HOW TO AVOID MASS TRANSFER LIMITATIONS IN OZONATION KINETICS OF PHENYLPHENOL ISOMERS?

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Dedicated to Prof. Ryszard Pohorecki on the occasion of his 80th birthday

Ozonation is a heterogeneous process of chemical absorption often controlled by a gas-liquid mass transfer rate. This paper presents the results of kinetics in a reaction between phenylphenol isomers and ozone. The degradation of phenylphenol isomers during ozonation proceeds quite fast. In order to avoid the influence of mass transfer limitation the kinetics experiments were conducted in a homogenous liquid-liquid system. The second-order rate constants were determined using classical and competition methods, which are especially recommended for fast reactions. The determined rate constants at pH 2 using the two different methods are almost the same. The increase of pH causes an increase of rate constants for the reaction of phenylphenol isomers with ozone.

Keywords: phenylphenol isomers, ozonation in homogenous system, ozonation kinetics, competition kinetics, classical kinetics

1. INTRODUCTION

Due to its properties ozone is used worldwide as a disinfectant and oxidant. The oxidation potential of molecular ozone at pH 0 is equal to 2.07 V (Oppenländer, 2003), and decreases with pH increase (Cotton and Wilkinson, 1973). This oxidant can react both with organic and inorganic compounds in two ways: directly and indirectly. The first pathways are relatively slow, and include a reaction of ozone molecules with a substrate. In aqueous solutions ozone is decomposed to hydroxyl radicals, which react much faster with substrates (indirect oxidation). Decomposition rate of ozone in aqueous solutions is influenced by many parameters, the most important of them include pH, temperature and concentration of organic and inorganic compounds. Direct oxidation is of primary importance under acidic conditions, and high pH results in dominance of degradation by hydroxyl radicals (Gottschalk et al., 2010). Ozonation is able to degrade pharmaceuticals (Adams et al., 2002; Rivas et al., 2009; Ternes et al., 2002), estrogens (Alum et al., 2004) as well as pesticides (Chelme-Ayala et al., 2011).

Ozonation or advanced oxidation using ozone can be carried out in homogeneous or heterogeneous systems in a bath, semi-bath or continuous flow mode. In heterogeneous gas-liquid systems, the reaction of ozone with a chemical compound is preceded by physical absorption of the gas in an aqueous solution, therefore mass transfer limitation should be taken into account. Mass transfer of ozone from the gas to the liquid phase can be influenced by various factors, including process parameters (gas flow rate and energy input), physical parameters (density, viscosity, surface tension) and geometry of the reactors can be distinguished (Gottschalk et al., 2010). The undoubted impact on the ozone absorption in the aqueous solution have simultaneous chemical reactions, which result in a

decrease of ozone concentration near to the interface, causing an increase of ozone molar flux. Kinetics of absorption with a simultaneous chemical reaction is one of the most difficult issues in environmental engineering, and it takes different notation forms depending on the reaction type, reaction order as well as reaction rate. In order to avoid mass transfer limitations in determining ozonation kinetics experiments should be carried out in a homogenous liquid-liquid system. In this case, the rate constant for direct reaction of ozone with chemical compounds can be determined by using classical or competition kinetics and a stopped-flow spectrometry system. The latter two methods are especially recommended for fast reactions (Gottschalk et al., 2000).

The competition kinetics method was developed by Hoigné and Bader (1976) and can be applied universally for direct or indirect reactions and for fast or slow reacting compounds (Chelme-Alaya et al., 2010; Karpel Vel Leitner and Roshani, 2010). In this method an oxidant reacts simultaneously with at least two compounds. One of them is considered as a reference compound with the known reaction rate constant while the other is a substance with an unknown reaction rate constant. The method assumes that the reaction between the oxidant and each target compound is second-order overall, and first-order with respect to both reactants (Benitez et al., 2006). The selection of reference compounds is a very important step, because they cannot be much more or less reactive than the target compound. Improperly selected reference compounds lead to large errors in determination of the reaction rate constants (Einschlag et al., 2003).

In stopped-flow experiments, ozone is applied in excess (at least 10-fold excess of the molar reaction requirements) and the pseudo-first-order reaction rate constant is estimated by monitoring the UV absorbance of the investigated compound. Subsequently, the second-order rate constant is determined from the double log plot of first-order rate constants versus ozone concentrations (Chelme-Ayala et al., 2010). The major advantages of this method are that very small amounts of reaction solutions are needed and the possibility for continuous monitoring of the reaction. On the other hand, this method is not appropriate if the investigated compound has the absorption spectrum in the same wavelength region as ozone and reaction products.

This article presents kinetics analysis of degradation phenylphenol isomers (PPs) in a homogenous liquid-liquid system by ozone. The selection of PPs was due to the fact that they are widespread in the water environment and possess oestrogenic and androgenic potential, which can adversely affect living organisms. The major aim of this study was to establish a database with second-order rate constants for the reaction of ozone and investigated compounds at different pH values using classical and competition methods.

2. MATERIAL AND METHODS

Ortho-phenylphenol (*o*-PP)($\geq$ 98.0%), *para*-phenylphenol (*p*-PP) (> 98%), butylparaben (BP) (> 99%), *tert*-butanol (*t*-BuOH) ($\geq$ 99.7%) were purchased from Fluka. *meta*-phenylphenol (*m*-PP) (85%) was from Aldrich and used after recrystalisation from methanol (POCH, Poland). The stock solutions of PP isomers and BP were prepared in distilled water treated in Millipore Milli-Q Plus System (18.2 MΩ), under sonication. Aqueous solutions of PP isomers and BP were made by diluting a proper amount of the stock solution. The pH of the reaction solution was adjusted by a phosphate buffer (H_3PO_4, KH_2PO_4, Na_2HPO_4, NaOH, all p.a., POCH, Poland) in the range from 2 to 10.

Experiments were carried out in a 1dm^3 glass reactor, immersed in a thermostatic bath to keep constant temperature at 20 °C within $\pm$ 0.5 °C. Agitation of the reaction mixture was provided by a magnetic stirrer working at 600 rpm. The reactor was additionally equipped with a porous plate to deliver ozone gas into the reaction solution. The reactor was operated in a semi batch mode (a heterogeneous gas–liquid system). Ozone was generated from pure oxygen in a BMT 802 ozonator. Ozone concentration in the gas stream in the inlet and outlet of the reactor was measured with an ozone analyser

(BMT 963 Vent). During the experiments samples were collected regularly for analysis. In order to remove the residual ozone from the samples, sodium sulfite solution (p.a., POCH, Poland) was added (Huber et al., 2003).

The kinetic experiments were performed at room temperature (20 ± 0.5 °C) in a homogenous system, in the presence of t-BuOH (0.05 M) used as OH radicals scavenger. Glass flasks (100 ml) with a the stopper were used as the reaction vessel in classical kinetic experiments. Kinetic runs were started by injecting, under rapid mixing, PP isomer stock solution into the flask containing the solution saturated with ozone at pH 2. During the experiments two sample series of reaction solution were taken: first for the analysis of PPs and second for ozone analysis.

Competition kinetic experiments were carried out in 10 ml vials. A detailed description of the kinetic method was given previously by Huber et al. (2003). BP was selected as a reference compound because a similar to target compound reaction rate constant was expected. Different concentrations of aqueous ozone ranging from 2 μM to 50 μM were added to a solution containing equal concentrations of PP isomer (5 μM) and the reference compound (5 μM) and the vials were then shaken vigorously. After ozone was completely consumed, the remaining concentrations of the target and reference compounds were analysed.

Ozone concentration in water solutions was determined by indigo method (Bader and Hoigne, 1981). The progress of PP isomers and BP degradation was monitored by chromatographic analysis performed on a HPLC Waters apparatus with a UV diode array detector using a Nova-Pak 150/C18 column, operated in an isocratic mode. The mobile phase was a mixture of methanol (Baker HPLC Analyzed, gradient grade) and acidified water (0.01% H_3PO_4) at the flow rate of $1 cm^3/min$.

3. RESULTS AND DISCUSSION

The degradation of PP isomers during ozonation was quite fast. For example, *m*-PP was almost completely removed after 4 min of ozonation carried out with ozone concentration in the gas stream equal to 21 g/Nm^3 (Fig. 1A). The increase of ozone content in the gas stream supplied to the reactor caused a higher ozone concentration in water solution (Fig. 1B), which accelerated degradation of PP isomers (Fig. 1A).
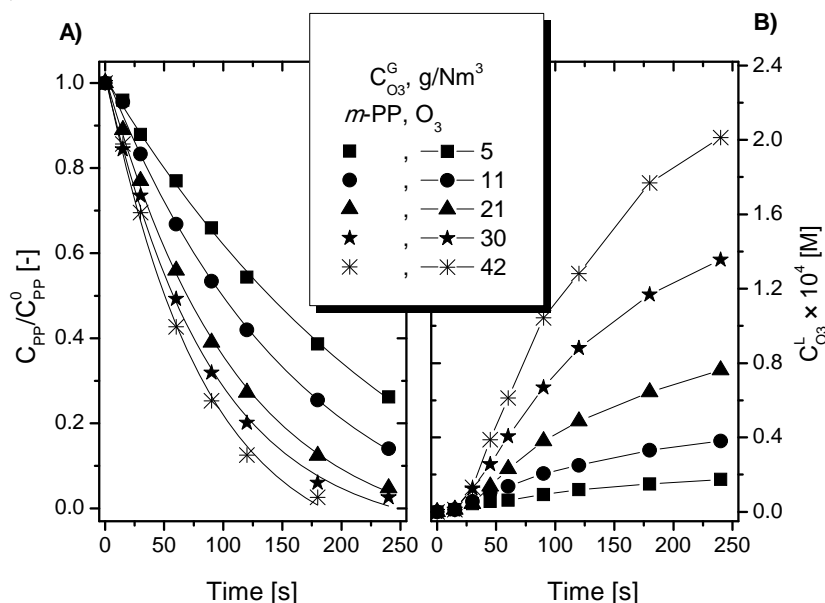

Fig. 1. Changes in *m*-PP relative concentration (A) and ozone concentration (B) in reaction solution during ozonation for various ozone contents in gas stream supplied to the reactor
(C_{mPP0} = 48 μM, Q_m = 35 dm^3/h, T = 20 °C, pH = 7)

The results of oxidation and reaction kinetics of *o*-PP during ozonation were discussed in our earlier work (Olak-Kucharczyk et al., 2012). In the present study two different approaches for measuring direct ozonation rate constants were used. First, classical kinetic experiments were performed. At pH 2 in the presence of t-BuOH. During ozonation time, PP isomers and ozone concentrations were changed according to the profiles presented in Fig. 2A. PP isomer ozonation was considered as a second-order reaction. The rates of ozone and PP isomer disappearance are formulated as follows:

$$\frac{dC_{PP}(t)}{dt} = -k_{O3PP}C_{PP}(t)C_{O3}(t) \tag{1}$$

$$\frac{dC_{O3}(t)}{dt} = -k_{O3PP}C_{PP}(t)C_{O3}(t) \tag{2}$$

where k_{O3PP} is the second-order rate constant. The following initial conditions were assumed:

$$C_{PP}(0) = C_{PP0} \tag{3}$$

$$C_{O3}(0) = C_{O30} \tag{4}$$

Subtraction of Eq. (2) from Eq. (1) yields in Eq. (5):

$$\frac{dC_{PP}(t) - dC_{O3}(t)}{dt} = 0 \tag{5}$$

From Eq. (5) it follows that:

$$C_{PP}(t) - C_{O3}(t) = C_0 \text{ and } C_0 = C_{PP0} - C_{O30} \tag{6}$$

After dividing Eq. (1) by $C_{PP}(t)$ and Eq. (2) by $C_{O3}(t)$ the following equations are obtained:

$$\frac{1}{C_{PP}(t)}\frac{dC_{PP}(t)}{dt} = -k_{O3PP}C_{O3}(t) \tag{7}$$

$$\frac{1}{C_{O3}(t)}\frac{dC_{O3}(t)}{dt} = -k_{O3PP}C_{PP}(t) \tag{8}$$

Further conversion leads to:

$$\frac{d \ln C_{PP}(t)}{dt} = -k_{O3PP}C_{O3}(t) \tag{9}$$

$$\frac{d \ln C_{O3}(t)}{dt} = -k_{O3PP}C_{PP}(t) \tag{10}$$

After subtraction of Eq. (10) from Eq. (9) we get:

$$\frac{d}{dt} \ln \frac{C_{PP}(t)}{C_{O3}(t)} = k_{O3PP}[C_{PP}(t) - C_{O3}(t)] \tag{11}$$

After integrating Eq. (11) and taking into account Eq. (6) the following dependence can be obtained:

$$k_{O3PP}t = \frac{1}{C_{PP0} - C_{O30}} \ln \frac{C_{PPt}C_{O30}}{C_{O3t}C_{PP0}} = A \tag{12}$$

Eq. (12) can be used to determine reaction rate constants of PP isomers with ozone. Results were plotted in the coordinate system (t, A) arising from Eq. (12) (Fig. 2B), where the slope of a rectilinear dependence corresponds to the second-order rate constant. Results are given in Table 1.
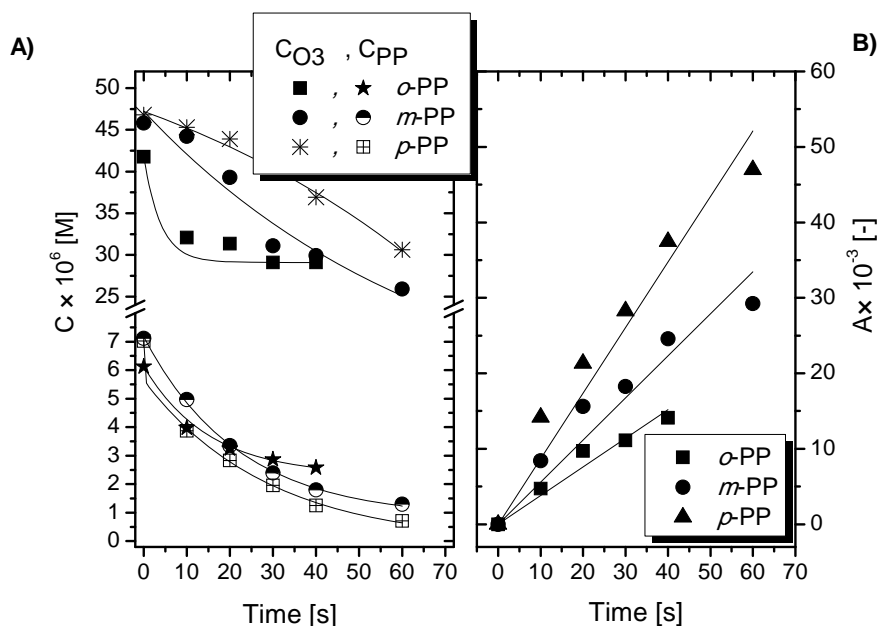
Fig. 2. Changes in PP isomers and ozone concentration during ozonation time (A). Determination of second-order rate constant for the reaction of ozone with PP isomers (B) (C_{oPP0} = 6.1 μM, C_{mPP0} = 7.1 μM, C_{pPP0} = 7.0 μM, C_{O30oPP} = 42 μM, C_{O30mPP} = 46 μM, C_{O30pPP} = 47 μM, C_{BuOH} = 0.05 M, T = 20 °C, pH = 2)

Table 1. Rate constants for PP isomers with ozone and values of constants used in calculations

Method	pH	k_{O3}, 1/(M·s)			
		BP	o-PP	m-PP	p-PP
classical	2	-	$(3.79 \pm 0.23) \times 10^2$	$(5.58 \pm 0.40) \times 10^2$	$(8.68 \pm 0.50) \times 10^2$
competition		[a]$(4.2 \pm 0.60) \times 10^2$	$(4.42 \pm 0.64) \times 10^2$	$(5.85 \pm 0.35) \times 10^2$	$(8.90 \pm 0.33) \times 10^2$
	6	[a]$(4.4 \pm 0.40) \times 10^5$	$(3.32 \pm 0.48) \times 10^5$	$(3.97 \pm 0.60) \times 10^5$	$(5.25 \pm 0.03) \times 10^5$
	10	[b]$(1.36 \pm 0.60) \times 10^9$	$(1.4 \pm 0.63) \times 10^9$	$(1.75 \pm 0.01) \times 10^9$	$(1.73 \pm 0.01) \times 10^9$

[a] value reported by Tay et al. (2010); [b] value calculated from Eq. (15)

The second approach for determination of direct ozonation constant rates was to use the method of competition kinetics. Experiments were conducted at pH ranging from 2 to 10. BP was used as a reference compound. The kinetics for simultaneous reactions for ozone with PP isomers and BP can be integrated and expressed as follows:

$$\ln \frac{C_{PPt}}{C_{PP0}} = k_a \ln \frac{C_{BPt}}{C_{BP0}} \tag{13}$$

$$k_a = \frac{k_{O3PP}}{k_{O3BP}} \tag{14}$$

where k_{O3PP} and k_{O3BP} are the second-order rate constants for the reaction of ozone with PP isomer and BP, respectively.

The plot of ln C_{PPt}/C_{PP0} versus ln C_{BPt}/C_{BP0} should result in a straight line (Fig. 3), with a slope equal to k_a. The determined k_a and Eq. (14) were used for calculation of the second-order rate constant of ozone with PP isomers. The values of reaction rate constants for BP necessary for calculations and the obtained results are given in Table 1. The second-order rate constant for the reaction BP with ozone at pH 10 was calculated using Eq. (15). The value of pK_a = 8.24 for BP (Błędzka et al., 2010) and other constants (Tay et al., 2010) necessary for calculations were taken from the literature.

$$k_{O3s} = k_{O3uds}\left(\frac{10^{-pH}}{10^{-pKa}+10^{-pH}}\right) + k_{O3ds}\left(\frac{10^{-pKa}}{10^{-pKa}+10^{-pH}}\right) \qquad (15)$$
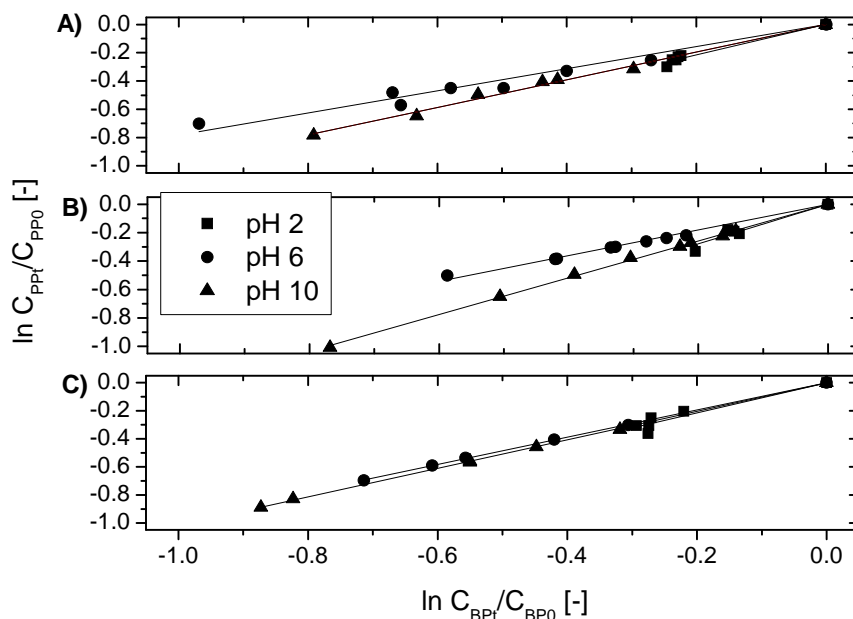

Fig. 3. . Determination of second-order rate constants for a reaction of ozone with *o*-PP
(A), *m*-PP (B) and *p*-PP (C) at different pH using competition kinetics
(C_{oPP0} = 6.5 μM, C_{mPP0} = 5 μM, C_{pPP0} = 5 μM, C_{O30} = (2-50) μM, C_{BuOH} = 0.5 M, T = 20 °C)

An attempt for the determination of kinetic parameters using stopped-flow spectrometry was also made. But in this case, estimation of reaction constant rates was impossible because PP isomers absorb the radiation in the same wavelength region as ozone (Olak-Kucharczyk et al., 2015), and reaction products (data not shown).
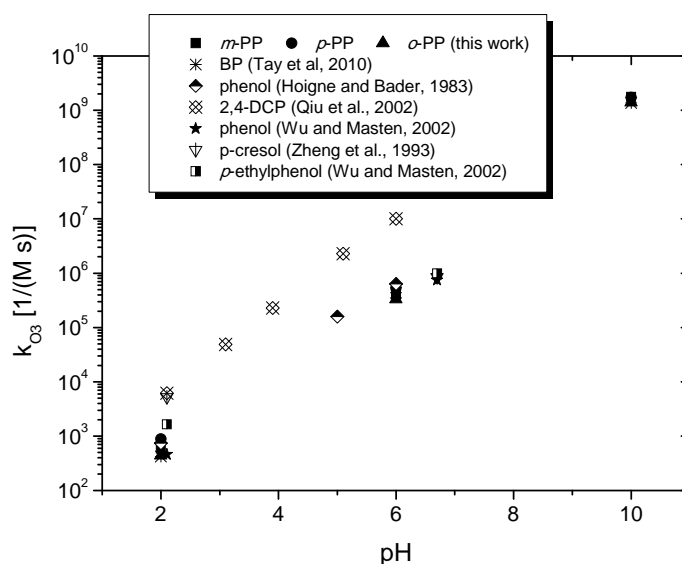

Fig. 4. Second-order rate constants different phenolic compounds

The determined rate constants for PP isomers at pH 2 using classical and competition methods are very similar. Higher values of rate constants obtained from the competition method can be explained by an error made in the selection of the reference compound. The rate constants for a reaction of PP isomers

with ozone increase with the pH increases, which is consistent with the literature data (Benitez et al., 2003; Qiu et al., 2002; Tay et al., 2010), because ozone reacts faster with the dissociated form of chemical compounds (Gottschalk et al., 2010). As can be seen in Fig. 4, the rate constants for PP isomers and phenol or different phenolic compounds are similar.

4. CONCLUSIONS

- In order to avoid the influence of mass transfer limitation, kinetics experiments were conducted in a homogenous liquid-liquid system using two different methods.

- Good agreement between the reaction rate constants determined with the classical and competition methods was observed.

- Determination of kinetic parameters based on stopped-flow spectrometry was found not to be possible because PP isomers have absorption spectra in the same wavelength region as ozone, and reaction products.

- The degradation of PP isomers during ozonation in a heterogeneous gas-liquid system proceeded quite fast, in particular a decrease of acidity resulted in an increase of the rate constants.

- The obtained rate constants for a reaction of ozone with PP isomers are similar to those of ozone with different phenolic compounds available in the literature.

SYMBOLS

C_i	molar concentration, M
C_{i0}	initial molar concentration, M
k	reaction rate constant, 1/(Ms)
pK_a	acid - base equilibrium constant
Q_m	volumetric flow rate of gas mixture, dm^3/h
T	temperature, ^{o}C
t	time, s

Superscripts

L	liquid
G	gas

Subscripts

0	initial conditions
t	time conditions
s	sum of disocciated and undissociated forms
ds	dissociated form
uds	undissociated form

Abbreviations

PP	phenylphenol

O₃	ozone
PPs	phenylphenol isomers
o-PP	*ortho*-phenylphenol
m-PP	*meta*-phenylphenol
p-PP	*para*-phenylphenol
BP	butylparaben
t-BuOH	*tert*-butanol

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