Ozonation of *p*-chlorophenol in aqueous solution

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Abstract

The ozonation of *p*-chlorophenol (CHP) in aqueous solution has been studied in the pH range 2.0–8.0, in the presence of *tert*-butyl alcohol, which prevents the activation of the radical mechanism of oxidation. Results indicate that the pH influences the system reactivity and that only a partial chlorine release is observed for lengthy ozonation too, after the complete substrate disappearance. For adopted experimental conditions the oxidation process develops under a quasi-diffusional regime of absorption with reaction, a transition domain between kinetic and diffusional regimes in which ozone and dissolved substances react exclusively in the liquid film. A proper mathematical model has been developed and used to simulate the system behaviour © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Chlorophenols are important intermediates for the production of pesticides, herbicides and dyes [1]. Their presence in the environment is often reported also as a consequence of their accidental formation during the disinfection of phenol-containing water by means of chlorination [2,3]. The toxicity of these substances to man and animals is comparable to that of phenol [4,5] and therefore great care is required to achieve a complete abatement of chlorophenols in water and wastewater.

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Many researchers [6–8] have reported that ozonation processes are capable of destroying this type of pollutants with consequent release of chloride ions in the solution, although complete reaction schemes are lacking. Less extensive work has been done to assess the reaction kinetics [3,9,10] with some discrepancies among reported findings.

In the present work the results of an investigation on the ozonation process of *p*-chlorophenol in aqueous solution in the pH range 2.0–8.0 are reported. A part of the work is focused on the kinetic analysis of the data collected during ozonation experiments performed in a semibatch reactor.

2. Experimental methods

Ozonation runs were performed in the experimental apparatus reported elsewhere [11] on buffered aqueous solutions of bidistilled water ($V_L = 0.8$ dm^3) containing *p*-chlorophenol (purchased from Aldrich, > 99% by weight). Solutions were buffered at different pHs by means of H_3PO_4, KH_2PO_4 and Na_2HPO_4 addition. The ionic strength was kept at a constant value of 0.1 mol dm^{-3} by using a proper amount of NaCl salt. Analytical samples for chloride analysis were obtained from ozonation runs on aqueous buffered solutions of *p*-chlorophenol whose ionic strength was adjusted by adding only phosphate salts. To prevent the activation of the radical mechanism of oxidation a volume (4.0×10^{-3} dm^3) of *tert*-butyl alcohol was added to the solution as radical scavenger for each run. The stirrer speed was adjusted at 380 rpm. An ozonised oxygen stream of 2% by volume obtained by an ozone-generator (Fischer 502) was fed at a flow rate of 36 dm^3 h^{-1} to a 1.090 dm^3 semi-batch glass reactor containing the aqueous solution. The ozone concentration in the outlet gaseous stream was evaluated by continuous UV monitoring at a wavelength of 253 nm by means of a Varian UV spectrophotometer equipped with a quartz cell (optical length = 3.0×10^{-2} dm). Analytical aqueous samples, withdrawn at different reaction times, were analyzed by means of a HPLC chromatograph (Hewlett Packard mod. 1090 II) equipped with a Spherisorb S5C6 reverse phase column and a UV–VIS detector ($\lambda = 280$ nm). The eluent was a 90:10 buffered solution ($H_2O:CH_3CN:H_3PO_4$ 500:25:2): CH_3CN at flow rate of 1.0 ml min^{-1}. The 1,2-phenylenediamine derivatizing method [12] and HPLC analyses with an Alltech OA-1000 acid column (detector: $\lambda = 280$ nm, eluent solution: $H_2O:H_2SO_4$ 500:0.8, flowrate: 0.8 ml min^{-1}) were also used for the determination of chemical intermediates. To detect the free chloride formation during the ozonation process an Orion 96-17B combination electrode was used. To identify chemical intermediates the following esterification procedure was carried out: an ozonised aqueous sample, after drying under vacuum, was dissolved in methanol acidified with H_2SO_4 (2% by volume). The mixture was kept for 6 h at reflux and then, after cooling, extracted with diethyl ether. Before the GC-MS injection, the organic fraction was gently evaporated to minimum liquid content using a dry stream of Nitrogen gas.

GC-MS analyses were performed by a Saturn 2000 apparatus (Varian) using a DB5 column with an Ion Trap detector. The flow rate of carrier gas (Helium) was 10 ml

min^{-1}. The injector temperature was set at 120°C. The following temperature ramp was used: 30°C for 5.0 min, 6.6°C min^{-1} up to 280°C, hold time 5.0 min.

Only analytical grade solvents were used (Sigma-Aldrich, USA or Carlo Erba Reagents, Italy)

3. Results and discussion

The results of the ozonation experiments performed at different pHs are reported in Fig. 1. In the pH range 2.0–6.0, the system reactivity increases with increasing pH. Due to the presence in the solution of *tert*-butyl alcohol, the intervention of the radical mechanism can be ruled out and the observed behaviour can be thus explained by considering that *p*-chlorophenol is an acid organic compound and that in aqueous solution it is present in dissociated and undissociated form whose relative occurrence is regulated by the pH ($pK_{CHP} = 9.2$ [9]). Since the direct (ionic) attack of ozone to aromatic substrates develops through an electrophilic mechanism, it is evident that
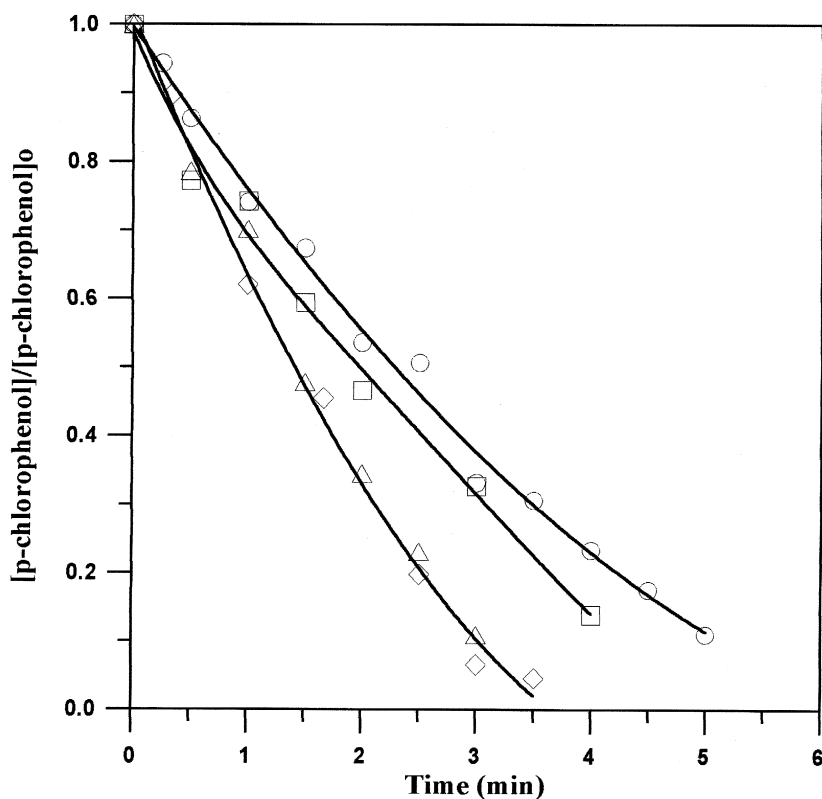

Fig. 1. Ozonation of *p*-chlorophenol at varying pH. ○ pH = 2.0 — ■ pH = 4.0 — △ pH = 6.0 — ◇ pH = 8.0. [*p*-chlorophenol]$_o$ = 1.0×10^{-3} mol dm^{-3} — $T = 25.0$°C — Ionic strength = 0.1 mol dm^{-3}.

higher the concentration of phenate-like form, higher is the reactivity. Further increases of the pH do not seem to have any influence on the system reactivity, probably because of the occurrence of mass-transfer limitations between gas and liquid phase. That is, at pH higher than 6.0 the rate of ozone attack to the organic substrate becomes too high and the transfer of ozone from the gas to the liquid phase is the rate determining step.

In Figs. 2 and 3 the concentration profiles of the substrate and chlorides are shown for ozonation experiments in the range $2.0 \leq pH \leq 8.0$. The diagrams indicate for each investigated pH that when *p*-chlorophenol disappears the chloride yields are far from the unity thus suggesting the presence in the reacting solution of not analyzed chlorine-con-taining intermediates.

A complete abatement of the investigated pollutant is observed in all the experiments when approximately two moles of ozone per mole of substrate are consumed (2.5 for experiments at pH = 5.0) (Table 1). Therefore, the formation of unsaturated, partially oxidized intermediates can be inferred.

After the disappearance of *p*-chlorophenol, the further admittance of ozone to the reactor results in the increase of the chloride concentration through the successive
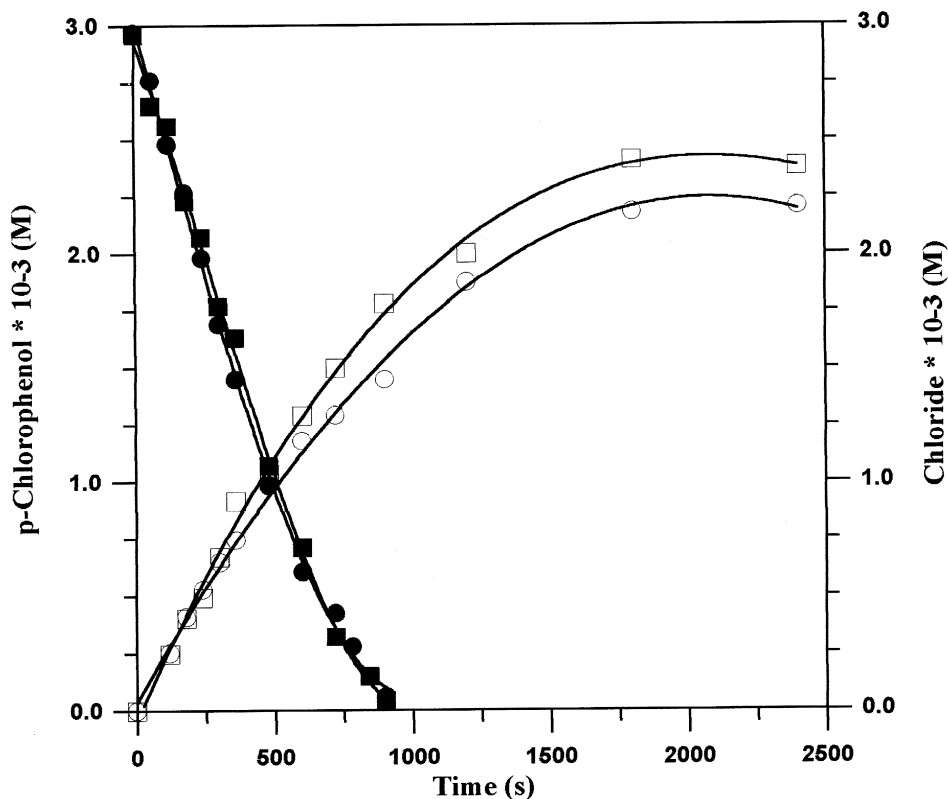

Fig. 2. Ozonation of *p*-chlorophenol. $T = 25°C$ — Ionic strength = 0.1 mol dm^{-3}. pH = 2.0, ■ *p*-chlorophe-nol, □ Cl$^-$; pH = 4.0, ● *p*-chlorophenol, ○ Cl$^-$.
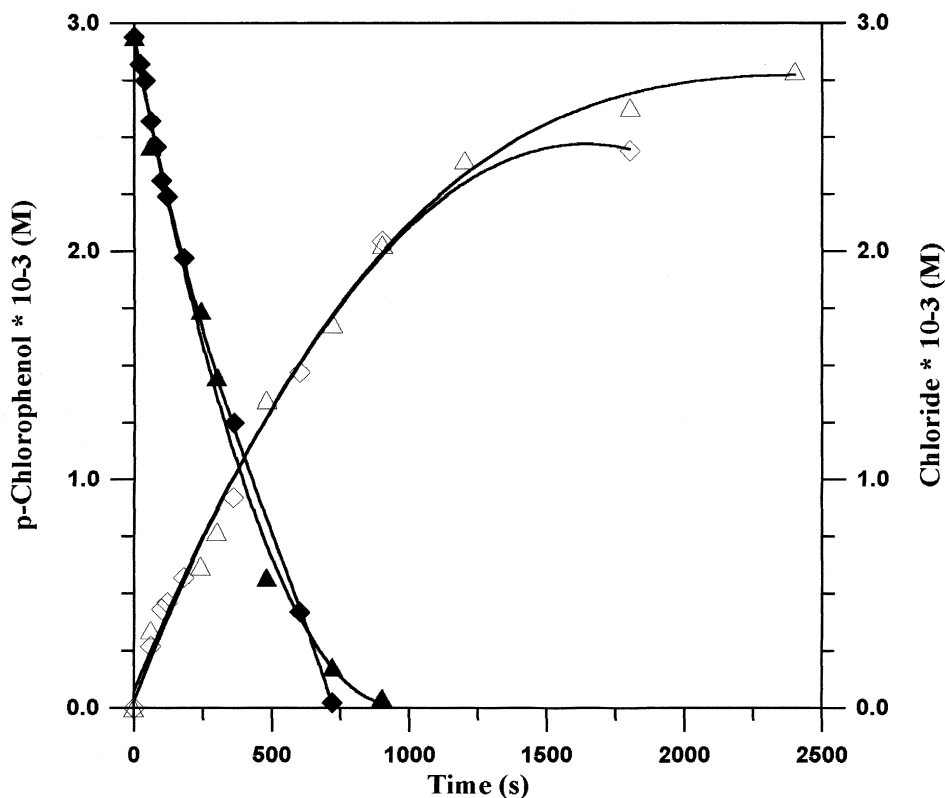
Fig. 3. Ozonation of p-chlorophenol. $T = 25°C$ — Ionic strength $= 0.1$ mol dm^{-3}. pH = 6.0, ▲ p-chlorophenol, △ Cl$^-$; pH = 8.0, ◆ p-chlorophenol, ◇ Cl$^-$.

oxidation of chlorine-containing intermediate compounds, although for the investigated reaction times, the chloride yields remain at values less than 1.0. This result can be probably ascribed to a low reactivity of chlorine-containing intermediates which could be completely destroyed only at very long reaction times. One of these compounds was detected and identified (Table 2) in the reacting solution by means of GC-MS analysis.
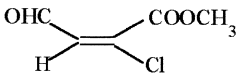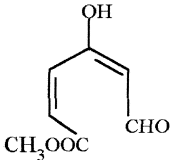
Table 1
Molar consumption ratio for ozonation of p-chlorophenol at different pH. $T = 25.0°C$ — $I = 0.1$ mol dm^{-3}

pH	p-Chlorophenol conversion (%)	Molar ratio consumption $(\Delta O_3)/(\Delta p\text{-Chlorophenol})$
2.0	95.6	2.1
3.0	83.5	2.2
4.0	93.3	2.1
5.0	95.1	2.5
6.0	88.0	1.8

Table 2
Derivatized by-products of ozonation of *p*-chlorophenol identified by means GC-MS instrumentation

	m/e
OHC—CH=CCl—COOCH$_3$ (H on left carbon)	148, 119, 88, 69, 59
(ring structure with OH, CH$_3$OOC, CHO)	156, 141, 127, 113, 85, 59

In Fig. 4 the distribution of identified intermediates and products is reported against the time along with the concentration profile of the substrate. It is evident that reported compounds account only partially for the converted *p*-chlorophenol and that less than 20% of carbon atoms are converted to CO_2.

When the activation of the radical mechanism is prevented, ozone attacks the substrate and the intermediates only with an electrophilic mechanism. Possible pathways through which the oxidation process develops are thus described in Scheme 1.

C_2 indicates two carbon atom compounds such as glyoxal and glyoxalic acid. As indicated in Table 2, compounds (A) and (B) were actually found in the reacting mixture.

Moreover, it can be observed that the compound (A) is characterized by a structure which is deactivated with respect to the electrophilic ozone attack due to the presence of electron withdrawing groups. When a compound like this is formed, it accumulates in the solution since its reactivity towards ozone is low, thus delaying the release of chloride ions. The formation of formic acid can be easily accounted for, according to the literature [13], by supposing that an *anomalous ozonation mechanism* is partially operating (Scheme 2):

4. Kinetic modeling

Experimental data were analyzed by means of proper kinetic models, which had been developed by coupling fluid dynamic and chemical sub-models. As it is generally known the oxidation processes develop in a gas–liquid reactor according to different regimes of absorption with reaction. With the exception of the diffusional regime, in all the other
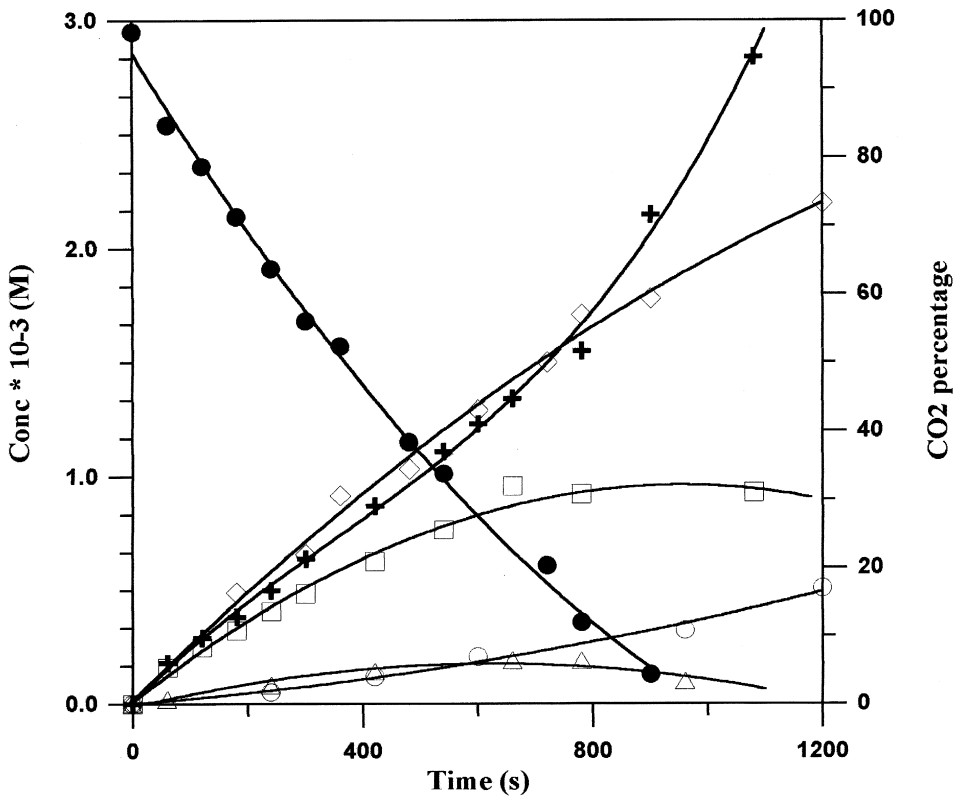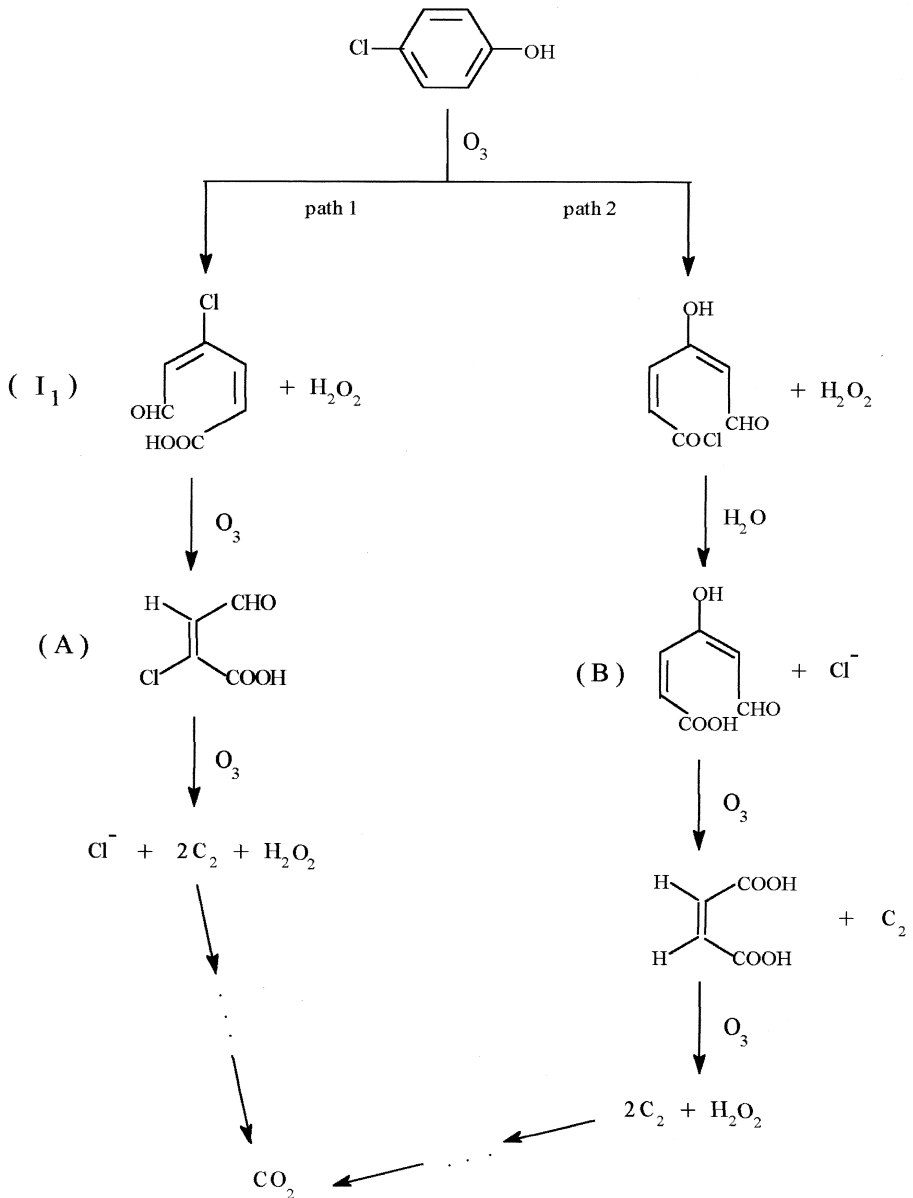
Fig. 4. Ozonation of *p*-chlorophenol and chemical intermediates at pH = 2.0, [*p*-chlorophenol]$_o$ = 3.0×10^{-3} mol dm^{-3} — T = 25.0°C — Ionic strength = 0.1 mol dm^{-3}. ● *p*-chlorophenol — ■ glyoxalic acid — △ maleic acid — ◇ chloride — + formic acid — ○ CO$_2$.

cases [14] the partial sensitivities of the rate of reaction with respect to kinetic parameters, $(\mathrm{d}R)/(\mathrm{d}K_i)$, are not negligible, thus enabling the best estimation of unknown parameters through the adoption of some optimization techniques [15]. Suitable fluid dynamic sub-models have been previously reported for the kinetic (slow and fast) [16] and the quasi-diffusional regime [17] for the ozonation processes of organic compounds. For each investigated chemical system a proper chemical sub-model should also be developed, by adopting a suitable reaction network.

Hoigné and Bader [9] reported a kinetic constant for *p*-chlorophenol between 6.37×10^2 dm^3 mol^{-1} s^{-1} and 3.40×10^7 dm^3 mol^{-1} s^{-1} in the pH range 2.0–6.0. To assess the relevant regime of absorption with reaction, the dimensionless Hatta's number, the ratio between characteristic reaction time and diffusion time, is generally used:

$$\mathrm{Ha} = \sqrt{\frac{D_{O_3}\, z\, k\, C_{\mathrm{In}0}}{\left(k_{\mathrm{L}}^0\right)^2}} \qquad (1)$$

Cl——⟨benzene⟩——OH

O_3

path 1   path 2

(I_1) Cl / OHC / HOOC ring $+ H_2O_2$ OH / CHO / COCl ring $+ H_2O_2$

O_3 H_2O

(A) H, CHO, Cl, COOH (B) OH / COOH / CHO ring $+ Cl^-$

O_3 O_3

$Cl^- + 2C_2 + H_2O_2$ H, COOH, H, COOH $+ C_2$

O_3

$2C_2 + H_2O_2$

CO_2

Scheme 1.

In a previous paper [17] it has been demonstrated that the ozonation processes in the same reactor develop under (slow/fast) kinetic regimes for Ha < 2.0, whereas for higher values of Ha (up to 25) the quasi-diffusional regime is established.
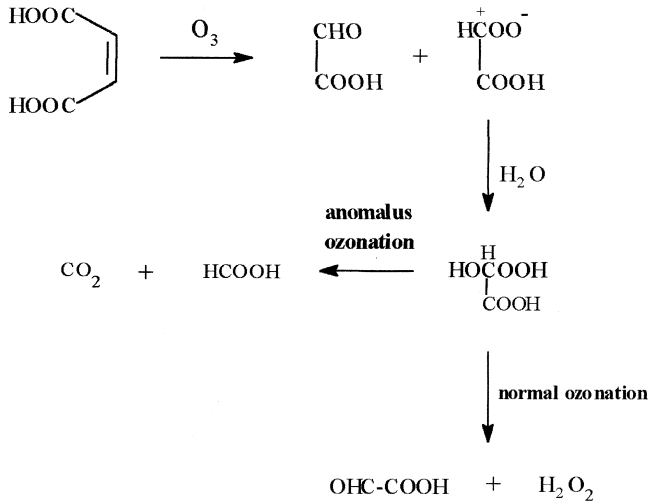
Scheme 2.

For p-chlorophenol ozonation, by taking into account the ozone diffusivity and the mass-transfer coefficient from the literature [18,19], Hoigné and Bader's data for k and a theoretical value of 3.0 for z, Ha numbers higher than 2.0 were obtained.

Therefore, it was assumed that the ozonation of p-chlorophenol developed in a quasi-diffusional regime of absorption with reaction. In this case an overall reaction:

$$p\text{-chlorophenol} + zO_3 \overset{k}{\rightarrow} \text{Products}$$
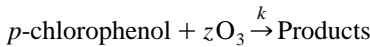
was adopted to describe the ozone attack to the substrate, where z, the stoichiometric coefficient, accounts also for ozone consumed by the intermediates. The complete model was thus developed by writing the differential mass balance equations for ozone in the three phases (bubble, $[O_3]_B$ and freeboard, $[O_3]_F$), each considered as a well-mixed stirred reactor and the substrate:

$$\frac{d[O_3]_B}{dt} = \frac{Q}{V_B}\left([O_3]_{\text{in}} - [O_3]_B\right) - \frac{k_L^o a [O_3]_B \alpha E}{V_B} V_L \tag{2}$$

$$\frac{d[O_3]_F}{dt} = \frac{Q}{V_F}\left([O_3]_B - [O_3]_F\right) \tag{3}$$

$$\frac{d[\text{CHP}]}{dt} = -\frac{k_L^o a [O_3]_B \alpha E}{z} \tag{4}$$

and by neglecting the rate of the spontaneous decomposition of ozone.

The Enhancement factor E was calculated through the following formulas:

$$E \approx \sqrt{1 + \text{Ha}^2} \tag{5}$$

This model was used to estimate the best values for k and z once the overall volumetric physical mass-transfer coefficient $k_L°a$ and Ostwald coefficient α had been evaluated for the experimental conditions of interest. In a previous paper the influence of ionic strength, pH and temperature upon α values had been investigated [20].

''Calibration'' runs, in which a substrate with known kinetic constant and z coefficient (fumaric acid, $k_{fum} = 6.0 \times 10^3$ dm^3 mol^{-1} s^{-1} at pH = 2.30, $z = 1.0$ [9]) was ozonised in the same reactor and experimental conditions as p-chlorophenol, were performed to estimate suitable values for $k_L°a$. In Fig. 5 the results obtained at stirring speed of 380 rpm and at varying ionic strength are shown.

As expected according to Hassan and Robinson's [21] findings the overall volumetric mass-transfer coefficient $k_L°a$ increases with increasing total ionic strength (largely due to an increase in $k_L°$).

The data collected during p-chlorophenol ozonation runs at pH between 2.0 and 6.0 were thus modeled by supposing that $z = a =$ constant in the time range $0 < t < t_M$. The time t_M bounds the domain of validity of the model since for $t > t_M$ the hypothesis of quasi-diffusional regime fails. The t_M value for each run were chosen by minimising the
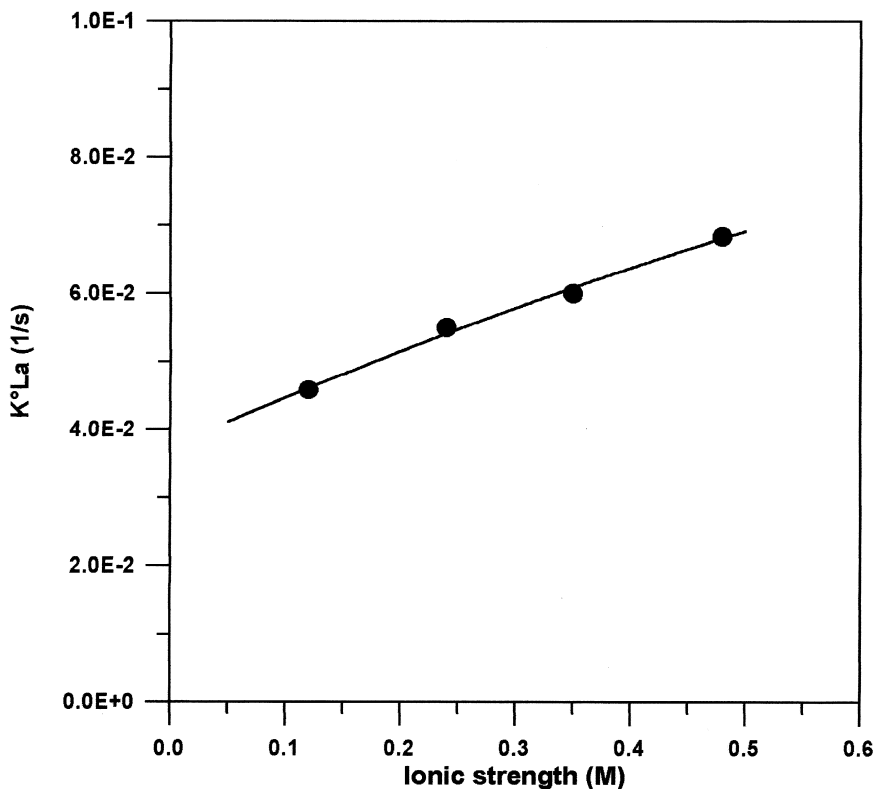

Fig. 5. Influence of ionic strength on $k_L°a$ during ozonation of fumaric acid. pH = 2.30 — $T = 25.0°C$ — Stirrer speed = 380 rpm.

standard deviation for ozone in the freeboard thus considering the overall ozone consumption as the most reliable and significant experimental information [18]. In Fig. 6 an example of fitting between calculated and experimental results is shown.

In Table 3 the best estimated kinetic constants and the values of *a* are reported along with percentage standard deviations for *p*-chlorophenol and ozone in the freeboard. The data in this table indicate that for $2.0 \leq pH \leq 6.0$ kinetic constants are estimated with a good accuracy and consistent values of parameter *a* are obtained in the different runs.

It is noteworthy to observe that a re-computation of Hatta's number with the data of *k* and *z* actually found (Table 3), for pH 2.0 and 3.0, gives values slightly lower than 2.0, although the agreement of estimated constants with the literature data and obtained standard deviations are rather satisfactory. This indicates that some uncertainties exist for Hatta's number value bounding the transition from fast kinetic to quasi-diffusional regime.

Higher values of percentage standard deviations are obtained at pH 5.0 and 6.0 probably due either to some model inadequacies when the system reactivity becomes too
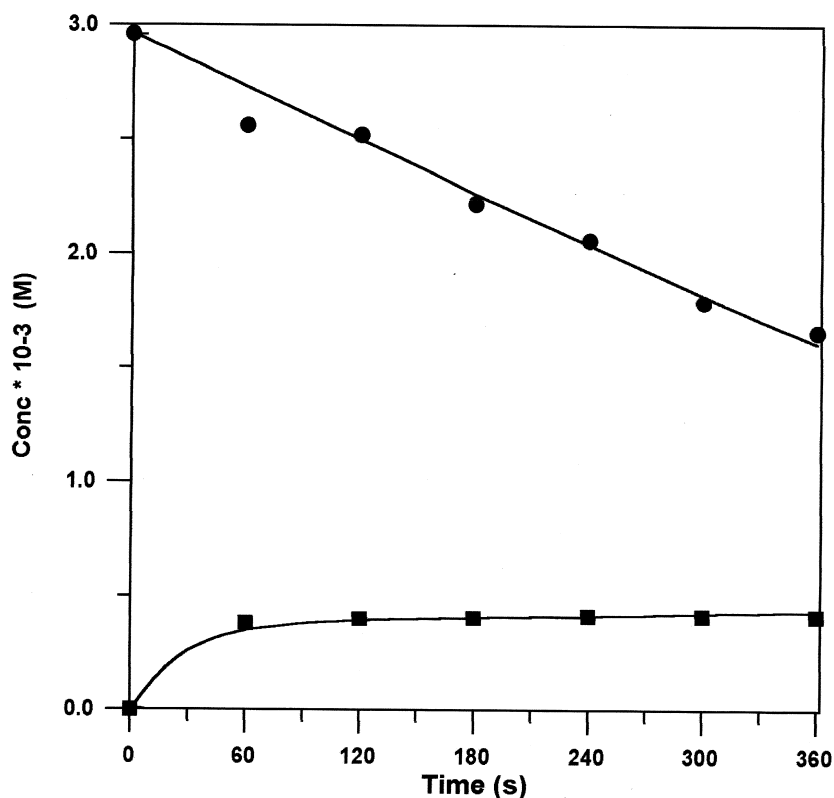

Fig. 6. Comparison between calculated and experimental results at pH = 3.0. $T = 25°C$ — $I = 0.1$ mol dm^{-3} in presence of *t*-BuOH, ● *p*-chlorophenol, ■ ozone in the freeboard.

Table 3
Kinetic parameters obtained from experimental runs at different pH values. $T = 25.0°C$, $I = 0.1$ mol dm^{-3}

pH	2.0[a]	3.0[a]	4.0[b]	4.5[b]	5.0[b]	6.0[b]
k (dm^3 mol^{-1} s^{-1})	$8.91 \times 10^2 \pm$ 1.01×10^2	$8.34 \times 10^2 \pm$ 2.18×10^2	$4.28 \times 10^3 \pm$ 5.92×10^2	$1.80 \times 10^4 \pm$ 2.83×10^3	$5.89 \times 10^4 \pm$ 9.29×10^3	$5.50 \times 10^5 \pm$ 1.45×10^4
a	$1.93 \pm$ 4.95×10^{-2}	$1.94 \pm$ 1.10×10^{-1}	$2.12 \pm$ 4.41×10^{-2}	$1.96 \pm$ 4.07×10^{-2}	$2.31 \pm$ 3.17×10^{-2}	$2.23 \pm$ 8.10×10^{-2}
% σ_{CHP}	2.69	3.99	3.15	4.40	7.65×10^{-1}	8.05
% $\sigma_{O_3 freeb}$	5.59	4.53	2.50	4.93	14.35	12.21

[a] [p-chlorophenol]$_o$ = 3.0×10^{-3} mol dm^{-3}.
[b] [p-chlorophenol]$_o$ = 1.0×10^{-3} mol dm^{-3}.

high [17] or to the difficulty to completely suppress the radical ozonation mechanism by means of tert-butyl alcohol addition.
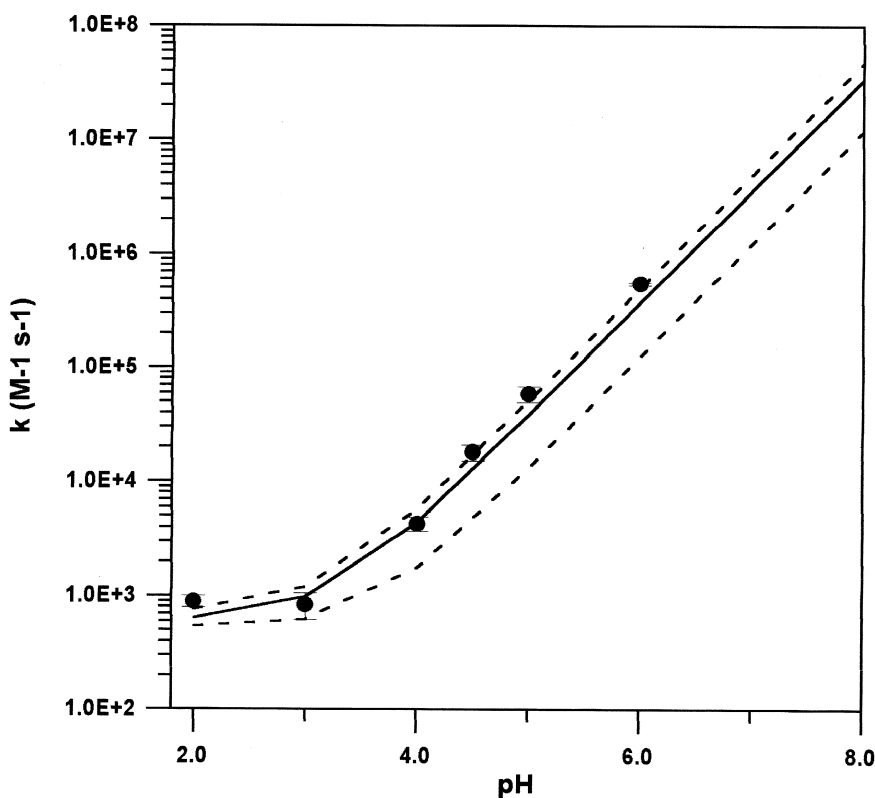

Fig. 7. Rate kinetic constants of p-chlorophenol ozonation continuous line: literature data from Hoigné and Bader [9], dashed lines: confidence zone for Hoigné and Bader's data full circles: present work.

The mean value found for $z = a \approx 2.0$ suggests that the ozonation of p-chlorophenol can be described by means of the following simplified scheme at least for reaction times $t < t_{\mathrm{M}}$:

$$p\text{-chlorophenol} + O_3 \xrightarrow{k} I_i \underset{\text{fast}}{\overset{O_3}{\rightarrow}} \text{Product}$$
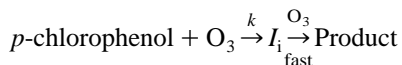
In Fig. 7 the comparison of the values found at different pH for k in the present work with those found by Hoigné and Bader is shown. Continuous and dashed lines have been calculated according to Hoigné's findings [9] by means of the following equation:

$$k = \frac{k_{\mathrm{PH}}}{\left(1 + \dfrac{K_{\mathrm{eq}}}{[\mathrm{H}^+]}\right)} + \frac{k_{\mathrm{P}-}\dfrac{K_{\mathrm{eq}}}{[\mathrm{H}^+]}}{\left(1 + \dfrac{K_{\mathrm{eq}}}{[\mathrm{H}^+]}\right)} \tag{6}$$

where k_{PH} and $k_{\mathrm{P}-}$ are respectively the kinetic constants for phenol-like and phenate-like forms.

Data shown in this figure indicate a good agreement between the results of the present investigation and those reported by Hoigné and Bader.

5. Conclusion

The ozonation of p-chlorophenol in aqueous solution was studied in the range 2.0–8.0, in the presence of $tert$-butyl alcohol which prevents the activation of the radical mechanism of oxidation. A partial chlorine release was observed during the ozonation runs. GC-MS analysis indicated the presence in the reacting mixture of at least one chlorine-containing unsaturated intermediate. As previously found for phenol, the pH of the solution strongly influences the substrate reactivity.

A proper mathematical model was built by considering that the oxidation process develops in a quasi-diffusional regime of absorption with reaction. The adoption of this model allowed the estimation of kinetic constant values in good agreement with those reported by others.

Nomenclature

C_{In0}	initial concentration of p-chlorophenol, mol dm^{-3}
D_{O_3}	diffusivity of ozone in water, dm^2 s^{-1}
E	Enhancement factor, defined by Eq. (5), dimensionless
H_{a}	Hatta number, defined by Eq. (1), dimensionless
k	rate constant of the p-chlorophenol ozonation, dm^3 mol^{-1} s^{-1}
K_{eq}	acid–base equilibrium constant for p-chlorophenol, mol dm^{-3}
k_{L}°	gas–liquid phase mass transfer coefficient without chemical reaction, dm s^{-1}
$k_{\mathrm{L}}^{\circ}a$	gas–liquid phase volumetric of mass transfer coefficient without chemical reaction, s^{-1}
I	ionic strength, mol dm^{-3}

$[O_3]_B$	ozone bubbles concentration, mol dm^{-3}
$[O_3]_F$	ozone freeboard concentration, mol dm^{-3}
$[O_3]_{in}$	initial ozone concentration in the gas phase, mol dm^{-3}
Q	gas flow rate, dm^3 s^{-1}
R	reaction rate, mol dm^{-3} s^{-1}
t	reaction time, s
t_M	maximum reaction time of validity of the model for a single run, s
V_B	bubbles volume, dm^3
V_F	freeboard volume, dm^3
V_L	reaction volume, dm^3
z	stoichiometric reaction coefficient, dimensionless

Greek Letters

α	Ostwald coefficient, dimensionless
σ	standard deviation, %

Acknowledgements

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