Chemical Engineering Journal 146 (2009) 486–497

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A reaction kinetic model for ozone decomposition in aqueous media valid for neutral and acidic pH

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ARTICLE INFO

Article history:
Received 26 May 2008
Received in revised form
28 September 2008
Accepted 4 November 2008

Keywords:
Ozone
Thermal decomposition
Semi-empirical kinetic model
Acidic and neutral conditions

ABSTRACT

A kinetic scheme for ozone decomposition in aqueous media has been developed. It can be applied for an extended range of pHs from acidic to neutral operating conditions. All experiments were made in a homogeneous medium under an assured kinetic controlling regime. Under no circumstances, a headspace existed in the reactor volume. The starting point of the reaction was always under the prerequisite of a true state of initial equilibrium conditions for the mixture water–ozone–oxygen. The model, that is not intended to be a true reaction mechanism, was derived from the 18 reaction steps mechanism proposed by Bühler et al. [R.E. Bühler, J. Staehelin, J. Hoigné, Ozone decomposition in water studied by pulse radiolysis. 1. HO_2/O_2^- and HO_3/O_3^- as intermediates, J. Phys. Chem. 88 (1984) 2560–2564] and Staehelin et al. [J. Staehelin, R.E. Bühler, J. Hoigné, Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO_4 as chain intermediates, J. Phys. Chem. 88 (1984) 5999–6004]. Most of the kinetic constants are known, but unfortunately they have not been obtained at the same pH (variations from 0.9 to almost 13 exist) and in one particular case was the result of a parametric estimation resorting to assumptions about the value of four other unknown constants in the proposed reaction sequence. With an accurate phenomenological modification represented by an analytical expression, a function of pH was introduced in what was found to be the most critical constant of the previously mentioned mechanism. The resulting set of reactions steps reproduces with very good agreement experiments made at pH 3, 4.8 and 6.3. These results should be useful to be applied as background information to analyze the use of ozone to degrading chlorinated organic compounds that render reaction by products (HCl), which reduce the pH of the reacting medium along the reaction evolution. Thus, the ultimate objective of this work is to derive a working and practical reaction sequence valid under these variable operating conditions.

1. Introduction

Ozone is considered to be an attractive alternative to chlorine for water and wastewater disinfection and for oxidation of various organic and inorganic contaminants. Additionally, it also can be used in combination with other remediation technologies to treat rather complex mixtures of wastewaters.

Decomposition of ozone in aqueous solution plays a very important role in the application of ozonation processes and has been studied for several decades. In spite of its high instability and faster oxidation capabilities, the decomposition mechanism of ozone is considered to be very complex and still not totally unveiled. Moreover, using ozone in the presence of other compounds, and even in the occurrence of small amounts of impurities, its decay in aqueous media is affected by a very large number of factors ([3] and literature cited therein). This work provides a revision of most of the research information available on ozonation reactions and processes up to the year 2002. This reference exempts us from a larger introduction on the subject. In a review of the literature on the kinetics of ozone decomposition, the most common observation is the reported disagreement among different research groups as to the reaction order of the decomposition reaction in very simplified kinetic expressions and the magnitude of the reaction rate constants in both, simplified and detailed mechanisms [3–6].

When studding ozonation reactions in aqueous solutions a distinction can be made concerning two main operating conditions: (i) to proceed in a homogeneous medium with ozone concentration never surpassing the saturation limit and avoiding the existence of a gaseous headspace and (ii) to undertake the reaction under heterogeneous conditions where at least two phases coexist and mass transfer problems constitute a significant part of the problem to tackle. This work was performed ensuring that the employed pro-

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doi:10.1016/j.cej.2008.11.001

Table 1
Mechanism A [1,2]. Kinetic scheme (pH ≅ acid to neutral).

Reaction	Kinetic constant	Reference
(1) $O_3 + OH^- \rightarrow HO_2^- + O_2$	$k_1 = 7 \times 10^4\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(2) $O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$	$k_2 = 2.2 \times 10^9\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(3) $HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^+$	$k_3 = 7.9 \times 10^5\ s^{-1}$	Westerhoff et al. [8]
(4) $O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$	$k_4 = 5 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$	Westerhoff et al. [8]
(5) $O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$	$k_5 = (1.6 \pm 0.2) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Sehested et al. [14]
(6) $O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet}$	$k_6 = (5.2 \pm 0.6) \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$	Bühler et al. [1]
(7) $HO_3^{\bullet} \rightarrow O_3^{-\bullet} + H^+$	$k_7 = (3.7 \pm 0.3) \times 10^4\ s^{-1}$	Bühler et al. [1]
(8) $HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2$	$k_8 = (1.009 \pm 0.06) \times 10^8\ cm^3\ mol^{-1}\ s^{-1}$	Bühler et al. [1]
(9) $O_3 + HO^{\bullet} \rightarrow HO_4^{\bullet}$	$k_9 = 2 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Staehelin et al. [2]
(10) $HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2$	$k_{10} = (2.8 \pm 0.3) \times 10^7\ cm^3\ mol^{-1}\ s^{-1}$	Staehelin et al. [2]
(11) $HO_2^- + H^+ \rightarrow H_2O_2$	$k_{11} = 5 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$	Westerhoff et al. [8]
(12) $H_2O_2 \rightarrow HO_2^- + H^+$	$k_{12} = 0.125\ s^{-1}$	Westerhoff et al. [8]
(13) $HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3$	$k_{13} = 5 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Staehelin et al. [2]
(14) $HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_2 + O_3$	$k_{14} = 5 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Staehelin et al. [2]
(15) $HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$	$k_{15} = 2.7 \times 10^{10}\ cm^3\ mol^{-1}\ s^{-1}$	Christensen et al. [15]
(16) $HO^{\bullet} + HO_2^- \rightarrow HO_2^{\bullet} + OH^-$	$k_{16} = 7.5 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Christensen et al. [15]
(17) $HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$	$k_{17} = 5.2 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Buxton et al. [16]
(18) $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$k_{18} = 8.3 \times 10^8\ cm^3\ mol^{-1}\ s^{-1}$	Bielski et al. [23]

Step no.	Employed pH in providing the data	Employed T (K) in providing the data	Observations
Mechanisms A (complement)			
1	11.85	293	Directly measured or without significant assumptions
2	12.98	293	Directly measured or without significant assumptions
3	7.5	296	Used in several reactions to verify its validity
4	7.5	296	Used in several reactions to verify its validity
5	9–10.3	Not specified	Directly measured or without significant assumptions
6	4	294	Directly measured or without significant assumptions
7	6.3–7.9	294	Directly measured or without significant assumptions
8	6.3–7.9	294	Directly measured or without significant assumptions
9	6.3–7.3	294	By parameter estimation with assumptions about steps 10, 13 and 14
10	6.3–7.3	294	Assumed with reference to similar reactions
11	7.5	296	Used in several reactions to verify its validity
12		296	Used in several reactions to verify its validity
13	6.3–7.3	294	Assumed with reference to similar reactions
14	6.3–7.3	294	Assumed with reference to similar reactions
15	7.8	293	Directly measured or without significant assumptions
16	7.8	293	Directly measured or without significant assumptions
17	7	294	Directly measured or without significant assumptions
18	0.9–1.7	296	Measured a this pH to make negligible other mechanism's reactions

Some of the constants were published without the confidence interval. Shading values indicate the largest differences in pH ranges.

cedure permanently kept the system within the boundaries of the first case. The main reason for this choice is that its objective was to develop an applied kinetic study and interferences with extraneous difficulties that could disguise the desired purpose were specifically avoided.

The stability of dissolved ozone in water has been found to be readily affected by ozone concentration, pH, ultraviolet light, and the presence of inhibitors or many other different forms of radical scavengers [3,7–9].

Since ozone is unstable in aqueous solution, its effectiveness as a disinfectant depends upon the rate at which it decomposes. Considering its behavior as a prospective oxidant, ozone can react via a direct reaction pathway involving molecular ozone or by an indirect route involving various highly reactive intermediates that arise from its decomposition [3]. Therefore, to be able to design an efficient ozonation system, it is important to determine a working equation for the kinetics of ozone decomposition including, as much as possible, the main variables affecting this rate. pH has been

Table 2
Mechanism B [9]. Kinetic scheme (pH ≅ basic).

Reaction	Kinetic constant	Reference
(1) $O_3 + OH^- \rightarrow HO_2^- + O_2$	$k_1 = 7 \times 10^4\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(2) $O_3 + HO_2^- \rightarrow HO_2^\bullet + O_3^{\bullet -}$	$k_2 = 2.2 \times 10^9\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(3) $HO_2^\bullet \rightarrow O_2^{\bullet -} + H^+$	$k_3 = 7.9 \times 10^5\ s^{-1}$	Westerhoff et al. [8]
(4) $O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$	$k_4 = 5 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$	Westerhoff et al. [8]
(5) $O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$	$k_5 = (1.6 \pm 0.2) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Sehested et al. [14]
(6) $O_3^{\bullet -} + H_2O \rightarrow HO^\bullet + O_2 + OH^-$	$k_6 = 2\text{–}3 \times 10^4\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(7) $O_3^{\bullet -} + HO^\bullet \rightarrow HO_2^\bullet + O_2^{\bullet -}$	$k_7 = 6 \times 10^{12}\ s^{-1}$	Tomiyasu et al. [9]
(8) $HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2$	$k_8 = 3 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(9) $HO_2^- + H^+ \rightarrow H_2O_2$	$k_9 = 5 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$	Westerhoff et al. [8]
(10) $H_2O_2 \rightarrow HO_2^- + H^+$	$k_{10} = 0.125\ s^{-1}$	Westerhoff et al. [8]
(11) $O_3^{\bullet -} + HO^\bullet \rightarrow O_3 + OH^-$	$k_{11} = 2.5 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$	Tomiyasu et al. [9]
(12) $HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$	$k_{12} = 2.7 \times 10^{10}\ cm^3\ mol^{-1}\ s^{-1}$	Christensen et al. [15]
(13) $HO^\bullet + HO_2^- \rightarrow HO_2^\bullet + OH^-$	$k_{13} = 7.5 \times\ cm^3\ mol^{-1}\ s^{-1}$	Christensen et al. [15]

Some of the constants were published without the confidence interval.

chosen to be the first influencing agent for this initial study. Considering possible applications related to chlorinated compounds, acidic conditions have been adopted to investigate the first significant variable. It should be noted that the ultimate objective of this work must not be considered the proposal of a complete set of new kinetic constants, nor of a new reaction mechanism. The maximum that can be expected from this point of view is the confirmation of the usefulness of some of the reaction sequences proposed in the literature [1,2,9]. Conversely, it should be regarded as a semi-empirical modification of one or more kinetic constants of accepted reaction schemes, searching for a precise functionality of the result with pH under acidic conditions (pH from 2 to 7). This development is to be used in the degradation of a particular family of chlorinated compounds that always produces an important end product (hydrochloric acid) that varies the pH during the course of the reaction.

The influence of pH on the decomposition reaction has also been the subject of several studies and again, the diversities among the different observations are notable. Gurol and Singer [4] reported a second-order reaction rate with respect to the ozone concentration, working in batch and in contact column reactors. In this case, the rate of ozone decomposition was found to be relatively insensitive to pHs below 4 and unusually low at acidic conditions. Above pH 4 the proposed model included a constant that was very dependent on the composition of the aqueous system. Garoma and Gurol [10] reported that, according to Gurol and Akata [11], the ozone photolysis was rather insensitive to pH in the range of 6–9.0. In their work on the degradation of *tert*-butyl alcohol with ozone + UV [10], they mentioned that the presence of $OH^\bullet$ radicals acted to neutralize the possibility of a decrease in the pH, by scavenging the carbon dioxide produced along the reaction, and maintaining the pH of the medium relatively stable. It should be mentioned, that in these two reports, UV radiation was used. Álvarez et al. [12] in a work concerning the effect of granular activated carbon (GAC) on the ozone decomposition suggested that pH is a variable of prime importance in ozone chemistry in aqueous solutions. In blank experiments performed between pH 3 and 9, they observed that ozone decay, interpreted in terms of first-order rate coefficients, increased with pH due to the intensification of the effect produced by the building up of $OH^\bullet$ radicals. Faria et al. [13] investigated several reaction order dependences with single kinetic expressions for ozone decomposition catalyzed by activated carbon, ending with the conclusion that, for the homogeneous decomposition of ozone, a second-order dependence provided a good representation of the experimental data, with an apparent second-order rate constant that was a strong function of the existing pH. In fact, they published a table of the type $k_{dec} = k_{dec}(pH)$; i.e. different rate constants depending upon the operating pH.

In a first stage, it seems appropriate to study ozone decomposition in the absence of inhibitors or other substances operating with similar consequences (pollutants for example), in order to progress, in successive systematic steps, to add more information to the existing literature related to the kinetics of ozone reactions in the presence of more complex mixtures. However, since the initial reaction conditions were always made under the premises of imposing true equilibrium exigencies for the mixture "water–ozone–oxygen", at this point, some of the initiators and promoters of ozone thermal decomposition were already present, an event that has to be taken into account when stating the initial condition in the solution of the proposed mathematical model.

The adopted experimental conditions could lead to the accumulation of hydrogen peroxide and its presence could modify the decomposition rates. There is not a full agreement on the effect of his second variable and measurements should be made on its concentration evolution. The details will be discussed in the section dedicated to the analysis of the experimental data.

With respect to ozone decomposition in water, complementing the information commented before for the case of ozone photolysis, there are two main, multiple-authors contributions. The predominant kinetic mechanisms proposed in the literature for ozone breakdown in pure water [1–3,9] are described in Tables 1 and 2. The principal difference between Mechanism A kinetic proposal [1–3] (known as the SBH model), and Mechanism B kinetic scheme [3–9] (known as the TFG model), is that the first proposition is said to be valid for neutral to acidic conditions while the second was developed for alkaline conditions. Thus, reactions (6–9) of

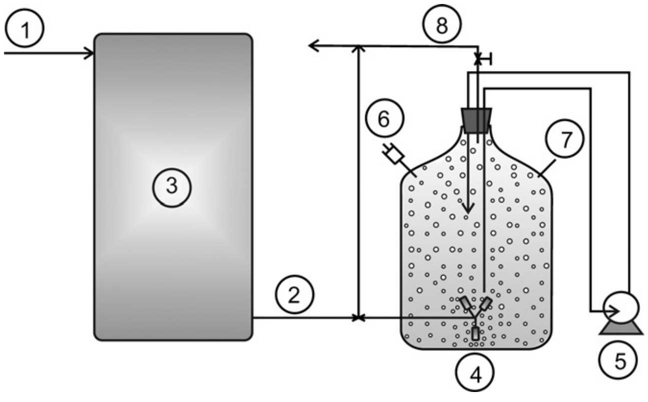

Fig. 1. Experimental setup. (1) O_2 inlet, (2) O_3/O_2 outlet, (3) ozone generator, (4) ozone solubilization reactor, (5) mixing pump, (6) sampling port, (7) complementary port and (8) O_3/O_2 purge.

the Staehelin et al. kinetic sequence [1,2] do not appear in this model, and consistent with this change, any termination reaction where the radical $HO_4^{\bullet}$ could had been participating was not included. In principle, the SBH model should be more apt for our purposes.

2. Experimental

2.1. Equipment and chemicals

The experimental setup used in this study is shown in Fig. 1 The reactor consisted of a tank made of glass, with circular cross section, and an effective volume of 11,500 cm^3. The tank filled with pure water (to avoid the existence of extraneous inhibitors or substances producing similar undesired effects) was fed from an ozone generator (Fischer 503 Ozone Generator, with a nominal input power of 350 W and an operating pressure of 0.5 atm.). The flow rate of the oxygen inlet gas to the generator was kept at 28 $cm^3\,s^{-1}$. The ozone percentage produced in the gas stream was controlled by changing the power input to the generator. To ensure good mixing, the volume contained in the reactor was continuously recirculated by means of a Masterflex pump. For the decomposition reaction, the reactor operated in a single aqueous phase, was tightly closed and did not had a gaseous head space above the water mixture to avoid the releasing of ozone from the homogeneous phase. The experimental system had a purge to maintain a constant pressure (1 atm.) during ozone solubilization.

The following reactants were used: (a) potassium indigo trisulfonate (Aldrich), (b) sodium phosphate monobasic (Anhedra, a.r., 99% plus), sulfuric acid (Cicarelli, p.a., 98% plus) and sodium hydroxide (Cicarelli, p.a., 99% plus). Oxygen gas was supplied in standard gas cylinders (99% plus).

2.2. Procedure

At the beginning of the experiences, the ozone-containing gas was purged out of the system, while the ozone generator was stabilized. For the batch experiments, the ozone-containing gas flowed to the well mixed reactor until the concentration of ozone in the aqueous phase reached equilibrium at 20 °C. At this point, the gas flow was switched off. This was the starting point of the decomposition reaction mixture. Thus, the initial condition starts from a steady-state equilibrium condition. Upon addition of Ozone, at steady state, the starting pH was 4.8. When initial reaction pH values smaller than 4 were desired, the pH was modified with dilute sulfuric acid solutions. Conversely, for pHs above 4, diluted NaOH solutions were added. Continuous sampling was made during Ozone solubilization, until constant readings were obtained. During the ozone decomposition, at defined time intervals, small aliquots of the solution were taken from a sampling port located near the top of the reactor and analyzed for the residual ozone concentration and hydrogen peroxide concentration. Simultaneously with each sampling, employing another port, an equivalent amount (equally small) of ozonated water was added to avoid the formation of a head space that would subtract ozone from the aqueous solution. Experimental runs where always triplicated.

The concentration of ozone in the aqueous phase was determined by the indigo blue method [17] and pH was controlled along the reaction using an Altronix digital thermo-pH-meter, provided with an Alpha-Altronix pH electrode Model PY-41. H_2O_2 was analyzed with spectrophotometric methods at 350 nm according to Allen et al. [18] employing a Cary 100 Bio UV–vis instrument. As any method that analyzes oxidizing agents, interferences by ozone must be removed. Following reference [19] a convenient method is striping with inert gases (and even with oxygen) from 1 to 5 min. We did blank essays and coinciding with the quoted reference, even longer purging periods (10 min) did not affect the existing hydrogen peroxide concentration. Employing nitrogen at 20 °C no measurable losses of H_2O_2 were found. With 1 min of ozone stripping, 95% of its concentration was removed. In this aspect, we found a significant difference with one aspect of the proposed method in reference [19]. Not even after 5 min of striping, it was sure that all the ozone was eliminated. Thus, parallel measurements with the technique proposed in reference [17] must be made in order to ensure the total removal of ozone. The complete withdrawal of interferences is very important, because hydrogen peroxide concentrations in the reacting medium are very low. For this reason, the original technique [18] was modified in two aspects: (i) after performing all the steps of the method, samples for the spectrophotometric analysis were subjected to lesser dilution and (ii) a 10 cm long cell was used in the spectrophotometer. In this way, concentrations as low as 10^{-13} $mol\,cm^{-3}$ could be measured with accuracy. The UV light absorbance of each sample also was measured in order to have information for future work. In both measurements, a Cary 100 Bio UV/visible spectrophotometer was used.

The same experimental procedure was repeated for pH values in the range from 3 to 6.3 to observe its effect on the steady-state initial concentration of ozone and hydrogen peroxide in water at 20 °C and afterwards, study the corresponding thermal decomposition reaction. For the preparation of each experimental run, the gas flow rate, the input power to the ozone generator and the partial pressure of ozone in the gas mixture were kept constant. The pH was changed as described above. At every employed initial pH, variations during the course of the reaction were minimal.

2.3. Experimental scope

All experiments were carried out within the following range of the significant variables: (1) ozone concentration between 1.3 and 2.7×10^{-7} $mol\,cm^{-3}$, (2) initial pH values between 3 and 6.3 and (3) the operating electric current intensity of the ozone generator between 1.2 and 2.6 A.

3. The mass balance

The mass balance is a very simple set of ordinary differential equations, for a well stirred, isothermal, batch reactor.

The reaction kinetics was formulated in terms of the mass action law for all the necessary reaction steps. In what follows, the procedure is illustrated with the mechanism proposed in Table 1 for the decomposition of ozone under acidic conditions. The inclusion of all the required reaction steps restrained the possibility of reaching a reasonable simple and useful analytical expression for ozone decomposition. Then, it became necessary to resort to the solution of a system of 12 ordinary differential equations (ODE), for the reactant species present in the system. These equations are:

$$\frac{dC_{O_3}}{dt} = -k_1 C_{O_3} C_{OH^-} - k_2 C_{O_3} C_{HO_2^-} - k_5 C_{O_3} C_{O_2^{\bullet -}} - k_9 C_{O_3} C_{HO^\bullet} + 2k_{13} C^2_{HO_4^\bullet} + k_{14} C_{HO_4^\bullet} C_{HO_3^\bullet} \quad (1)$$

$$\frac{dC_{HO_2^-}}{dt} = k_1 C_{O_3} C_{OH^-} - k_2 C_{O_3} C_{HO_2^-} - k_{11} C_{HO_2^-} C_{H^+} + k_{12} C_{H_2O_2} - k_{16} C_{HO^\bullet} C_{HO_2^-} \quad (2)$$

$$\frac{\mathrm{d}C_{\mathrm{HO}_2^\bullet}}{\mathrm{d}t} = k_2 C_{\mathrm{O}_3} C_{\mathrm{HO}_2^-} - k_3 C_{\mathrm{HO}_2^\bullet} + k_4 C_{\mathrm{O}_2^{\bullet-}} C_{\mathrm{H}^+} + k_{10} C_{\mathrm{HO}_4^\bullet} + k_{15} C_{\mathrm{OH}^\bullet} C_{\mathrm{H}_2\mathrm{O}_2} + k_{16} C_{\mathrm{HO}^\bullet} C_{\mathrm{HO}_2^-} - k_{18} C^2_{\mathrm{HO}_2^\bullet} \quad (3)$$

$$\frac{\mathrm{d}C_{\mathrm{O}_3^{\bullet-}}}{\mathrm{d}t} = k_2 C_{\mathrm{O}_3} C_{\mathrm{HO}_2^-} + k_5 C_{\mathrm{O}_3} C_{\mathrm{O}_2^{\bullet-}} - k_6 C_{\mathrm{O}_3^{\bullet-}} C_{\mathrm{H}^+} + k_7 C_{\mathrm{HO}_3^\bullet} \quad (4)$$

$$\frac{\mathrm{d}C_{\mathrm{O}_2^{\bullet-}}}{\mathrm{d}t} = k_3 C_{\mathrm{HO}_2^\bullet} - k_4 C_{\mathrm{O}_2^{\bullet-}} C_{\mathrm{H}^+} - k_5 C_{\mathrm{O}_3} C_{\mathrm{O}_2^{\bullet-}} \quad (5)$$

$$\frac{\mathrm{d}C_{\mathrm{HO}_3^\bullet}}{\mathrm{d}t} = k_6 C_{\mathrm{O}_3^{\bullet-}} C_{\mathrm{H}^+} - k_7 C_{\mathrm{HO}_3^\bullet} - k_8 C_{\mathrm{HO}_3^\bullet} - k_{14} C_{\mathrm{HO}_4^\bullet} C_{\mathrm{HO}_3^\bullet} \quad (6)$$

$$\frac{\mathrm{d}C_{\mathrm{OH}^\bullet}}{\mathrm{d}t} = k_8 C_{\mathrm{HO}_3^\bullet} - k_9 C_{\mathrm{O}^3} C_{\mathrm{OH}^\bullet} - k_{15} C_{\mathrm{OH}^\bullet} C_{\mathrm{H}_2\mathrm{O}_2} - k_{16} C_{\mathrm{OH}^\bullet} C_{\mathrm{HO}_2^-} - k_{17} C^2_{\mathrm{OH}^\bullet} \quad (7)$$

$$\frac{\mathrm{d}C_{\mathrm{H}^+}}{\mathrm{d}t} = k_3 C_{\mathrm{HO}_2^\bullet} - k_4 C_{\mathrm{O}_2^{\bullet-}} C_{\mathrm{H}^+} - k_6 C_{\mathrm{O}_3^{\bullet-}} C_{\mathrm{H}^+} + k_7 C_{\mathrm{HO}_3^\bullet} - k_{11} C_{\mathrm{HO}_2^-} C_{\mathrm{H}^+} + k_{12} C_{\mathrm{H}_2\mathrm{O}_2} \quad (8)$$

$$\frac{\mathrm{d}C_{\mathrm{OH}^-}}{\mathrm{d}t} = -k_1 C_{\mathrm{O}_3} C_{\mathrm{OH}^-} + k_{16} C_{\mathrm{OH}^\bullet} C_{\mathrm{HO}_2^-} \quad (9)$$

$$\frac{\mathrm{d}C_{\mathrm{HO}_4^\bullet}}{\mathrm{d}t} = k_9 C_{\mathrm{O}_3} C_{\mathrm{OH}^\bullet} - k_{10} C_{\mathrm{HO}_4^\bullet} - k_{13} C^2_{\mathrm{HO}_4^\bullet} - k_{14} C_{\mathrm{HO}_4^\bullet} C_{\mathrm{HO}_3^\bullet} \quad (10)$$

$$\frac{\mathrm{d}C_{\mathrm{O}_2}}{\mathrm{d}t} = k_1 C_{\mathrm{O}_3} C_{\mathrm{OH}^-} + k_5 C_{\mathrm{O}_3} C_{\mathrm{O}_2^{\bullet-}} + k_8 C_{\mathrm{HO}_3^\bullet} + k_{10} C_{\mathrm{HO}_4^\bullet} + k_{14} C_{\mathrm{HO}_4^\bullet} C_{\mathrm{HO}_3^\bullet} + k_{18} C^2_{\mathrm{HO}_2^\bullet} \quad (11)$$

$$\frac{\mathrm{d}C_{\mathrm{H}_2\mathrm{O}_2}}{\mathrm{d}t} = k_{11} C_{\mathrm{HO}_2^-} C_{\mathrm{H}^+} - k_{12} C_{\mathrm{H}_2\mathrm{O}_2} + k_{13} C^2_{\mathrm{HO}_4^\bullet} + k_{14} C_{\mathrm{HO}_4^\bullet} C_{\mathrm{HO}_3^\bullet} - k_{15} C_{\mathrm{OH}^\bullet} C_{\mathrm{H}_2\mathrm{O}_2} + k_{17} C^2_{\mathrm{OH}^\bullet} + k_{18} C^2_{\mathrm{HO}_2^\bullet} \quad (12)$$

The system of 12 ODEs was solved with a four order, variable step, modified Runge-Kutta method for stiff problems, using a commercial code, and the concentration of ozone and hydrogen peroxide were calculated as a function of the reaction time. The concentration of both stable species was also measured at $t = 0$ to account for the initial conditions in Eqs. (1) and (12). The initial values of the concentrations of the reactions involving intermediate-unstable species were obtained from the data in reference [8]. The values resulting from the solution of the set of Eqs. (1)–(12) after application of the computer program did not indicate the need to modify those initial conditions. Initially, the computer program used the kinetic constants reported in Table A. The solution of these simulations can be compared with the experimental data.

4. Preliminary results

In the case of the rate constants corresponding to Mechanism A (the SBH model) compiled by reference [3] there are some limitations and weaknesses in the reported information that are worthy to discuss. (i) The known constants have been obtained in eight different research groups; (ii) not all the available kinetic constants were obtained at the same pH. In fact variations from 0.9 to 12.98 exist in the reported values (see Table 1, second part) and it has been well established that the reaction rate increases very significantly from acidic conditions to pH values up to 9–10; (iii) even if not with very significant modifications, not all the values were obtained at the same temperature; (iv) one of the kinetic constant (corresponding to step 9) was obtained by parameter estimation, assuming plausible values for the kinetic constants corresponding to steps 12 and 13 (and two more steps, not finally included among the 18 steps of Table A) based on information existing for a "similar" reaction step (step 17 in Table A); these "assumed" figures were latter on included in the above mentioned compilation of known kinetic constants as true values.

As a way of an important example of the described problems, reference [20] initially used in their work the SBH model and derived different values of the parameters. Moreover, under no circumstances they could conciliate this mechanism with the used experimental data (taken from reference [9]) a result that should not be a surprise because the employed data in the quoted reference [9] were obtained at pH between 12 and 13. Finally, in reference [20] the value of kinetic constant $k_9 = 2 \times 10^{12}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ (as listed in Table 1) was used at a pH between 12 and 13. It is very unusual that the same value had been reported before by reference [2] for pH 6.3–7.3.

Thus from the very beginning, the set of not quite compatible compiled numerical values of the kinetic constants of sequence A, known as the one most probably mechanism for alkaline to neutral operating conditions [3], cannot be thought as conclusive. This is so, because those kinetic constants have never been fully validated under identical experimental conditions regarding pH. Furthermore, never have they been published as a "single set of values" with complete information about its variations for a given confidence interval; i.e. they cannot be thought as indubitable and confirmed values to represent correctly the reaction evolution in a given pH or to be valid for the full range of pHs from acidic to neutral conditions. In fact, the authors that separately published all the original values, have never made this claim.

However, in the absence of better information, these mechanisms (models SBH and TGB) will be the starting basis for this work. Here, it is proposed to apply the models with the reported values of the reaction kinetic steps parameters to the realistic operation of a well-stirred, isothermal reactor. Thus, the experimental data will be compared with the result of solving the set of ordinary differential equations (ODE) derived from the mass balance of the reactor [for example, Eqs. (1)–(12) and its initial conditions for mechanisms A] using the existing information about the specific rate constants of the chosen reaction steps. At different pHs (under neutral and/or acidic conditions), a full agreement should be the most desired result. However, as it was discussed previously and will be shown below, this was a very optimistic approach. Hence, if this expectancy is not fulfilled, additional studies will be necessary to introduce some modifications. In this study, it was decided to resort to a phenomenological approach based on the existing information. As indicated before, the final objective is to have a workable kinetic model apt for reactions where the pH may decrease during the process, to be useful for reactor design purposes. Therefore, we need this information to develop, in a forthcoming application (in a certainly more complex mixture) the reaction that includes the spontaneous decomposition of ozone combined with the ozone degradation process of chlorinated organic compounds. This process produces hydrochloric acid that modifies the pH along the reaction. Hence, the only way to obtain a valid kinetic expression useful for this application is to be in the possession of well-characterized kinetic parameters of the thermal decomposition

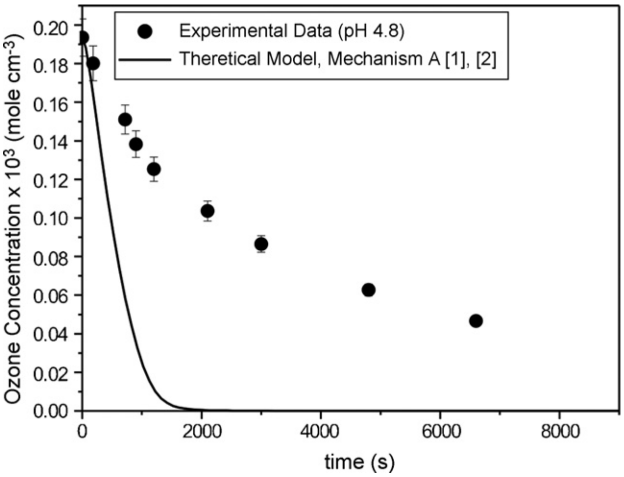

Fig. 2. The SBH model (A) versus experimental data.

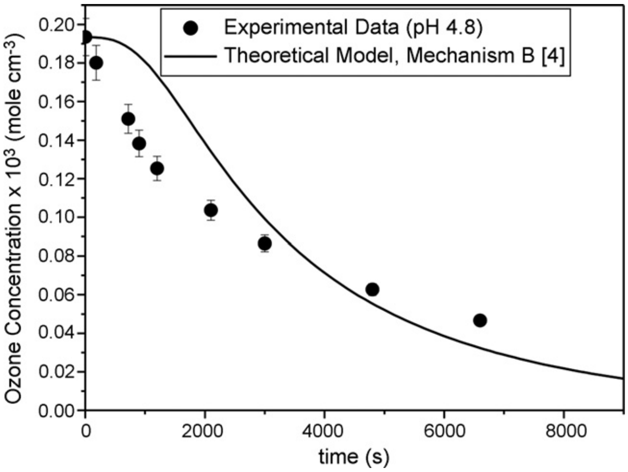

Fig. 3. The TFG model (B) versus experimental data.

of ozone at different operating pHs (in this case from neutral to acidic conditions). Consequently, if the initial trial fails, the proposed approach is to investigate the possibility of describing the reaction performance with one set of steps having one or more modified kinetic parameters from the original data, with a known functional dependence with respect to pH. In the worse circumstance, the compiled values of constants taken from published data will have resulted very good initializing conditions for the solution of the complete set of differential equations representing the complete process and estimate the corresponding new values.

4.1. Staehelin, Bühler and Hoigné kinetic scheme or the SBH model [1,2]

The reaction was carried out at pH ≅ 4.8.

With this scheme, the ozone reaction evolution is shown with a solid line in Fig. 2. Comparing these results with the experimental data, as an anticipated possibility, this set of 12 equations, solved with the compiled kinetic constants inconsistently extracted from the literature, does not represent the reaction performance at pH 4.8. Theoretical simulations differ quite significantly from experiments. One or more numerical values of the reported parameters are not compatible with these results. Needless is to say that this a corroboration of the presumption made at the beginning of this section and clearly ratified by the complete information provided in Table 2. Moreover, in most of the cases the confidence interval for the reported constants were not given in the original publications and, as indicated in the table, some of the constants were the result of assumptions made by analogy with “similar” reactions steps.

4.2. Tomiyasu–Fukutomi–Gordon kinetics scheme or the TFG model [3–9]

The reaction was carried at pH ≅ 4.8.

In spite of being a mechanism proposed for alkaline conditions, in this case the agreement is somewhat better (Fig. 3), but not fully satisfactory. However, this apparent improvement is to some extent surprising because the experimental runs (always triplicated) were made at acidic pH. The problems and limitations indicated above for the values of the employed constants are about the same.

5. Quali-quantitative study of the reported kinetic constants

This section is an intent to obtain some guidance concerning the possible ways to solve the problems described in the previous one; i.e. to search for an indication as to the best way to use the available information to reach our previously stated objectives.

5.1. Effect on the overall reaction rate, changing systematically, for each reaction step, the value of the corresponding specific reaction constant

One problem that needs to be scrutinized is related to the already mentioned difficulties concerning the consistency of the numerical values of the reported kinetic constants. It seemed important to know how much, hypothetical differences in the reported values of the specific constants, could affect the outcome of the final reaction results. This is just some sort of crude approximation, because many of the reaction steps are not independent. Thus, only a qualitative analysis can be made to know how much variation on the overall reaction rate is produced by separate and systematically changing the individual values of the kinetic constants of each of the 18 reaction steps, one order of magnitude greater and one order of magnitude smaller than the published data. The selection of the magnitude of this change is an arbitrary decision. Other modification could have been chosen as well; but for this approximation it is as good as any other. Calculated values correspond to the following equation:

$$\text{Result of the solution of the set of 12 ODE} \rightarrow \langle \mathrm{R}_{\mathrm{O}_3} \rangle_{\mathrm{V}_\mathrm{R}} = \left\langle \frac{\mathrm{d}C_{\mathrm{O}_3}}{\mathrm{d}t} \right\rangle_{\mathrm{V}_\mathrm{R}} \tag{13}$$

In Eq. (13) $\langle\cdot\rangle$ represents an average value over the whole reactor volume. For a well-stirred batch reactor, this average accurately represents the experimental measurement of the changes in the Ozone concentration, as a consequence of the proposed separate changes in each of the parameters of the reaction steps.

The results are summarized for kinetic scheme A in Table 3. Leaving aside equilibrium reaction steps, for reasons that will be apparent below, as far as this work is concerned, the small effect produced by changes in the kinetic constant of reaction R_5 in any sense and in the kinetic constant of reaction R_9 particularly when it is decreased, contrast with the significant variations in constants k_2 and k_{10} to k_{14}.

Table 3
Qualitative effect on the overall reaction rate, by changing separately each of the published values of the kinetic constants, one order of magnitude greater and one order or magnitude smaller.

Constant	Effect on the overall rate	
	One order of magnitude smaller	One order of magnitude greater
k_1	Moderate change (+)	Almost none
k_2	Moderate change (−)	Significant change (+)
k_3	Almost none	Almost none
k_4	Almost none	Almost none
k_5	Almost none	Almost none
k_6	None	None
k_7	None	None
k_8	Small change (−)	Moderate change (+)
k_9	None	Small change (+)
k_{10}	Moderate change (−)	Significant change (+)
k_{11}	Significant Change (+)	Moderate change (−)
k_{12}	Moderate change (−)	Significant change (+)
k_{13}	Significant change (+)	Small change (−)
k_{14}	Significant change (+)	Small change (−)
k_{15}	No change	No change
k_{16}	No change	No change
k_{17}	No change	No change
k_{18}	No change	No change

5.2. *Values of the individual rates of each reaction step considering the concentration changes during 8000 s of reaction evolution*

Consider what seems to be the most recognized reaction scheme and, in principle, with known limitations, valid for acidic or neutral conditions (Mechanism A). The variation of the value of each reaction step from the initial point ($t = 0$) to an arbitrarily chosen point ($t = 8000$ s) are shown in Table 4. Note that these values correspond to each step and are not represented by Eq. (13). From these values it was possible to construct Fig. 4(a), which represents the maximum value that takes each of the individual reaction steps. In this way it is clear to see that reactions R_5, R_6, R_9 and R_{11}, play an important role. At the end of the reaction, R_3, R_4, R_7, R_8, R_{10}, and R_{12} seem to have comparable values with R_5, R_6, R_9 and R_{11}, but in all these cases, the results are five order of magnitude smaller because the overall reaction is almost completed; this comparison can be seen from the graphic illustration in Fig. 4(b). It should be noted that reactions R_6 and R_{11} are equilibrium reactions with R_7 and R_{12}, respectively. Thus changes in the H^+ concentration will affect both reactions in the same way. This leaves us with mainly reactions R_5 and R_9. It is assumed that they are the two steps more apt to investigate the possible influence of the pH in the global reaction result. This working assumption does not imply that the other steps on the proposed mechanism are unimportant. It is just an initial guess to develop a phenomenological correction. However, according to Table 1 (first part) one should not be surprised if step 9 turns up to be, as far as the pH is concerned, the most influential step.

Table 4
Reaction rate variation for each of the proposed steps.

Reaction	Reaction rate: mol cm^{-3} s^{-1}		
	$t = 0$ s	$t = 8000$ s	R_{max}
R_1	3.39×10^{-15}	6.54×10^{-25}	3.39×10^{-15}
R_2	4.52×10^{-13}	1.69×10^{-21}	4.25×10^{-13}
R_3	7.90×10^{-10}	4.26×10^{-10}	1.10×10^{-9}
R_4	1.99×10^{-9}	4.26×10^{-10}	1.99×10^{-9}
R_5	3.09×10^{-6}	8.26×10^{-11}	3.09×10^{-6}
R_6	2.07×10^{-5}	1.10×10^{-10}	2.07×10^{-5}
R_7	3.70×10^{-7}	2.78×10^{-11}	3.70×10^{-7}
R_8	1.10×10^{-6}	8.26×10^{-11}	1.10×10^{-6}
R_9	3.86×10^{-6}	8.26×10^{-11}	3.86×10^{-6}
R_{10}	2.80×10^{-7}	8.26×10^{-11}	1.01×10^{-6}
R_{11}	1.99×10^{-5}	6.32×10^{-10}	1.99×10^{-5}
R_{12}	2.50×10^{-12}	6.32×10^{-10}	6.56×10^{-10}
R_{13}	5.00×10^{-14}	4.35×10^{-21}	6.53×10^{-13}
R_{14}	5.00×10^{-14}	1.11×10^{-21}	1.59×10^{-13}
R_{15}	2.70×10^{-16}	1.17×10^{-14}	3.09×10^{-14}
R_{16}	7.50×10^{-14}	4.08×10^{-19}	7.50×10^{-14}
R_{17}	5.00×10^{-14}	1.46×10^{-15}	5.00×10^{-14}
R_{18}	8.30×10^{-18}	2.41×10^{-18}	1.60×10^{-17}

Errors are the one existing in the original values of the employed kinetic constants (Table 1).

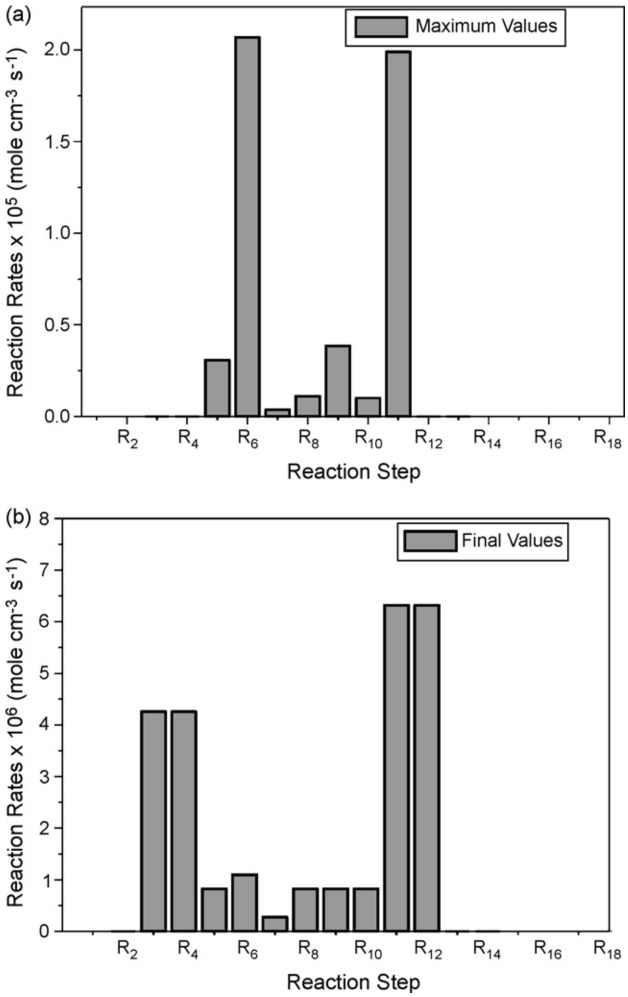

Fig. 4. (a) Relative maximum values of the 18 reaction steps of Mechanism A and (b) the same results after 8000 s of reaction time.

5.3. *The experimental time required to reach 30% conversion of ozone as a function of the reaction*
pH (from pH 3 to pH 6.3)

It is very important to note the effect that the aqueous solution pH has on the overall reaction rate. Above pH 7, due to the stated objectives of this work, the pH effect was not studied. However, this does not mean that for pHs higher than 7 changes may be negligible; this conclusion could be substantiated with the information included in Table 2. Fig. 5 shows this effect for acidic conditions. The time required to reach 30% decomposition varies from 5400 s at pH 3 to 300 s at pH 6.3. This major change is in agreement with previous observations reported by other authors mentioned in the Introduction Section. Consequently, considering the objective of

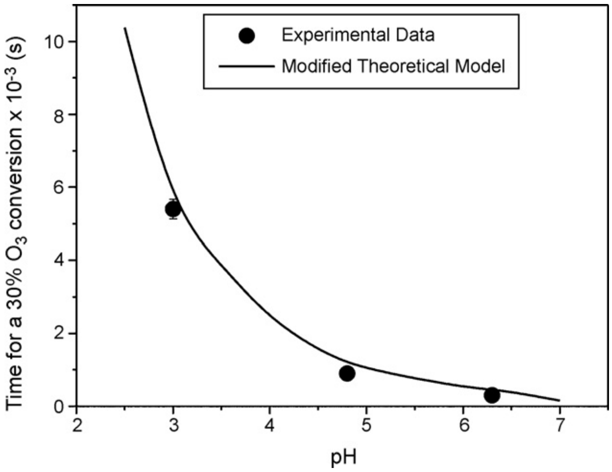

Fig. 5. Reaction time for a 30% conversion of ozone as a function of pH.

this research, it was decided to search for a function of the existing pH to correct, as an empirical – phenomenological – approximation, the effects on the most influential reaction rate constants.

5.4. The decomposition reaction of ozone

Again, an assumption is made. It is proposed to start by considering, out of the 18 steps of the reaction mechanism, the ones directly involved in the decomposition of Ozone as given by

$$\frac{dC_{O_3}}{dt} = -k_1 C_{O_3} C_{OH^-} - k_2 C_{O_3} C_{HO_2^-} - k_5 C_{O_3} C_{O_2^{\bullet -}} - k_9 C_{O_3} C_{HO^\bullet} + 2k_{13} C^2_{HO_4^\bullet} + k_{14} C_{HO_4^\bullet} C_{HO_3^\bullet} \tag{14}$$

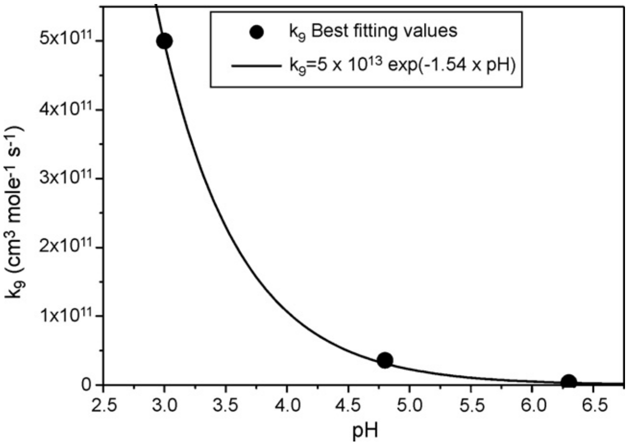

Fig. 6. Experimental representation of the variation of constant the k_9 as a function of pH.

Let us analyze the contribution made by each of these five reactions to the decomposition of ozone. The results are given in Table 5. It can be seen that at pH 4.8 and 6.3 the step corresponding to R_5 contributes to 44.35 and 96.18%, respectively, of the reaction product. At pH 3 and 4.8, the step corresponding to R_9 is responsible for 99.76 and 55.59% of the total reaction product. However, one must keep in mind that the complete reaction mechanism of 18 steps, does not represent, not even approximately, the experimental data at pH ≅ 4.8. As said before, this was an understandable outcome.

6. Effect of the reaction pH

Considering previous results it was decided to study the possibility of representing the experimental data of a set of runs performed a three different pHs, estimating new values of the rate constant k_9. With this purpose, comparing the laboratory results

Table 5
Incidence of reactions R_1, R_2, R_5, R_9, R_{13} and R_{14} on the rate of ozone decomposition as a function of pH, employing published values of the rate constants.

Reaction and pH	Rates in units of mole cm^{-3} s^{-1}			% of Total at $t = 0$
	$t = 0$ s	$t = 1000$ s	$t = 3000$ s	
$-k_1 C_{O_3} C_{OH^-}$				
3	1.35×10^{-16}	0	0	0.000035
4.8	8.53×10^{-15}	1.00×10^{-18}	0	0.001228
6.3	2.70×10^{-13}	0	0	0.002663
$-k_2 C_{O_3} C_{OH_2^-}$				
3	4.25×10^{-13}	0	0	0.1097
4.8	4.25×10^{-13}	0	0	0.0612
6.3	4.25×10^{-13}	0	0	0.004195
$-k_5 C_{O_3} C_{O_2^{\bullet -}}$				
3	4.90×10^{-13}	1.11×10^{-11}	5.92×10^{-12}	0.1266
4.8	3.08×10^{-10}	4.18×10^{-11}	0	44.345
6.3	9.74×10^{-9}	0	0	96.179
$-k_9 C_{O_3} C_{OH^\bullet}$				
3	3.86×10^{-10}	1.11×10^{-11}	5.90×10^{-12}	99.76
4.8	3.86×10^{-10}	4.18×10^{-11}	0	55.593
6.3	3.86×10^{-10}	0	0	3.8114
$-k_{13}(C_{HO_4^\bullet})^2$				
3	1.00×10^{-17}	1.56×10^{-18}	4.46×10^{-19}	0.000003
4.8	1.00×10^{-17}	2.28×10^{-17}	0	0.000001
6.3	1.00×10^{-17}	0	0	0
$-k_{14} C_{HO_3^\bullet} C_{HO_4^\bullet}$				
3	7.5×10^{-18}	1.99×10^{-19}	5.7×10^{-20}	0.000002
4.8	7.5×10^{-18}	2.91×10^{-8}	0	0.000001
6.3	7.5×10^{-18}	0	0	0

Errors are the one existing in the original values of the employed kinetic constants (Table 1).

Table 6
Incidence of reactions R_1, R_2, R_5, $R_{9,}$ R13 and R_{14} on the rate of ozone decomposition as a function of pH, employing the set of kinetic constants calculated in this work.

Reaction and pH	Rates in units of mole cm^{-3} s^{-1}			% of Total at $t = 0$
	$t = 0$ s	$t = 1000$ s	$t = 3000$ s	
$-k_1 C_{O_3} C_{OH^-}$				
3	1.35×10^{-16}	0	0	0.000014
4.8	8.53×10^{-15}	0	0	0.00271
6.3	6.00×10^{-13}	2.63×10^{-11}	5.45×10^{-12}	0.0061
$-k_2 C_{O_3} C_{OH_2^-}$				
3	4.25×10^{-13}	0	0	0.439
4.8	4.25×10^{-13}	1.00×10^{-16}	0	0.135
6.3	1.00×10^{-17}	8.80×10^{-18}	3.80×10^{-19}	0.0000001
$-k_5 C_{O_3} C_{O_2^{-\bullet}}$				
3	4.90×10^{-13}	1.08×10^{-11}	5.71×10^{-12}	0.50
4.8	3.08×10^{-10}	2.14×10^{-11}	9.50×10^{-12}	97.95
6.3	9.74×10^{-9}	2.60×10^{-11}	5.00×10^{-12}	99.98
$-k_9 C_{O_3} C_{OH^\bullet}$				
3	9.57×10^{-11}	1.08×10^{-11}	5.71×10^{-12}	99.1
4.8	6.01×10^{-12}	2.14×10^{-11}	9.49×10^{-12}	1.91
6.3	6.00×10^{-13}	2.63×10^{-11}	5.45×10^{-12}	0.00616
$-k_{13}(C_{HO_4^\bullet})^2$				
3	1.00×10^{-17}	8.80×10^{-19}	8.80×10^{-19}	0.000010
4.8	1.00×10^{-17}	5.83×10^{-18}	1.15×10^{-18}	0.000003
6.3	1.00×10^{-17}	1.48×10^{-18}	4.16×10^{-18}	0.0000001
$-k_{14} C_{HO_3^\bullet} C_{HO_4^\bullet}$				
3	7.15×10^{-18}	1.12×10^{-18}	4.80×10^{-20}	0.000008
4.8	7.15×10^{-18}	7.42×10^{-19}	1.46×10^{-19}	0.000002
6.3	7.15×10^{-18}	1.88×10^{-19}	5.30×10^{-20}	0.0000001

With the exception of k_9, errors are the one existing in the original values of the employed kinetic constants (Table 1).

with the solution of the set of 12 ODE corresponding to the mass balances, it was permitted a change in one of the values of the reported kinetic constants. Al the other values are considered now as good initializing values for our parameter estimation. Then, with a multiparameter regression program based in the Levenberg–Marquardt optimization algorithm (Levenberg [21] and Marquardt [22]) it was possible to estimate the best fitting value for k_9; i.e. k_9 was the only constant that was set totally free. All other kinetic constants were kept within the same range of figures of the results published in the literature. The following result was obtained:

Published value: $k_9 = (2.00 \pm 0.5) \times 10^{12}$ cm^3 mol^{-1} s^{-1};
Value at pH 3: $k_9 = (5 \pm 0.04) \times 10^{11}$ cm^3 mol^{-1} s^{-1} (decreased);
Value at pH 4.8: $k_9 = (3.60 \pm 0.1) \times 10^{10}$ cm^3 mol^{-1} s^{-1} (decreased);
Value at pH 6.3: $k_9 = (3.10 \pm 0.01) \times 10^{9}$ cm^3 mol^{-1} s^{-1} (decreased).

These values are reliable due to the sharp convexity observed in the obtained objective function and consequently, disguised, unobserved minima can be safely disregarded.

These last three results can be plotted as it is done in Fig. 6. The result represents the pH dependence of k_9 according to the following equation:

$$k_9 = 5 \times 10^{13}\ \exp(-1.54 \times \text{pH}) \quad \text{with}\, R^2 = 0.999 \tag{15}$$

It is possible to repeat now a table equivalent to Table 5, but employing this new set of parameters. Table 6 shows the results.

The very significant effect of the reaction pH on the decomposition rate of ozone is clearly shown in the simulation results shown in Fig. 7. These results corroborated the reported results in references [12,13].

Employing only this functionality of k_9 with the pH, all runs were very well represented, resorting to only one modification in one of the kinetic constants of the 18 steps kinetic scheme.

Fig. 8(a)–(c) give three typical examples of the goodness of this semi-empirical kinetic scheme.

Fig. 9 shows a compendium of all the experimental points employing this approximation. It can be seen that the agreement between the experimental data and the values obtained with computed simulations of the model, resulting from including the pH dependence on the kinetic constant k_9 is very good. Once more, it should be emphasized that this result is not a reaction mechanisms in the strict sense employed usually in mechanistic modeling, but a very useful result for further applications of Ozone in decontamination of pollutants having reaction products that affect the aqueous environment pH during the reaction evolution. It is also clear, that the presence of other typical scavengers reported in the literate [3] could make necessary to add more steps to the reaction scheme.

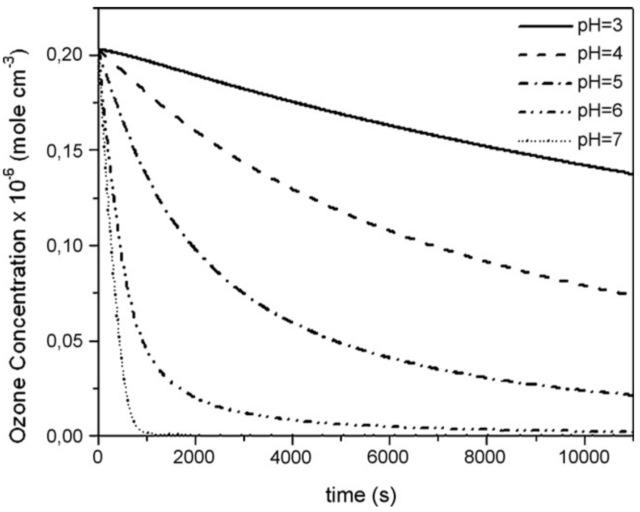

Fig. 7. Sensibility of the ozone decomposition rate. pH is the parameter.

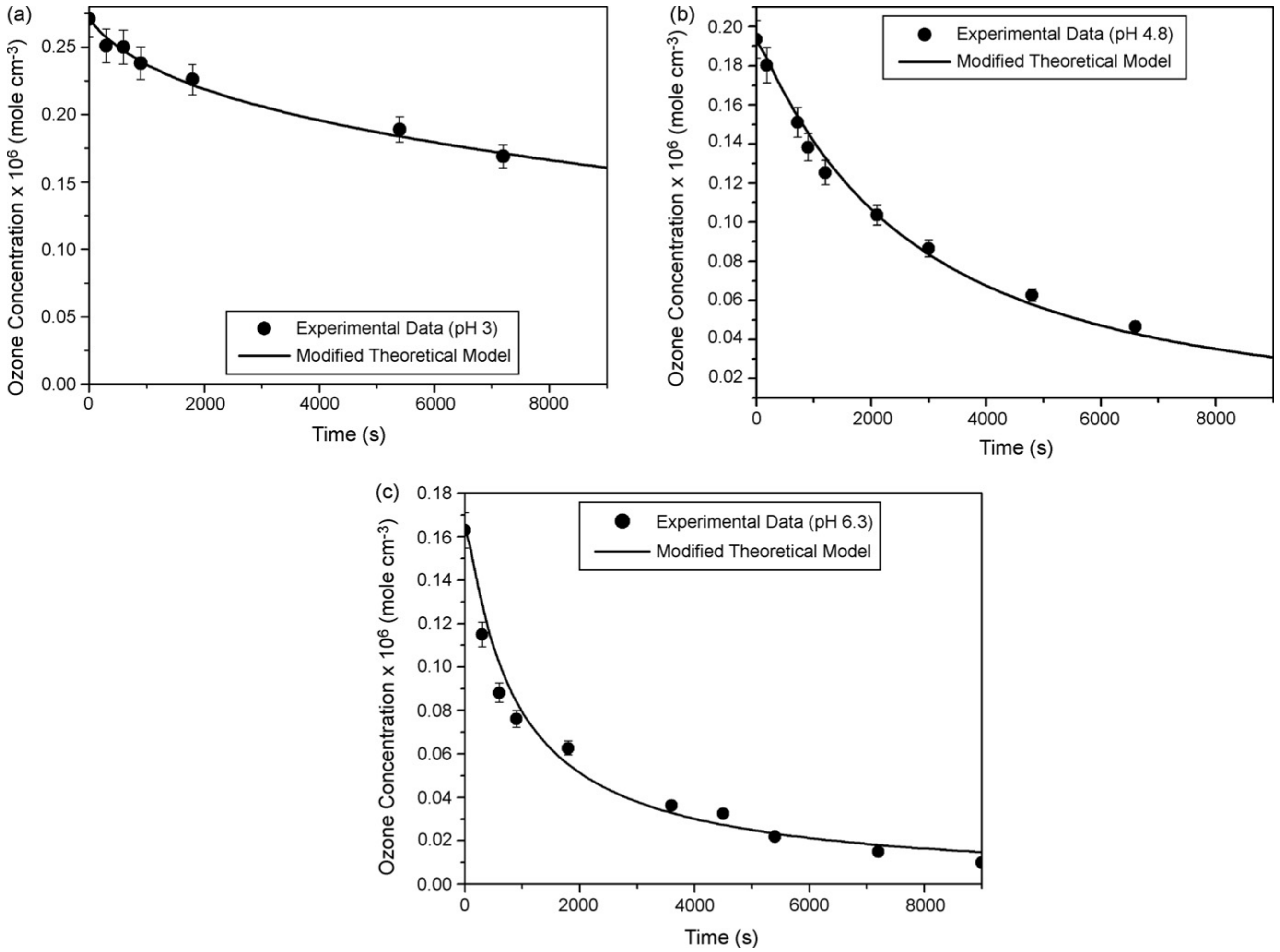

Fig. 8. Complete model versus experimental data. (a) pH 3, (b) pH 4.8 and (c) pH 6.3.

It was not possible to repeat this performance with an equivalent study made with the kinetic constant k_5. Its sensitivity to pH variations was very poor and no improvements were observed as compared with the results already reported in Fig. 2.

Even with a pH dependent, pseudo-kinetic parameter, neither a simple first-order nor a simple second-order reaction kinetic (with respect to $(C_{O_3})^2$ or to C_{O_3} and C_{OH^-}), can be used to represent the reaction evolution in a pH range from 3 to 6.3. They can only be used at a fixed pH, with a different value of the constant for each case, unless a rather complex function of pH is introduced in the single parameter equation.

7. Effect of the initial concentration of hydrogen peroxide

There are two different opinions in the references quoted up to now concerning the effect of the hydrogen peroxide concentration on the rate. On one hand, reference [1] indicates very clearly that the H_2O_2 produced by Ozone decomposition reacts too slowly with O_3, to interfere with the scale of their own experiments. On the other hand, reference [9] indicated that when the pH is increased (no initial value is given) traces (no numerical values are reported) of hydrogen peroxide may affect the ozone decomposition. Finally, reference [19] starting from an initial value of H_2O_2 equal to zero and ozone concentrations from 167 to 790 μM, shows in its Fig. 1 an increase in the hydrogen peroxide concentration during the first part of the reaction. Afterwards, it reaches

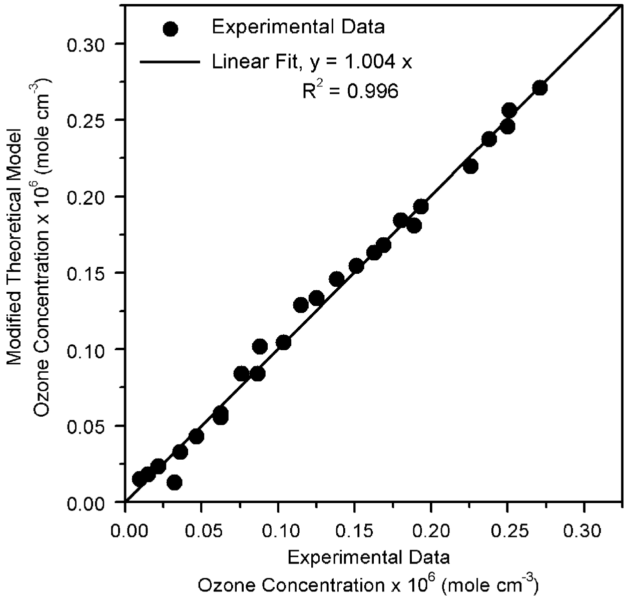

Fig. 9. Simulation of all the experimental points (each one triplicated) employing the model with $k_9 = k_9(\mathrm{pH})$ versus experimental data. $R^2 = 0.99$.

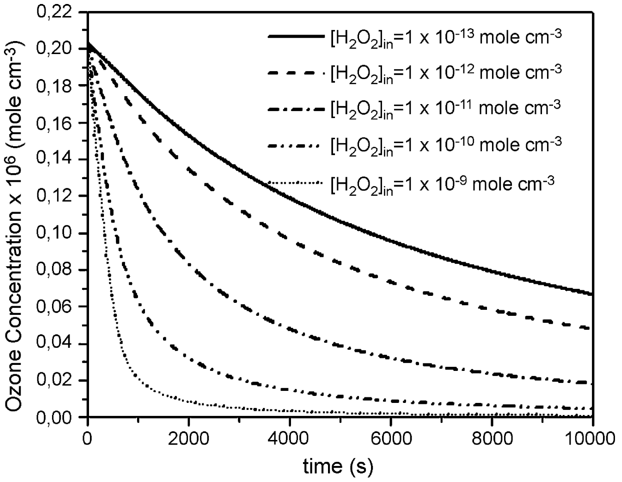

Fig. 10. Sensibility of the ozone decomposition rate. Initial H_2O_2 concentration is the parameter.

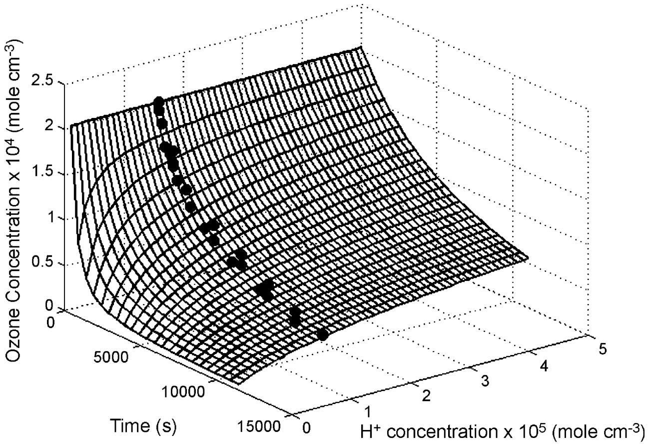

Fig. 11. Three-dimensional representation of the parametric sensitivity of the ozone decomposition rate with respect to pH. Initial H_2O_2 concentration is 3×10^{-12} mol cm^{-3}. Black circles are experimental data for pH ≅ 4.8. The pH is expressed in terms of hydrogen ion concentration to facilitate legibility of the data.

a sort of plateau that depends on the ozone initial concentration. Is in the order of 1 μM. However, it is important to mention that the employed purging time to remove ozone was 5 min, a time that according to our previously described method in Section 2, in our experiments, was not sufficient to eliminate completely all the existing ozone in the sample. In this reference, no information is given concerning the accuracy of the employed method to measure either the ozone concentration or the hydrogen peroxide concentration.

In our case, we started from a solution that had been previously saturated with ozone till the point of absorption equilibrium, and the initial concentration of hydrogen peroxide should be different from zero. We made measurements according to the method described in Section 2.2 and we found, at pH ≅ 4.8 and an initial ozone concentration of 2×10^{-7} mol cm^{-3}, an initial H_2O_2 concentration from 3 to 5×10^{-12} mol cm^{-3}. During the reaction, this concentration showed slight variations that alternates in a smooth manner from ≅4 to 1×10^{-12} mol cm^{-3}. These values are very close to those predicted by the simulation results obtained under these operating conditions: a value that started from the initial condition of 3×10^{-12} mol cm^{-3} and show some changes to finally reach a value almost equal to the starting one. The initial concentration of hydrogen peroxide has a very important effect on the rate of ozone decomposition, in agreement with the conclusions indicated by reference [9] even at not too high pHs. As shown in Fig. 10, with simulated results with our model, it is very important to known the initial condition of the reaction as well as the H_2O_2 concentration evolution along the process. In our case, since we started from a previous operation of saturation of ozone in the solution, it is conceivable that the reaction starts from the plateau that seems to have been observed by reference [19]. Afterwards, it maintains approximately the same value during the whole reaction time; i.e. under these operating conditions, no significant effects could have been detected because the H_2O_2 concentration remained approximately constant.

8. Parametric sensitivity

Under our operating conditions (pure water and absence of scavengers), two variables seem to have a very important effect on the ozone decomposition rate: (i) the pH and (ii) the initial concentration of hydrogen peroxide. Besides the results shown in Figs. 7 and 10, it seems important to display in a three-dimensional diagram, the parametric sensitivity of the reaction rate with respect to these variables and the way that the proposed model accounts for them.

Fig. 11 illustrates the effect of the reaction pH (from 3 to 6) in a plot of the variation of ozone concentration as a function of time. In the plot, to avoid the rather awkwardly representation of the logarithmic function, the pH has been transformed to hydrogen ion concentration. The black dots are our experimental results for pH ≅ 4.8. It can be seen that the model accurately represents the experimental data in a field of significant variations of the rate with the variable under analysis. In other words, the model is very sensitive to pH variations. The experimental data at pH ≅ 3 and pH ≅ 6.3, not included in the plot to facilitate its legibility, show the same precise adjustment.

Finally, a similar reasoning can be made with respect to the effect of the most significant stable by-product of the reaction: oxygen and hydrogen peroxide. The first one is, in the last instance, the one that is very stable, but does not have an important effect on the performance. On the other hand, hydrogen peroxide could have a strong influential effect on the rate. The sensitivity of the model to this variable is shown in a three-dimensional representation in Fig. 12. It can be seen that within the range of explores values of the

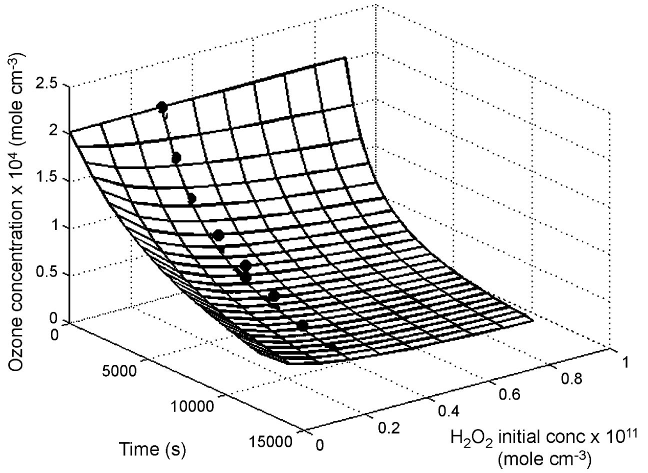

Fig. 12. Three-dimensional representation of the parametric sensitivity of the ozone decomposition rate with respect to the initial concentration of H_2O_2. Plot corresponds to pH 4.8. Black circles are experimental data for H_2O_2 concentration equal to 3×10^{-12} mol cm^{-3} and pH ≅ 4.8.

parameter (10^{-10} to 10^{-13} mol cm^{-3}) and, in this particular case for pH 4.8, that with an outcome not so dramatic than the pH, the effect is still very important. The experimental data for pH ≅ 4.8 and an initial H_2O_2 concentration equal to 3×10^{-12} mol cm^{-3} shows good agreement with the model. Similar results were obtained for pH ≅ 3 and 6.3 (not shown in the figure).

9. Conclusions

A semi-empirical model, based on a widely accepted 18 steps reaction mechanism that is said to be valid for acidic and neutral operating conditions, has been developed that represents the decomposition reaction of ozone in aqueous media at pHs range from 3 to 6.3.

The proposed modification makes use of published kinetic constants that were obtained under different operating conditions (particularly the value of the pH) as initializing conditions for the parameter estimation, and adjusts the pH functionality, with a very precise empirical equation, that introduces a modification in the value of only one critical constant (for the step $[O_3 + HO^{\bullet} \xrightarrow{k_9} HO_4^{\bullet}]$).

This correction was amenable of a simple analytical representation. Under these conditions, theoretical simulation results for pH values from almost neutral to rather weak acidic conditions, can represent, with good accuracy, the experimental data.

These results will be very important, as a background information, to apply Ozone in degrading organic pollutants whose reaction products during the mineralization process decrease the pH of the reacting system.

The reaction is very sensitive to the operating pH and this behavior is shown in a three-dimensional parametric sensitivity diagram that is constructed from the model. When the experimental data are plotted in this diagram, they show very good agreement.

It was also found that the concentration of hydrogen peroxide formed as a reaction intermediary and by-product at very low concentrations, can affect the reaction rate in a very significant manner. The developed model also shows this important affect and represents adequately the observed parametric sensitivity.

Acknowledgements

Thanks are given to Universidad Nacional del Litoral, CONICET and Agencia Nacional de Promoción Científica y Tecnológica for financial help. M.E.L. is grateful to the CONICET doctoral fellowship.

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