitution and undergoes very selective reactions. The second pathway is constituted by the action of radical species generated from the ozone decomposition, mainly hydroxyl radicals, and the result are very fast reactions with organic compounds with overall second order rate constants in the range $1 \times 10^8 - 1 \times 10^{10}$ l/(mol s) [5,11], although less selective reactions than the first pathway. This ozone decomposition is accelerated rapidly by the increase in the pH, specially in alkaline solutions, and therefore, this hydroxyl radical reactions would play an important role at basic solutions.

However, at the low pH values of work of this research, it can be expected a very slow ozone decomposition, and accordingly, an insignificant formation of hydroxyl radicals. In addition, the tert-butanol added to the solutions is a well known scavenger of hydroxyl radicals [12]. Therefore, the oxidation by hydroxyl radicals does not play a significant role in this case, and the only pathway is the direct oxidation between molecular ozone and the 4-CP. So, the increase in the reaction rate is due to the acidic nature of the 4-CP as will be discussed later more extensively in Section 3.4.

Once the influence of the operating variables is established, the kinetic study is performed in order to determine the overall rate constant for the direct reaction between ozone and

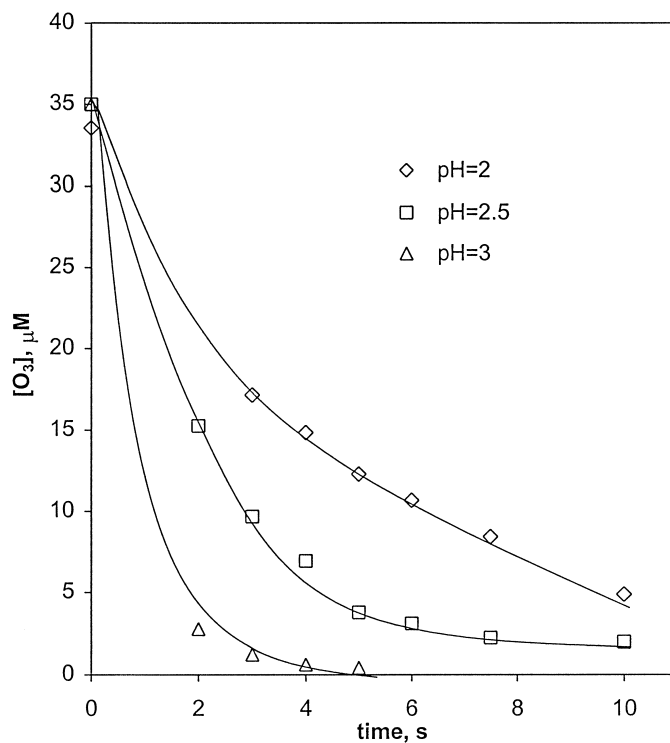


Fig. 2. Influence of the pH on the ozone concentration decay at $[4\text{-CP}]_0 = 4 \times 10^{-4}$ M.

this compound at the mentioned pH values. As several authors pointed out [9,13–15,22] these reactions of ozone with dissolved organic substances, like CPs, are assumed to be first order with respect to each reactant, yielding an overall second-order kinetics. Therefore, the ozone disappearance reaction rate can be expressed in the form

$$-\frac{d[\text{O}_3]}{dt} = k_{\text{O}_3}[\text{O}_3][\text{CP}] \quad (2)$$

where k_{O_3} is the overall second-order rate constant. As the 4-CP concentration is present in excess in comparison to the dissolved ozone (around 10 times higher), the reaction becomes of pseudo-first order. This aspect is also pointed out by the shape of the lines of Fig. 2 which looks like a first-order kinetics with respect to the ozone disappearance. Therefore, the rate equation can be written in the form

$$-\frac{d[\text{O}_3]}{dt} = k'_{\text{O}_3}[\text{O}_3] \quad (3)$$

The integration of Eq. (3) between the initial time and any time of reaction leads to

$$\ln \frac{[\text{O}_3]_0}{[\text{O}_3]} = k'_{\text{O}_3} t \quad (4)$$

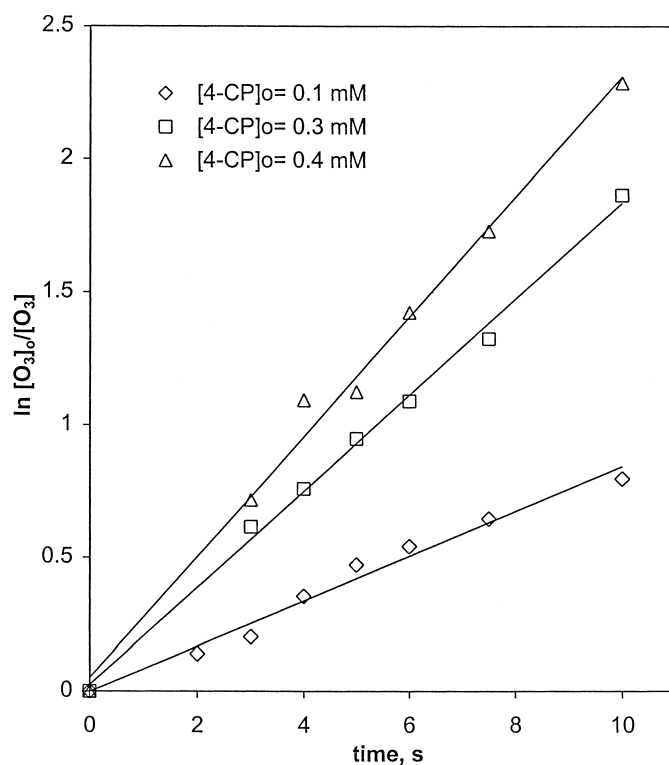


Fig. 3. Determination of the first-order rate constant k'_{O_3} for 4-CP ozonation at pH=2.

According to this equation a plot of $\ln([O_3]_0/[O_3])$ versus reaction time must lead to a straight line for each experiment, whose slope is the pseudo first-order rate constant k'_{O_3} . Fig. 3 shows this plot in the experiments conducted at pH=2 taken as example, with similar plots for the remaining pH. As can be observed, points lie satisfactorily around straight lines, and after regression analysis, the k'_{O_3} values were obtained with correlation coefficients higher than 0.99 in all cases, which confirm the goodness of the proposed kinetics. With those values and the 4-CP concentrations, the overall rate constants k_{O_3} were calculated, their values being depicted in Table 1 for every pH. As can be observed again, as in the disappearance curves of ozone (Fig. 2), there is a direct effect of the pH on this rate constant, which increases with the increase of this variable. Another values found in the literature for the overall rate constant of the reaction between ozone and 4-CP are the following: Trapido et al. [14] proposed a value of 850 l/(mol s) at pH 2.5, in the same range as the value obtained in this work of 1536 l/(mol s). On the contrary, Kuo and Huang [16] obtained a very large rate constant of 23 600 l/(mol s); however, their experiments were conducted in unbuffered solutions (with the pH value about 5.1), and therefore, it is not possible to conduct an exact comparison. In addition, at this higher pH=5.1, it can be expected a larger contribution to the global reaction of the dissociated form of 4-CP which provides an increase of the overall rate constant, as will be discussed in Section 3.4.

Table 1
Overall rate constants for the ozonation of CPs

Compound	k_{O_3} (l/(mol s))		
	pH=2	pH=2.5	pH=3
4-CP	655	1586	2437
2,4-DCP	1886	5110	9167
2,4,6-TCP	9488	20686	47477
2,3,4,6-TeCP	15036	36509	80967
4-CGC	39159	43223	138211
TeCC	25667	60294	54110

3.3. Heterogeneous ozonation of CPs: competitive method

The results of Trapido et al. [8] in the ozonation of some of the CPs of this study in acidic media (pH=2.5) revealed that the degradation rate of the direct reaction between ozone and these CPs increased as follows: 4-CP < 2,4-DCP < 2,4,6-TCP < 2,3,4,6-TeCP. This trend was also confirmed by our results in a previous research carried out at pH=2 for the heterogeneous ozonation of this group of CPs [17], where the addition of substituent chlorine atoms to the aromatic ring increased the global reaction rate of CPs with ozone. Therefore, it is not possible to conduct experiments of the remaining CPs degradation by ozone in a homogeneous reaction system, like those experiments for the ozonation of 4-CP described in the preceding Section 3.2, due to the extremely fast decomposition rate that impede to follow the reaction.

To solve this situation, in this second stage, the evaluation of the overall rate constants for the ozonation of the remaining CPs (2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, TeCC and 4-CGC) was conducted by a competitive kinetic model proposed by Gurol and Nekouinaini [9], which consists of the simultaneous degradation of mixtures of organic compounds in a heterogeneous reaction system. In every mixture, one of the organic substances is a reference compound, whose degradation rate constant is previously known; the remaining substances constitute the target compounds, whose rate constants are unknown. This dynamic approach has been previously used with success by several authors [9,13,15,18,22] for the oxidation of some organic compounds by oxidants like ozone, UV radiation or hydroxyl radicals.

In addition, this procedure is reliable when measuring the rates of fast reactions in aqueous solutions, and is based on assuming that the reaction between the oxidant and the organic follows an overall second-order kinetics, and more specifically, of first order with respect to both reactants. Both conditions are fulfilled in the ozonation of the phenolic derivatives of the present case which follow that kinetics [9,13–15,22].

According to those considerations, in this specific case of ozonation of CPs mixtures, the rate expression of disappearance for each chlorophenol 'i' and the reference chlorophenol 'R' will be

$$-\frac{d[CP_i]}{dt} = k_i[O_3][CP_i] = \frac{k_{O_3i}}{z_i}[O_3][CP_i] \quad (5)$$

$$-\frac{d[CP_R]}{dt} = k_R[O_3][CP_R] = \frac{k_{O_3R}}{z_R}[O_3][CP_R] \quad (6)$$

Table 2
Ozonation of mixtures of CPs

Mixture	Reference	Target
1	4-Chlorophenol	2,4-Dichlorophenol
2	2,4-Dichlorophenol	2,4,6-Trichlorophenol
3	2,4,6-Trichlorophenol	2,3,4,6-Tetrachlorophenol
4	2,3,4,6-Tetrachlorophenol	Tetrachlorocatechol
5	2,4,6-Trichlorophenol	4-Chloroguaiacol

where CP_R represents the reference chlorophenol and CP_i each target chlorophenol; k_{O_3R} and k_{O_3i} the overall ozone disappearance rate constants for the reference and target compounds, respectively; k_R and k_i the overall CP disappearance rate constants for the reference and target compounds, respectively; and z_R and z_i the stoichiometric ratios for the direct reaction between ozone and the reference and target CPs, respectively.

By dividing both Eqs. (5) and (6), and integrating between $t=0$ and $t=t$, it is obtained

$$\ln \frac{[CP_i]_0}{[CP_i]} = \frac{z_R k_{O_3i}}{z_i k_{O_3R}} \ln \frac{[CP_R]_0}{[CP_R]} \quad (7)$$

As it has been previously explained, the stoichiometric ratio experimentally deduced in this study was in all cases 2 mol of ozone consumed per mol of CP degraded; therefore, $z_R/z_i=1$. Thus, a plot of $\ln([CP_i]_0/[CP_i])$ against $\ln([CP_R]_0/[CP_R])$ must yields a straight line whose slope is the ratio of rate constants. As k_{O_3R} is known, the value for the rate constant k_{O_3i} in every experiment conducted can be calculated for each target compound.

For this purpose, in this research simultaneous ozonation experiments of couples of CPs were conducted (with initial CP concentration of 2×10^{-4} M in all cases) by varying the pH (2, 2.5 and 3), and maintaining the constant temperature at 20°C and the ozone partial pressure in the gas phase at 90 Pa. Table 2 summarises the selected ozonated mixtures (obviously, the first reference compound used was 4-CP, since its kinetics was studied and its rate constants were evaluated before in Section 3.2), and Fig. 4 shows the plots obtained according to Eq. (7) corresponding to mixtures 1, 3 and 5 taken as examples, at pH=2. As can be observed, points lie very satisfactorily around straight lines, confirming the goodness of the model used. Similar plots were obtained for the rest of the mixtures ozonated.

After least square regression analysis in all cases, the slopes were deduced, and with the corresponding k_{O_3R} values, the k_{O_3i} rate constants were evaluated for all the CPs. These values are also depicted in Table 1: as can be seen, they increase with the increase of the pH for all the CPs; as well as with the substitution degree in the aromatic ring in the specific sequence 4-CP to 2, 3, 4, 6-TeCP.

3.4. Determination of the ozonation rate constants for the non-dissociated and dissociated species

When acidic organic compounds, like these CPs, are dissolved in water, their reaction rates with oxidant agents can vary substantially with the pH of the medium. It is due to the fact that the non-dissociated and dissociated forms of the acidic substances, whose relative

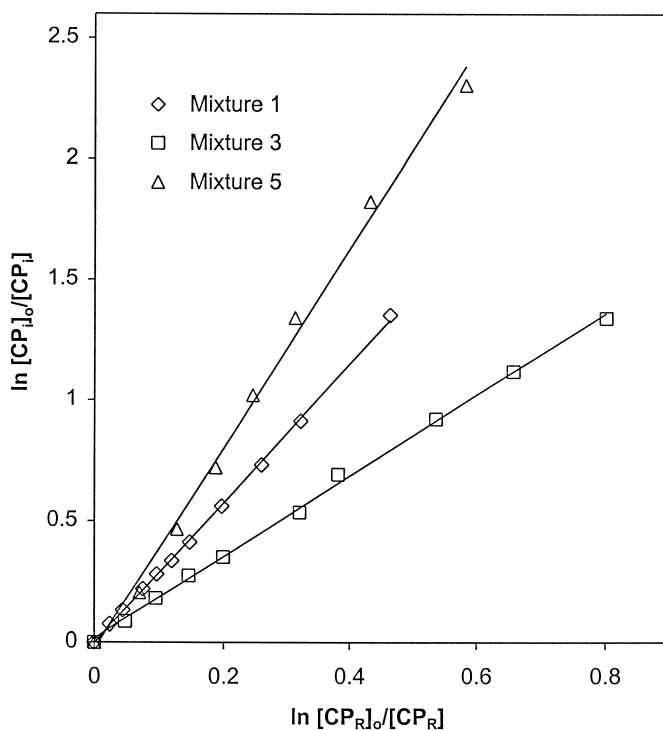


Fig. 4. Determination of the k_{O_3i}/k_{O_3R} ratio for the simultaneous ozonation of mixtures 1, 3 and 5.

presence in aqueous solutions depends on the pH, present a different reactivity towards the oxidants. Therefore, the overall reaction rate for the oxidation of the acidic substances strongly depends on the degree of dissociation, and consequently, on the pH of the solution. So, it is essential to evaluate the specific oxidation rate constants of both forms in which every organic pollutant can dissociate in water, in order to establish the global kinetics of their oxidation reactions at the pH of some natural waters and wastewaters. This aspect has a considerable importance for the design of reactors for water treatment processes.

According to these considerations, another objective of the present study is to evaluate the specific ozonation rate constants for the non-dissociated and dissociated species of the CPs studied from the experimental results obtained for the overall rate constants k_{O_3} in the preceding Sections 3.2 and 3.3. Once the specific rate constants for the ozonation of both species are evaluated, it would be possible to predict the overall rate constants of the CPs at whichever pH of the water, including the alkaline pHs where those constants have not been previously determined experimentally.

The acidic CPs can dissociate in the form



Thus, according to Eq. (2), the disappearance rate of ozone can be written as

$$r_{O_3} = k_{O_3}[O_3][CP]_{tot} = k_{CP^-}[O_3][CP^-] + k_{CP}[O_3][CP] \quad (9)$$

where k_{O_3} is the mentioned overall ozonation reaction rate constant based on the total concentration of chlorophenol present $[CP]_{tot}$, its values already determined in Sections 3.2 and 3.3 and depicted in Table 1; and k_{CP^-} and k_{CP} are the specific rate constants for the ozone disappearance by means of the anionic and neutral species, CP^- and CP , respectively.

The relative amount of CP^- and CP species present in the solution can be calculated from α , the degree of dissociation, defined as

$$\alpha = \frac{[CP]}{[CP^-] + [CP]} = \frac{[CP^-]}{[CP]_{tot}} \quad (10)$$

On the other hand, the degree of dissociation can be also determined from the pH of the solution and the dissociation constant K_a of the acid

$$\alpha = \frac{1}{1 + ([H^+]/K_a)} \quad (11)$$

Then, with Eqs. (9) and (10), it is finally obtained

$$k_{O_3} = \alpha k_{CP^-} + (1 - \alpha)k_{CP} \quad (12)$$

As Eq. (11) shows, it is necessary to know the pK_a values of the CPs studied for the evaluation of α . These values for the sequence 4-CP to 2,3,4,6-TeCP were obtained from the literature [13,19,22], while the pK_a for TeCC and 4-CGC were experimentally determined according to the procedure described by Qiu et al. [20]; all of these pK_a are showed in Table 3 for each CP. Thus, by using the pK_a and pH values in every experiment, the α values were calculated from Eq. (11); then, the use of the overall rate constants k_{O_3} at those pH (2 and 3) and Eq. (12) allows determining the unknown rate constants k_{CP^-} and k_{CP} , whose average values are also listed in Table 3.

The k_{CP} constants obtained for 4-CP, 2,4-DCP and 2,4,6-TCP can be compared to those proposed by Hoigne and Bader [13,22] for this rate constant, whose values were, respectively, 600, $<1.5 \times 10^3$ and $<10 \times 10^3$ l/(mol s). Therefore, there is a satisfactory agreement in the ozonation rate constant for the non-dissociated form of these compounds.

From the values given in Table 3, it can be seen higher reaction rate constants and subsequently larger reactivities of ozone towards dissociated species (phenolate ions) than those towards non-dissociated species, this aspect also being previously pointed out by several authors [5,13,21,22]. On the other hand, and specifically for the sequence 4-CP to 2,3,4,6-TeCP,

Table 3
Rate constants for the non-dissociated and dissociated species

Compound	pK_a	k_{CP^-} (l/(mol s))	k_{CP} (l/(mol s))	$(k_{O_3})^a$ (l/(mol s))
4-CP	9.2	3.9×10^9	608	1385
2,4-DCP	7.8	6.1×10^8	1569	4618
2,4,6-TCP	6.1	5.6×10^7	5953	19997
2,3,4,6-TeCP	5.4	1.9×10^7	9545	34646
4-CGC	9.5	5.7×10^{10}	37655	43101
TeCC	5.7	6.7×10^7	15656	57677

^a Calculated theoretically at pH=2.5.

it is also observed an inverse trend of reactivities for the non-dissociated CPs and their phenolates ions: thus, for the non-dissociated forms, the most reactive is 2,3,4,6-TeCP (larger k_{CP}), followed by 2,4,6-TCP, 2,4-DCP and 4-CP; on the contrary, for the phenolates forms, the sequence of reactivity is: 4-CP > 2,4-DCP > 2,4,6-TCP > 2,3,4,6-TeCP. In addition, the k_{CP^-} rate constants and the reactivities of 4-CGC and TeCC dissociated species are in the same range than those of 4-CP and 2,3,4,6-TeCP, respectively, as could be expected according to the similar chemical structures of both couples of compounds: one and four substituent chlorine atoms, respectively. The higher rate constants for both forms of 4-CGC with ozone could be attributed to the presence of the methoxy group in the aromatic ring. This is a known donor-electron group, and therefore, could increase the electronic density of the ring and activate the electrophilic attack of ozone.

Finally, in order to validate the obtained rate constant values, some comparisons between calculated and experimental results can be performed. Firstly, with the determined specific rate constants k_{CP^-} and k_{CP} , the overall constants k_{O_3} at pH=2.5 for all the CPs are calculated by means of Eq. (12), with the corresponding α obtained from Eq. (11) and the pK_a of each CP. The deduced values are also showed in Table 3, and when compared to the experimental ones for this rate constant at pH=2.5 which are depicted in Table 1, an excellent agreement between both groups can be seen. Secondly, the k_{O_3} overall rate constants are later calculated by means of Eq. (12) for the whole pH range, and Fig. 5 shows their evolution with the pH

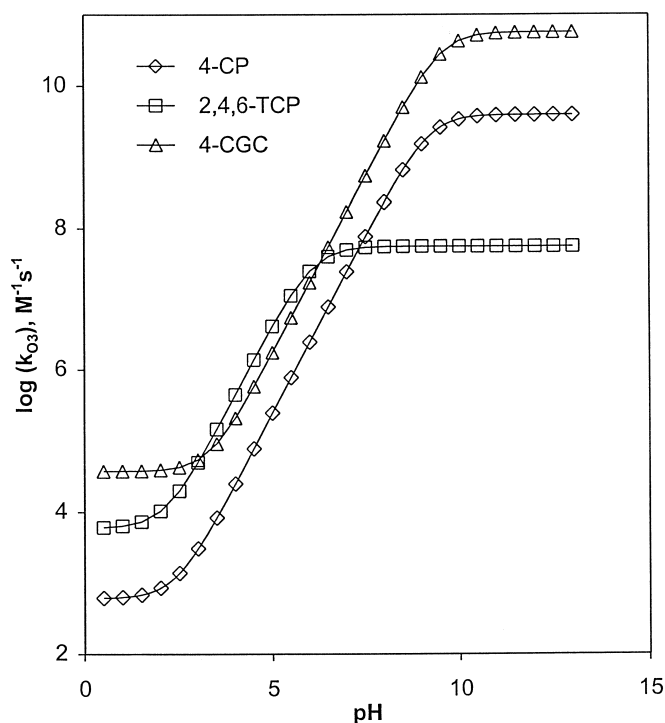


Fig. 5. Evolution of the k_{O_3} rate constant with the pH for the ozonation of 4-CP, 2,4,6-TCP and 4-CGC.

for 4-CP, 2,4,6-TCP and 4-CGC taken as examples. Similar trends were observed in the k_{O_3} evolution for 4-CP and 4-CGC, and a quite different trend for 2,4,6-TCP. Taking into account that an increase in the rate constants means an increase in the reactivity of the CP considered towards ozone, the mentioned trends indicate the sequence of reactivities of those compounds through this whole range of pH. In a parallel way, three ozonation experiments (at pH 2, 6 and 9, respectively) in heterogeneous conditions of mixtures of the mentioned

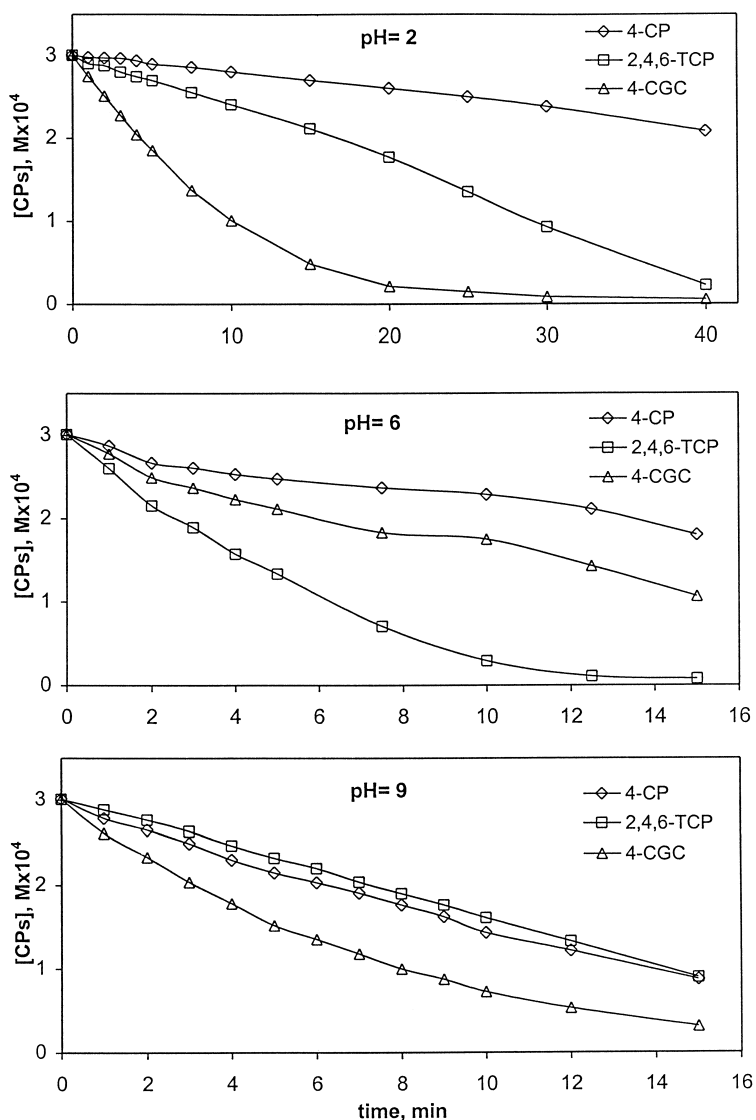


Fig. 6. Decomposition curves for the ozonation of 4-CP, 2,4,6-TCP and 4-CGC in experiments at pH=2, 6 and 9.

three CPs were conducted, and the CP concentrations were followed with reaction time, and plotted in Fig. 6. From this figure, the following sequences of reactivities are observed: at pH=2, 4-CGC > 2,4,6-TCP > 4-CP, while at pH=6, 2,4,6-TCP > 4-CGC > 4-CP, and at pH=9, 4-CGC > 4-CP > 2,4,6-TCP. Therefore, these experimental trends of reactivity agree perfectly with the trends of k_{O_3} calculated theoretically at those pHs as can be observed in Fig. 5. In conclusion, these agreements between experimental and theoretical results confirms the goodness of the procedure followed for the evaluation of overall rate constants k_{O_3} and specific rate constants k_{CP^-} and k_{CP} , and the subsequent reactivity of ozone towards each CP.

4. Conclusions

Previous experiments for the determination of the stoichiometric ratio between ozone and each CP studied revealed that 2 mol of ozone are consumed per mol of CP degraded. The results obtained in the ozonation of 4-CP in an homogeneous system at 20°C indicated that the initial chlorophenol concentration and the pH exert a positive influence on the disappearance rate of ozone. In the acidic conditions of the experiments (pH=2, 2.5 and 3), the direct pathway is the only reaction that takes place, and no contribution to the global reaction of the radical pathway can be expected. The overall rate constants obtained for this direct reaction varies from 655 l/(mol s) at pH=2 to 2437 l/(mol s) at pH=3.

The ozonation experiments of mixtures of two CPs in heterogeneous conditions allow evaluation of the overall rate constants for the reaction between ozone and each CP, the values obtained ranging between 1886 l/(mol s) at pH=2 for 2,4-DCP and 138 211 l/(mol s) at pH=3 for 4-CGC. Due to the fact that the second-order rate constants increase with the pH as a consequence of the increase in the degree of deprotonation of the dissolved CPs, this degree of dissociation is calculated at every pH for each CP and the specific rate constants for the ozone consumption with the dissociated and the non-dissociated forms are evaluated. The values obtained are significantly higher for the ozonation of the dissociated species, and the k_{CP^-} constants decrease in the sequence 4-CP to 2,3,4,6-TeCP, while the k_{CP} constants present an inverse trend in that series. Finally, the experimental results obtained for k_{O_3} at pH=2.5, and the sequence of reactivities established for three CPs taken as examples (4-CP, 4-CGC and 2,4,6-TCP) agree satisfactorily with the theoretical values calculated for both parameters, confirming the adequacy of the model used for the evaluation of the different rate constants for the ozonation reactions of the CPs studied.

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