

Kinetics of the ozonation of muconic acid in water

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Received 22 March 2006; received in revised form 25 May 2006; accepted 26 May 2006

Available online 3 June 2006

Abstract

The removal of muconic acid (specifically *trans-trans*-butanedioic acid) with ozone from water has been studied for kinetics purposes. Concentrations of muconic acid of 4.4×10^{-4} M are completely removed with ozone in less than 14 and 9 min at pH 3 and 7, respectively, and 3×10^{-4} M of ozone in the gas. The positive influence of pH was due to the more reactive muconic acid dissociated form with ozone. The process can be described as a second order irreversible gas–liquid reaction developing in the moderate kinetic regime of absorption. At the experimental conditions investigated no free radical reactions are present and muconic acid is entirely oxidized by molecular ozone. Rate constants of the direct reaction between muconic acid and ozone were found to be 1.6×10^4 and $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C, pH 3 and 7, respectively, according to film theory. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ozone; Muconic acid; Ozonation kinetics; Water pollution; Kinetic modelling

1. Introduction

Phenol compounds are one of the principal groups of organics present in wastewater because of their wide use in industrial processes and social activities [1–3]. As a consequence, studies on technologies for their removal from water abound in literature [4–6]. Among these technologies, chemical oxidation (in many cases using ozone as oxidant) deserves a special attention, due to high reaction rates that oxidants have with nucleophilic centers of phenols [7]. During ozonation of phenols compounds of different nature, but specifically polyphenols, unsaturated and saturated carboxylic acids and aldehydes are formed [8]. One of these intermediates is muconic acid or butanedioic acid, an unsaturated carboxylic acid with two double bonds that react fast with ozone [9]. Literature reports most of the kinetics of the reactions between these intermediates and ozone but that of the ozone–muconic acid reaction still remains unknown. Knowledge of the kinetics of this reaction is needed for kinetic modelling purposes. Therefore, the objective of this paper was to determine the rate constant of the direct reaction of ozone and muconic acid to further apply it in phenol ozonation kinetic modelling.

2. Materials and methods

Muconic acid (specifically *trans-trans*-butanedioic acid) was obtained from Sigma–Aldrich and used as received. Ozone was generated from pure oxygen in a Sander laboratory ozonator able to produce 6 g of ozone per hour. Pure water was obtained from a Milli-Q Millipore system.

Ozone absorption experiments were carried out in a 30 cm long, 7.5 cm i.d. bubble column provided with a porous plate (16–40 μm) at its bottom and inlets and outlets for feeding and exiting the gas, sampling and measuring temperature. These dimensions and the very fine bubbles circulating through the column allowed the perfect mixing conditions to be reached as also checked by tracer analysis [10]. The reactor was charged with pure water or with an aqueous buffered solution of muconic acid (4.4×10^{-4} M) at pH 3 or 7. Phosphoric acid and sodium hydroxide were used to buffer the aqueous solution and reach a 2×10^{-3} M ionic strength.

In some experiments, ozone was absorbed in pure water also buffered at pH 3 and 7 to determine the Henry law constant and the ozone solubility in water. Also, ozone decomposition was followed in some other experiments at pH 7 to determine the rate constant of the ozone decomposition reaction. Finally, in other group of experiments ozone was absorbed at pH 3 in aqueous solutions of 5,5',7 potassium indigo trisulfonate to determine the volumetric mass transfer coefficient of the system following the method of Ridgway et al. [11].

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The concentration of muconic acid was followed spectrophotometrically by measuring the absorbance at 264 nm since at these conditions there are no interferences of secondary products as literature reports [9]. Ozone concentration in the gas was measured iodometrically by absorbing the ozone containing gas in acid potassium iodide aqueous solutions and using sodium thiosulfate to reduce the liberated iodine. In water, ozone concentration was followed with the Karman Indigo method [12].

3. Results and discussion

3.1. Ozone decomposition and absorption experiments in pure water

In a first series of experiments ozone was decomposed in water at pH 7 to determine the rate constant of the self decomposition reaction needed to further determine the ozone solubility or the corresponding Henry's law constant. Ozone decomposition kinetics in water followed a first order reaction has already been reported in literature. The rate constant obtained was found to be $6.2 \times 10^{-4} \text{ s}^{-1}$ at pH 7. Then, ozone absorption in pure water was accomplished. Fig. 1 shows the evolution of ozone concentration in water for two experiments carried out at pH 3 and 7. As can be seen from Fig. 1, dissolved ozone concentration first increases and after a few minutes reaches a plateau value of 7.0 and $5.7 \times 10^{-5} \text{ M}$ at pH 3 and 7, respectively. The increase of concentration with the decrease of pH can be due to two factors: the increasing ozone decomposition with pH and the salting out effect of the different distribution of ions (from phosphoric acid) at pH 3 and 7 [13]. In our case, the difference in ozone solubility was likely due to the second factor: the salting-out effect since the rate constant of ozone decomposition was negligible against the volumetric mass transfer coefficient as shown below.

The volumetric mass transfer coefficient was obtained from the method of Ridgway et al. [11]. A value of 0.016 s^{-1} was

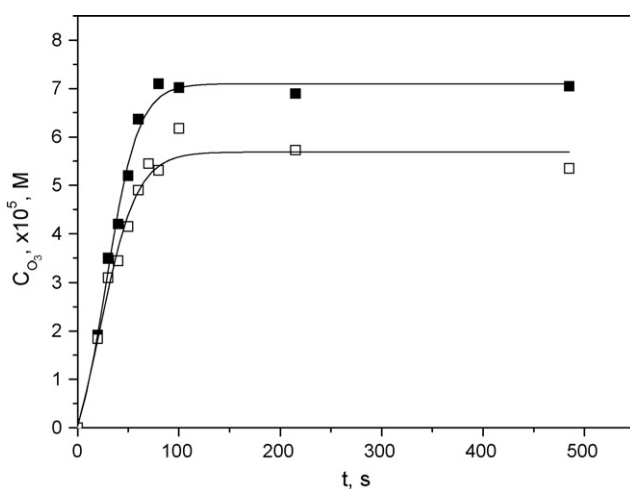


Fig. 1. Evolution of dissolved ozone concentration during the ozone absorption in pure water. Experimental conditions: 20 °C, 28.8 L h⁻¹; ionic strength: $2 \times 10^{-3} \text{ M}$. Ozone concentration in the inlet gas and pH: (■) $2.52 \times 10^{-4} \text{ M}$ and 3; (□) $2.67 \times 10^{-4} \text{ M}$ and 7.

found which is in accordance with the figure of this kind of coefficient expected in bubble columns [14].

For ozone absorption experiments in pure water in a semi-batch reactor with perfect mixing conditions, the ozone mass balance equation in bulk water is:

$$\frac{dC_{O_3}}{dt} = k_{1a}(C_{O_3}^* - C_{O_3}) - k_d C_{O_3} \quad (1)$$

where k_{1a} and k_d are the volumetric mass transfer coefficient and the rate constant of the ozone decomposition reaction, respectively, and $C_{O_3}^*$ and C_{O_3} the ozone concentrations at the gas–water interface or ozone solubility and the dissolved ozone concentration, respectively. At steady state conditions, Eq. (1) reduces to:

$$C_{O_3}^* = C_{O_{3ss}} \left[1 + \frac{k_d}{k_{1a}} \right] \quad (2)$$

with $C_{O_{3ss}}$ being the ozone concentration at steady state (see Fig. 1). Given the very low value of k_d compared to k_{1a} , from Eq. (2) is deduced that the ozone solubility coincides with the ozone concentration at steady state. At pH 3 this conclusion also holds since the ozone decomposition rate constant (not calculated) is much lower than at pH 7. Then, from Fig. 1, values of $C_{O_{3ss}}$ and hence the ozone solubility, $C_{O_3}^*$, can be read. Once $C_{O_3}^*$ is known, application of Henry's law allows the determination of the equilibrium constant, He:

$$P_{O_3} = He C_{O_3}^* \quad (3)$$

where P_{O_3} is the ozone partial pressure in the exiting gas due to perfect mixing conditions. Then, with the experimental values of the ozone partial pressure Henry's law constant was determined to be 86.2 and 101.8 atm M⁻¹ at pH 3 and 7, respectively. These values are on the order of magnitude of other that can be found in literature from empirical correlations [15,16].

3.2. Ozone absorption experiments in muconic acid aqueous solutions

In Fig. 2 the evolution of the muconic acid concentration against reaction time for ozone experiments at pH 3 and 7 is shown. As can be seen, at a given reaction time, muconic acid concentration diminishes as pH increases. This can be due to two reasons: the effect of free radical reactions of increasing importance with the increasing pH in ozone systems and the dissociating character of muconic acid, with the dissociated form being more reactive towards ozone than the non-dissociating one. In our case, the dissociating character of muconic acid is likely the reason. At pH 3 no free radicals are practically formed from ozone decomposition [17] and at pH 7, the reaction of ozone decomposition, responsible of the formation of free radicals, is still very low so that it can be classified as a very slow gas–liquid reaction [18]. Since, the reaction of muconic acid and ozone is faster it seems reasonable to admit that there is no competition between both reactions and the dissolved ozone is only consumed in direct reactions (with muconic acid and intermediates) in water. In any case, the absence of free radical reactions was checked by repeating the ozone–muconic acid experiment

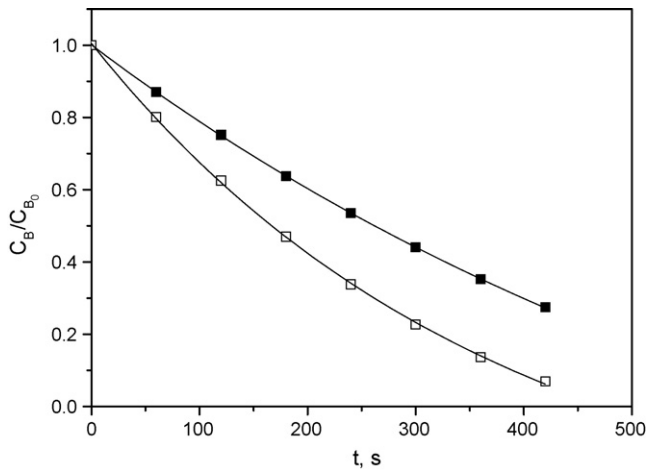


Fig. 2. Evolution of dimensionless concentration of muonic acid in water with time during its ozonation. Experimental conditions: 20°C, 28.8 L h⁻¹; ionic strength: 2 × 10⁻³ M; muonic acid initial concentration: 4.45 × 10⁻⁴ M (average value). Ozone concentration in the inlet gas and pH: (■) 2.90 × 10⁻⁴ M and 3; (□) 3.09 × 10⁻⁴ M and 7.

in the presence of *t*-butanol, a strong hydroxyl free radical scavenger [19]. The results (not shown) indicated no influence of the presence of *t*-butanol on the muonic acid removal rate. Hence, muonic acid is exclusively removed through its direct reaction with ozone.

3.3. Determination of the rate constant of the direct reaction: ozone–muonic acid

During the ozonation experiments of muonic acid in water the dissolved ozone concentration was zero, regardless of the pH. This means that the reaction developed in the fast or moderate instantaneous regime of ozone absorption. This, also, supports the previous conclusions on the negligible importance of free radical reactions to remove muonic acid with ozone. Thus, as is known [18] for pH lower than 12 the ozone decomposition reaction, while ozone is being absorbed in water, develops in the very slow kinetic regime and, hence, this reaction can not compete with a fast or moderate reaction of ozone (in this case, the ozone–muonic acid reaction).

Due to the fast removal of muonic acid from water (less than 15 min at the conditions applied, see Fig. 2), a fast pseudo first order kinetics for the ozone–muonic acid reaction was first assumed. At these conditions, the process kinetics obeys the following equation [14]:

$$N_{O_3} = aC_{O_3}^* \sqrt{kC_B D_{O_3}} \quad (4)$$

where N_{O_3} is the ozone absorption rate, a the specific interfacial area, k the rate constant of the muonic acid–ozone reaction, C_B the concentration of muonic acid and D_{O_3} is the ozone diffusivity in water. On the other hand, a mass balance of muonic acid in water, taking into account perfect mixing conditions and semibatch reactor (batch for the water phase) is:

$$-z \frac{dC_B}{dt} = N_{O_3} \quad (5)$$

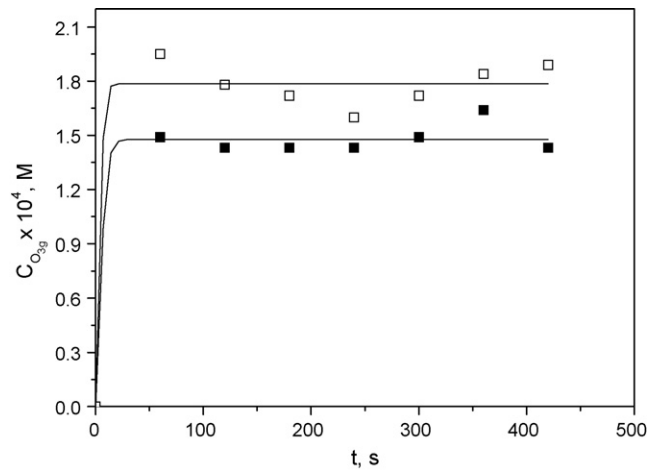


Fig. 3. Evolution of ozone concentration in the exiting gas from the reactor with time during the muonic acid ozonation in water. Experimental conditions: 20°C, 28.8 L h⁻¹; ionic strength: 2 × 10⁻³ M; muonic acid initial concentration: 4.45 × 10⁻⁴ M (average value). Ozone concentration in the inlet gas and pH: (■) 2.90 × 10⁻⁴ M and 3; (□) 3.09 × 10⁻⁴ M and 7.

with z being the stoichiometric coefficient of the ozone–muonic acid reaction, moles of ozone consumed per mole of muonic acid consumed. Substitution of Eq. (4) into Eq. (5) gives:

$$-z \frac{dC_B}{dt} = aC_{O_3}^* \sqrt{kC_B D_{O_3}} \quad (6)$$

Eq. (6) can be analytically solved when $C_{O_3}^*$ stays constant throughout the reaction period considered. This concentration is obtained from the concentration of ozone in the gas leaving the reactor, because of perfect mixing conditions and negligible gas phase mass transfer resistance [20]. Then, according to Henry and perfect laws:

$$C_{O_3}^* = \frac{C_{O_{3g}} RT}{He} \quad (7)$$

where $C_{O_{3g}}$ is the concentration of ozone in the exiting gas, R the gas perfect law constant and T is the temperature. As shown in Fig. 3, concentration of ozone in the exiting gas increases during approximately the first minute of reaction to become stationary. Then, from this short initial time, t_i , $C_{O_{3g}}$ and, then, $C_{O_3}^*$ are constants. Hence, once Eq. (7) has been substituted in Eq. (6) and variables have been separated, Eq. (6) can be integrated between t_i and t , to yield:

$$\begin{aligned} \sqrt{C_B} &= \sqrt{C_{B0}} - \frac{aC_{O_{3g}} RT}{zHe} \sqrt{kD_{O_3}} (t - t_i) \\ &= \sqrt{C_{B0}} - \chi(t - t_i) \end{aligned} \quad (8)$$

According to Eq. (8) a plot of its left side against $(t - t_i)$ should lead to a straight line. From the slope of this line the rate constant of the muonic acid reaction can be obtained. This plot is shown in Fig. 4 for the experiments at pH 3 and 7. As can be seen experimental points are situated around straight lines which comports Eq. (8). From the slopes of straight lines obtained from least squares analysis, k was found to be: 5.8 × 10⁹ and 1.7 × 10¹⁰ M⁻¹ s⁻¹ at pH 3 and 7, respectively, once data of

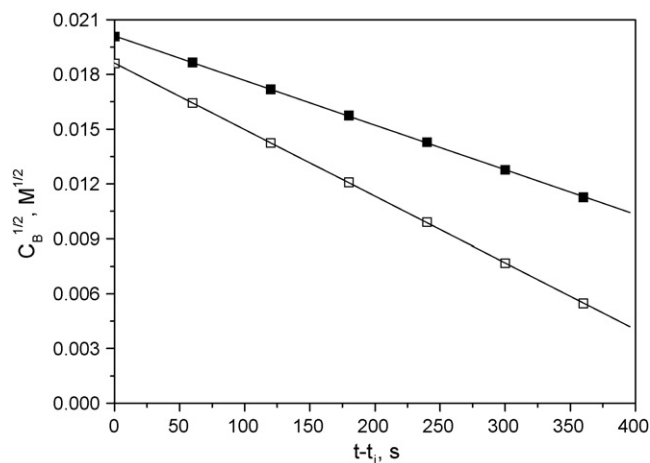


Fig. 4. Checking Eq. (8) for rate constant determination of the reaction between ozone and muonic acid in water. Kinetic regime assumed: fast of pseudo first order. Experimental conditions as in Fig. 2.

rest of parameters included in χ were considered (see Table 1 for parameter values). Among these parameters, the stoichiometric ratio, z , was found to be 1 mol of ozone consumed per mol of muonic acid consumed, determined experimentally in this work following a procedure already published [24]. Once the rate constant of the reaction was known, Hatta values were obtained and compared to the corresponding instantaneous reaction factor, E_i , values, to confirm that the kinetic regime of ozone absorption was fast of pseudo first order. Both parameters are defined as [14]:

$$\text{Ha} = \frac{\sqrt{kD_{\text{O}_3}C_{\text{B}}}}{k_1} \quad (9)$$

and

$$E_i = 1 + \frac{zD_{\text{B}}C_{\text{B}}}{D_{\text{O}_3}C_{\text{O}_3}^*} \quad (10)$$

Condition for a fast of pseudo first order kinetic regime is:

$$3 < \text{Ha} < \frac{E_i}{2} \quad (11)$$

However, this condition was not fulfilled for the ozone–muonic acid reaction. Hatta values were higher than 24 while those of $E_i/2$ varied between 0.5 and 2. As a consequence the values of k were recalculated by assuming a second order

Table 1
Experimental parameters used for rate constant determination^a

Parameter	Value	Reference
z	1	This work
a^b (m^{-1})	232	This work
He (atm M^{-1})	86.3 at pH 3; 101.8 at pH 7	This work
D_{O_3} ($\text{m}^2 \text{s}^{-1}$)	1.65×10^{-9}	From [21]
D_{B} ($\text{m}^2 \text{s}^{-1}$)	6.75×10^{-10}	From Wilke–Chang equation, [22]
k_1a (s^{-1})	0.016	This work
k_1 (m s^{-1})	6.9×10^{-5}	From [23]

^a Data for 20 °C.

^b Determined as k_1/a .

reaction in the moderate-fast kinetic regime [14]. For these regimes, the ozone absorption rate is:

$$N_{\text{O}_3} = k_1aC_{\text{O}_3}^*E \quad (12)$$

with E , the reaction factor, being:

$$E = \frac{\text{Ha}\sqrt{(E_i - E)/(E_i - 1)}}{\tanh[\text{Ha}\sqrt{(E_i - E)/(E_i - 1)}]} \quad (13)$$

The kinetic model of the ozonation for this kinetic regime is finally:

$$-z \frac{dC_{\text{B}}}{dt} = k_1aC_{\text{O}_3}^*E \quad (14)$$

Eq. (14) was solved finding, with a trial and error procedure, the value of k that minimizes, between t_i and a given time t , the sum of the squares of the differences between the actual and calculated muonic acid removal rates. Figs. 5 and 6 show the best fitting obtained at pH 3 and 7 with the values of k of 1.6×10^4 and $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively. As can be seen, calculated and experimental values coincide for reaction times approximately lower than 200 and 350 s at pH 3 and 7, respectively (notice that t_i was lower than 60 s). The deviations observed at higher reaction times are likely due to the competition of ozone reactions with by-products of muonic acid ozonation (for example: the reaction of ozone with maleic or fumaric acid, [24]). According to these results, during the first minutes of reaction, only the muonic acid–ozone reaction develops, while for higher reaction times, other ozone direct reactions compete. Finally, values of the Hatta number (Eq. (9)) were recalculated with the new values of k . In these cases, Ha always resulted to be lower than 3, regardless of the pH value. This allowed us to confirm the moderate kinetic regime of ozone absorption [14] and the validity of the procedure applied for kinetic determination.

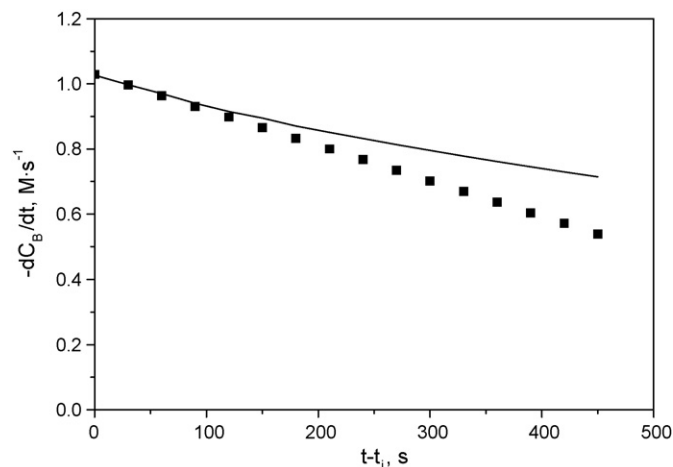


Fig. 5. Comparison between experimental and calculated accumulation rates of muonic acid in water to determine the rate constant of the reaction between ozone and muonic acid. Kinetic regime assumed: moderate. Experimental conditions as in Fig. 2 and pH 3. Black squares are experimental points. Continuous line represents calculated results.

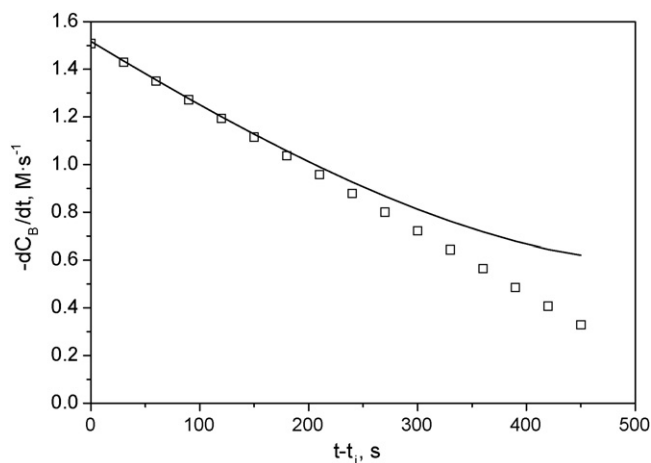


Fig. 6. Comparison between experimental and calculated accumulation rates of muonic acid in water to determine the rate constant of the reaction between ozone and muonic acid. Kinetic regime assumed: moderate. Experimental conditions as in Fig. 2 and pH 7. Empty squares are experimental points. Continuous line represents calculated results.

4. Conclusions

In this work the following conclusions have been reached:

- The reaction between ozone and muonic acid in water proceeds fast although it develops in the moderate kinetic regime of ozone absorption.
- pH is an important variable that affects the ozonation rate in a positive manner. However, pH influence is not due to contribution of free radical reactions, a common way through which ozonation of organics in water takes place but to the more reactive dissociated form of muonic acid towards molecular ozone, through double bond ozonolysis (Criegee mechanism [24]).
- The stoichiometric ratio of the direct ozone–muonic acid reaction was found to be 1 mol of ozone consumed per mol of muonic acid consumed.
- Application of film theory to experimental results of muonic acid ozonation leads to the determination of the rate constant of the reaction that resulted to be 1.6×10^4 and $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 7, respectively.

Acknowledgements

This work has been supported by the CICYT of Spain and the European Region Development Funds of the European Commission (Project PPQ2003/00554).

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