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This document is the Accepted Manuscript version of a Published Work that appeared in final form in [Chemical Engineering and Processing: Process Intensification ]. To access the final edited and published work see [https://doi.org/10.1016/j.cep.2009.11.016]."

### Testing a KrCl excilamp as new enhanced UV source for 4-chlorophenol degradation: experimental results and kinetic model. M. Gomez<sup>1</sup>, M.D. Murcia<sup>1</sup>, J.L. Gomez<sup>1\*</sup>, G. Matafonova<sup>2</sup>, V. Batoev<sup>2</sup>, N. Christofi<sup>3</sup> <sup>1</sup>Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain <sup>2</sup>Baikal Institute of Nature Management, Siberian Branch of Russian Academy of Sciences, Sakhyanova 6, Ulan-Ude 670047, Russia <sup>3</sup>Pollution Research Unit, School of Life Sciences, Napier University, Merchiston Campus, Edinburgh EH10 5DT, Scotland UK. <sup>1\*</sup>Corresponding author: J.L. Gomez, Tel: (34) 968367351, Fax: (34) 968364148; E-mail: carrasco@um.es Keywords: 4-chlorophenol, kinetic model, photodegradation, UV, excilamp Abstract Excilamps are new UV sources with great potential for application in wastewater treatment. In the present work, a KrCl excilamp emitting radiation at 222 nm has been used for the photodegradation of 4-chlorophenol within a range of concentrations from 50 to 500 mg $L^{-1}$ . The photodegradation process has been shown to form two main photoproduct intermediates, benzoquinone and hydroquinone. Total removal of 4-chlorophenol was shown for all concentrations assayed, and, for both main intermediates, residual concentrations of 20-30 % of the initial concentration of 4-chlorophenol remained. Their increasing presence with increasing initial concentrations of 4-chlorophenol had the effect of decreasing the removal efficiency of the photoproducts. In order to simulate the process and scale-up a simplified kinetic model has been developed and validated from the experimental data. Nomenclature

- 32 a = model parameter defined in Eq. (30), mM min<sup>-1</sup>
- $a_1 = model parameter defined in Eq. (22), dimensionless$

 $a_2$  = model parameter defined in Eq. (23), dimensionless b = model parameter defined in Eq. (30),  $mM^{-1}$  $b_1 = model parameter defined in Eq. (22), min^{-1}$  $b_2 = model parameter defined in Eq. (23), min<sup>-1</sup>$ BQ = benzoquinone  $c_1$  = model parameter defined in Eq. (22), min<sup>-1</sup>  $c_2 = model parameter defined in Eq. (23), min<sup>-1</sup>$ 4CP = 4-chlorophenol HQ = hydroquinone $I_0$  = intensity of total radiation, W cm<sup>-2</sup>  $I_A$  = intensity of absorbed radiation, W cm<sup>-2</sup>  $I_T$  = intensity of transmitted radiation, W cm<sup>-2</sup> k = pseudo-first order rate constant for 4-chlorophenol photodegradation, min<sup>-1</sup>  $k_1$  = kinetic constant for HQ formation from 4CP, min<sup>-1</sup>  $k_2$  = kinetic constant for BQ formation from 4CP, min<sup>-1</sup>  $k_3$  = kinetic constant for HQ decomposition to final products, min<sup>-1</sup>  $k_4$  = kinetic constant for BQ decomposition to final products, min<sup>-1</sup> L = optical pathway, cmt = reaction time, min $X_{BQ}$  = benzoquinone conversion, dimensionless  $X_{4CP}$  = 4-chlorophenol conversion, dimensionless  $X_{HO}$  = hydroquinone conversion, dimensionless [BQ] = concentration of benzoquinone at time t, mM  $[BQ]_0$  = initial concentration of benzoquinone, mM [4CP] = concentration of 4-chlorophenol at time t, mM  $[4CP]_0$  = initial concentration of 4-chlorophenol at time t, mM [HQ] = concentration of hydroquinone at time t, mM  $[HQ]_0$  = initial concentration of hydroquinone, mM Greek symbols  $\alpha$  = proportionality constant defined in Eq. (27), mM min<sup>-1</sup> cm<sup>2</sup> W<sup>-1</sup>  $\varepsilon = \text{molar absortivity. cm}^{-1} \text{ mol}^{-1} L$ 

### 68 Introduction

Chlorophenols are usually found in the wastewaters of numerous industries including the pulp and paper, wood, steel and other metals, petroleum refining, resins and plastic based industries, being commonly released from these industrial wastewaters to the environment [1, 2]. They are widely considered as priority pollutants and can be rather persistent causing severe environmental problems. One example is the Lake Baikal ecosystem (World Nature Heritage Site since 1996), where chlorophenols are released into the lake as by-products of the bleaching of crude pulp with active chlorine in the Baikalsk pulp and paper mill located directly on the southern shore of the lake [3].

Physical, chemical and biological methods have been utilised in the removal of these toxic compounds, however, a definitive solution remains [4-13]. Among the methods considered, photochemical degradation of the contaminants in water is of particular interest and potential. The combined use of UV radiation and strong chemical oxidizing agents constitutes one type of the advanced oxidation processes (AOPs), that can be particularly effective in the removal of toxic chlorophenols from water and wastewater [14-18]. Although there are numerous investigations on the photochemical transformation of chlorophenols using single UV radiation in combination with various AOPs agents, it is still a field of research in view of the development and application of novel sources of UV radiation. In general, the high-, medium- and low-pressure UV mercury lamps, at a wavelength of primarily 254 nm, are typically used in photolysis of chlorophenols [19-21], and, frequently, catalysts have been used to improve the process efficiency, titanium dioxide being the most common [22-25].

Among other UV radiation sources, attention is focusing on the development of excimer lamps and excilamps and their use in the destruction of toxic organic pollutants from wastewater [26, 27]. Excimer lamps, or excilamps, are a class of spontaneous radiation sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers). They emit a narrow-band ultraviolet radiation. Excilamps are attractive alternatives to commonly used mercury lamps and lasers for applications in pollution control technology because of the absence of 101 elemental mercury, long lifetime (from 1000 to 10000 h), geometric freedom, high102 photon flux and other advantages [28].

As far as we are aware there are no kinetic studies related to excilamps. However, numerous studies can be found in the area of photocatalytic processes based on UV mercury lamps and the use of catalysts such as titanium dioxide [22-25]. The kinetic models proposed in those previous studies are basically of two types: the lineal model based on first order kinetics and the Lagmuir-Hinshelwood non-lineal model, which involves a prior adsorption process of the photocatalytic substrate on the catalyst surface and its subsequent degradation.

It is known that a thorough understanding of degradation processes and their simulation is vital in order to predict the behaviour of treatment systems and the scaling up of the processes [29, 30]. With this appreciation, the present work deals with the use of a KrCl excilamp for 4-chlorophenol photodegradation and, additionally, in the development of a simplified photolytic kinetic model based on the experimental data and applicable to the progress curves of 4-chlorophenol and the two main intermediates, hydroquinone and benzoquinone.

 

## 120 Materials and Methods

4-chlorophenol (99%), *p*-benzoquinone (98%) and hydroquinone (99%) were all
purchased from Sigma-Aldrich.

A KrCl excilamp with output power of 5 W was used for photodegradation experiments. The typical spectrum of this lamp emitting UV radiation at 222 nm (the band of the KrCl molecule) is shown in Fig. 1. The excilamp was of cylindrical geometry covered by a metal case having an UV exit window with an area of 75  $cm^2$ , and was purchased from Institute of High Current Electronics of Russia. The exit window was oriented vertically in close proximity to a quartz tube with an operating length of 22 cm and external diameter of 2.6 cm. 4-chlorophenol at the required concentrations, ranging from 50 to 500 mg  $L^{-1}$  (0.389 to 3.891 mM) was dissolved in 10 ml of distilled water, placed into the quartz tube covered with a reflector and 

Any 4-chlorophenol remaining after the treatment and the two main photoproducts of the photodegradation process, benzoquinone and hydroquinone, were determined by HPLC analysis, at 283 nm for 4CP and HQ and 237 nm for BQ, using a Varian Prostar 210 chromatograph with UV-VIS detector and a C18 reverse phase column. The mobile phase was a mixture of methanol, acetic acid and water (60:2.5:37.5 v/v) with a flow rate of 1 ml min<sup>-1</sup>. Retention times were 6.2, 2.1 and 2.4 min for 4chlorophenol, hydroquinone and benzoquinone, respectively. **Results and Discussion 4-chlorophenol photodegradation** 

The results obtained in the photodegradation process with the KrCl excilamp, for the series of initial 4-chlorophenol concentrations ranging from 50 to 500 mg  $L^{-1}$ (0.389–3.891 mM), are shown in Figures 2-(A) to 2-(D).

157 Changes of 4-chlorophenol concentration with time are shown in Figure 2-(A) 158 and the generation of hydroquinone and benzoquinone can be observed in Figures 2-159 (B) and 2-(C), respectively. The temporal evolution of the sum of these three 160 components, being approximately the equivalent of the total organic load that has not 161 been degraded to low molecular weight compounds, is shown in Figure 2-(D).

163 It can be seen from Figure 2-(A), that the excilamp can achieve total 4-164 chlorophenol degradation with exposure times up to 5 minutes, for an initial 165 concentration of 50 mg  $L^{-1}$  (0.389 mM), and 90 minutes for 500 mg  $L^{-1}$  (3.891 mM). 166 As for the two main intermediates of the photodegradation process, hydroquinone and

# 134 irradiated at room temperature (23–25 $^{0}$ C) under static conditions.

average radiation intensity delivered to the solution was  $2.47 \text{ mW cm}^{-2}$ .

The output power of the excilamp was measured with a H8025-222 photodetector

(Hamamatsu Photonics KK) and was tested using an electrochemical actinometer. The

benzoquinone, it is evident that, initially, an increase in concentrations takes place and these reach maxima afterwhich there are decreases. The exception is seen in the assays with the higher chlorophenol concentration, where the photoproduct concentration fails to peak. Hydroquinone concentration attains higher values than benzoquinone, which is fully removed in assays with low initial 4-chlorophenol concentrations suggesting low stability and, consequently, more favoured degradation.

In Figure 2-(D), the curves corresponding to the total sum of 4-chlorophenol, hydroquinone and benzoquinone concentrations, regardless 4-chlorophenol initial concentration, show a continuous decreasing trend, showing that the excilamp is capable of completely degrading the compounds after an appropriate operation time. With the exposure time used in the present work, the residual organic load, represented by the previously mentioned curves, remains between 20 and 30% of the initial 4-chlorophenol concentration corresponding to non-chlorinated compounds, with lower toxicity and adequate for subsequent biodegradation.

#### Theoretical Analysis: Kinetic model for the photodegradation of 4-chlorophenol

Taking into account the experimental results obtained, as well as a previously proposed mechanism [20], a simplified kinetic model has been proposed for the photodegradation process and applied to the main components of the degradation system: 4-chlorophenol, hydroquinone and benzoquinone. A simplified scheme of the process is shown and the kinetic equations are developed and integrated as follows:

- **Reaction scheme**

The simplified reaction scheme includes a parallel mechanism for the 4-chlorophenol (4CP), which is degraded to hydroquinone (HQ) and benzoquinone (BQ), followed by a series mechanism for hydroquinone and benzoquinone. Other minor photoproducts that may be finally degraded to CO<sub>2</sub> and H<sub>2</sub>O, are not considered. The main reactions are the following ones:

	200	$\mathbf{k}_1$	
1 2	201	$4CP \rightarrow HQ$	(1)
3 4	202		
5	203	k <sub>2</sub>	
0 7	204	$4CP \rightarrow BQ$	(1)
8 9	205		
10 11	206	$\mathbf{k}_3$	
12 13	207	$HQ \rightarrow Final Products$	(3)
14 15	208		
16	209	$\mathbf{k}_4$	
17 18	210	$BQ \rightarrow Final Products$	(4)
19 20	211		
21 22	212	where: BO = Benzoquinone: HO = Hvdroquinone	
23	213		
24	214		
26 27	215	Mass balance differential equations for 4-chlorophenol, hydroquinone	and
28 29	216	benzoquinone	
30 31	217		
32 33	218	From the above kinetic scheme the following mass balance	differential
34	219	equations can be formulated:	
35 36	220	equations can be formalated.	
37 38	220		
39 40	221	$\frac{d(4CP)}{dt} = -(k_1 + k_2)[4CP]$	(5)
41 42	222		
43		d[HO] . [OH]	
44 45	223	$\frac{1}{dt} = k_1 [4CP] - k_3 [HQ]$	(6)
46 47	224		
48 49	225		( <b>7</b> )
50 51	225	$\frac{dt}{dt} = \kappa_2 [4CP] - \kappa_4 [BQ]$	(7)
52 52	226		
55	227	Under the following initial conditions:	
55 56	228		
57 58	229	$t = 0; [4CP] = [4CP]_0; [HQ] = [BQ] = 0$	(8)
59 60	230		
61			
62 63			7
64 65			7

Equations (5), (6) and (7) have analytical solution and concentrations of 4CP, HQ and BQ along time are given by:  $[4CP] = [4CP]_0 e^{-(k_1+k_2)t}$ (9)  $[HQ] = \frac{k_1 [4CP]_0}{k_2 - (k_1 + k_2)} \left( e^{-(k_1 + k_2)t} - e^{-k_3 t} \right)$ (10) $[BQ] = \frac{k_2 [4CP]_0}{k_4 - (k_1 + k_2)} \left( e^{-(k_1 + k_2)t} - e^{-k_4 t} \right)$ (11)Conversions of 4-chlorophenol, hydroquinone and benzoquinone For 4CP, HQ and BQ, conversions are defined by the following equations, respectively:  $X_{4CP} = \frac{[4CP]_0 - [4CP]}{[4CP]_0}$ (12) $X_{HQ} = \frac{[HQ]}{[4CP]}$ (13) $X_{BQ} = \frac{[BQ]}{[4CP]}$ (14)These conversion expressions, apart from being used to normalize the value of the different compounds concentrations ranging from 0 to 1, represent the fraction of the initial 4CP degraded after a time t and the fraction of 4CP converted to HQ and BQ, respectively but not degraded to more simple molecular forms. As a consequence, the conversion values give some relevant information related to the state of the 4CP photodegradation process.

From the above defined conversions, Eqs. (12) to (14), we have:

 $[4CP] = [4CP]_0(1 - X_{4CP})$ (15)6 7 8 9  $[HQ] = [4CP]_0 X_{HO}$ (16) $[BO] = [4CP]_0 X_{PO}$ (17)And by substituting in Eqs. (9), (10) and (11):  $X_{4CP} = (1 - e^{-(k_1 + k_2)t})$ (18) $X_{HQ} = \frac{k_1}{k_3 - (k_1 + k_2)} \left( e^{-(k_1 + k_2)t} - e^{-k_3 t} \right)$ (19) $X_{BQ} = \frac{k_2}{k_4 - (k_1 + k_2)} \left( e^{-(k_1 + k_2)t} - e^{-k_4 t} \right)$ (20)Solving the model: fitting procedure and parameters determination. In order to fit the experimental data, Eqs. (18) to (20) have been defined as user functions in the software Sigma Plot V8.2, as follows:  $X_{4CP} = \left(1 - e^{-kt}\right)$ (21) $X_{HO} = a_1 \left( e^{-b_1 t} - e^{-c_1 t} \right)$ (22) $X_{BO} = a_2 (e^{-b_2 t} - e^{-c_2 t})$ (23)The definition of these new parameters, k, a<sub>1</sub>, b<sub>1</sub>, c<sub>1</sub>, a<sub>2</sub>, b<sub>2</sub> and c<sub>2</sub>, related to the model original ones, makes it easier to formulate the previous equations in the Sigma Plot workspace and, in addition, avoids the presence of parameter subtraction in the denominator leading, sometimes, to an error in the parameter determination This

frequently occurs when they have similar values with the difference approaching zero in some of the iterations carried out by the software calculation method.

 The result of fitting the 4CP, HQ and BQ conversion values to Eqs. (21), (22) and (23) is shown in Figure 3-(A), 3-(B) and 3-(C), respectively. The points correspond with the experimental conversion data and the solid continuous lines with the values calculated with the model. Additionally, for all the mentioned compounds, the conversion values obtained with the model have been plotted versus the experimental ones (Figure 4). An excellent degree of agreement is obtained, with  $R^2$ =0.9974. As for the model constants corresponding to Eqs. (21), (22) and (23), their values are presented in Tables 1 to 3, as well as their confidence intervals for a significance level of 95%.

The constants units shown in Tables 1 to 3, according to Eqs. (21), (22) and (23), are min<sup>-1</sup> in all cases, except for the constants  $a_1$  and  $a_2$  from Eqs. (22) and (23), which are dimensionless. In all cases the constant value depend on the initial 4CP concentration, decreasing when this concentration increases. However, a first order reaction constant is theoretically independent from the reactant initial concentration.

A simple explanation for the variation of the constants values with 4CP initialconcentration is proposed below.

# 311 Model parameters and Lambert-Beer law

The photodegradation of 4CP as well as the process intermediates requires radiation adsorption to take place. When a radiation of intensity  $I_0$  penetrates a tube containing the 4CP solution, part of this initial radiation is absorbed and another part is transmitted through the sample. The following equation applies:

 $I_0 = I_A + I_T \tag{24}$ 

319 Where:

- $I_A = absorbed intensity$
- $I_T$  = transmitted intensity

323 On the other hand, according to Lambert-Beer Law, when a radiation follows 324 a distance L (optical pathway), through a sample of concentration  $C_A$  in an absorptive 325 species, A, with a molar absorptivity  $\varepsilon$ , the transmitted intensity is given as follows:

$$I_{\rm T} = I_0 e^{-\varepsilon L C_{\rm A}} \tag{25}$$

By substituting (25) in (24) the following value for  $I_A$  can be obtained:

$$I_{A} = I_{0} \left( 1 - e^{-\varepsilon L C_{A}} \right)$$
(26)

Only the absorbed intensity can produce a photochemical reaction. Considering that all the species presented (4CP, HQ, BQ and minor degradation products) have a similar molar absorptivity value, then the absorbed intensity is given by the equation (26), being  $\varepsilon$  an average value for all the compounds, and C<sub>A</sub> the total concentration, which can be taken approximately as the initial 4CP concentration, [4CP]<sub>0</sub>, since all molecular species presented at the beginning of the reaction are formed in the ratio 1:1 from 4CP.

Based on these hypotheses, the 4CP removal rate will be proportional to the absorbed intensity fraction for this compound which is proportional to the product of the total absorbed intensity and the molar fraction of 4CP, as follows:

 $\frac{d[4CP]}{dt} = -\alpha I_0 \left(1 - e^{\epsilon L[4CP]_0}\right) \frac{[4CP]}{[4CP]_0}$ 

Where α is a proportionality constant. The previous equation can be rewritten in thefollowing way:

$$\frac{d[4CP]}{dt} = -k[4CP]$$
(28)

351 This equation corresponds to an apparent first order kinetic where constant k depends352 on the 4CP initial concentration as indicated:

(27)

$$k = \alpha I_0 \frac{\left(1 - e^{-\varepsilon L[4CP]_0}\right)}{\left[4CP\right]_0}$$
(29)

This is the kind of expression:

$$k = a \frac{\left(1 - e^{-b[4CP]_0}\right)}{[4CP]_0}$$
(30)

Using the Sigma Plot V8.2 software, the values of 4CP k constant have been fitted to equation (30) and the values  $a = 0.366 \text{ mM min}^{-1}$  and  $b = 96.58 \text{ mM}^{-1}$ obtained with a regression coefficient of R = 0.987. The results in Figure 5-(A) show a good degree of agreement. Figure 5-(B) shows the calculated values of k plotted against the experimental ones. A similar dependence with initial 4CP concentrations has been assumed for the other constants and this hypothesis has been validated in Figure 5-(C), where it is evident that these constants are proportional to the k values. It can also be observed from Figure 5-(C) that the lines corresponding to the parameters b<sub>1</sub> and b<sub>2</sub> are very close, which is in good agreement with the fact that both parameters are theoretically equivalent to the sum  $k_1 + k_2$ . In addition, the value of  $c_2$ is considerably higher than the other constants values, due to the higher capacity of degradation of BQ.

When the proportionality between the model parameters and the constant k were proved, the theoretical values of these parameters was calculated and plotted, together with the experimental ones, against the 4CP initial concentration. The result is shown in Figure 5-(D) providing validation of the proposed hypotheses.

### 378 Conclusions

 The experimental data show that by using excilamps, total 4-chlorophenol photodegradation can be achieved without additional use of catalysts. For the main photoproducts, hydroquinone and benzoquinone, the removal efficiency is higher at low chlorophenol concentrations, and residual concentrations, equivalent to about 20–

30% of initial 4-chlorophenol amount, remain with higher concentration used. With the aim of process simulation and scale-up, a kinetic model has been developed and validated with the experimental data, the model parameters being determined from the fitting of the experimental data to the model. A good fitting between experimental and calculated data was obtained, with a standard deviation of 1.63% and  $R^2 = 0.9974$ . which confirms the validity of the model and the parameters used. Additionally, the application of the Lambert-Beer law results is an approximated interpretation for the variation of the model parameters with initial 4-chlorophenol concentrations.

- Acknowledgements

This study was made possible with funding from the Royal Society of Edinburgh to 

G. Matafonova and from a grant to M. Gómez and M. D. Murcia from Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain).

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Figure 1



Figure 2



Figure 3



Figure 4



Figure 5

### **Figure captions:**

Figure 1. Emission spectrum of KrCl excilamp with the maximum wavelength of 222 nm. The intensity (I) is given in relative units (r.u.).

Figure 2. Progress curves for 4-chlorophenol, (A), hydroquinone, (B), benzoquinone, (C), and for the sum, (D), for the different 4-chlorophenol concentrations tested: ◆ 0.389 mM; ■ 0.778 mM; ▲ 1.167 mM; X 1.946 mM; \* 2.724 mM and • 3.891 mM.

**Figure 3.** Conversion variation with time for 4-chlorophenol, (**A**), hydroquinone, (**B**), and benzoquinone, (**C**), for the different 4-chlorophenol concentrations tested:  $\blacklozenge$  50 mg L<sup>-1</sup>;  $\blacksquare$  100 mg L<sup>-1</sup>;  $\blacktriangle$  250 mg L<sup>-1</sup>; x 500 mg L<sup>-1</sup>; + 350 mg L<sup>-1</sup>; \* 500 mg L<sup>-1</sup>; - model.

**Figure 4.** Experimental and calculated conversion of 4-chlorophenol, hydroquinone and benzoquinone, for all experimental conditions assayed.

**Figure 5.** Fit of experimental values of k to Eq. (30), (**A**); experimental and calculated values of k, (**B**); dependence of the model parameters on k, (**C**), and dependence of the model parameters on initial 4-chlorophenol concentration, (**D**).

[4CP]₀ (mg L <sup>-1</sup> )	[4CP]₀ (mM)	k (min⁻¹)
50	0.389	1.004 ± 0.024
100	0.778	$0.445 \pm 0.007$
150	1.167	0.222 ± 0.006
250	1.946	0.137 ± 0.009
350	2.724	0.088 ± 0.005
500	3.891	0.048 ± 0.001

 Table 1. Model parameters for 4-chlorophenol.

[4CP]₀ (mg L <sup>-1</sup> )	[4CP]₀ (mM)	a <sub>1</sub> (dimensionless)	b₁ (min⁻¹)	c₁ (min⁻¹)
50	0.389	1.373 ± 0.215	0.117 ± 0.025	0.355 ± 0.061
100	0.778	0.448 ± 0.026	0.035 ± 0.007	0.547 ± 0.054
150	1.167	0.388 ± 0.046	0.030 ± 0.005	0.338 ± 0.057
250	1.946	0.276 ± 0.060	0.020 ± 0.006	0.202 ± 0.056
350	2.724	0.212 ± 0.041	0.000 ± 0.003	0.094 ± 0.024
500	3.891	0.188 ± 0.044	$0.000 \pm 0.003$	0.046 ± 0.012

 Table 2. Model parameters for hydroquinone.

[4CP]₀ (mg L <sup>-1</sup> )	[4CP]₀ (mM)	a <sub>2</sub> (dimensionless)	b₂ (min⁻¹)	c₂ (min⁻¹)
50	0.389	1.041 ± 0.150	0.510 ± 0.026	1.028 ± 0.060
100	0.778	0.137 ± 0.012	0.045 ± 0.010	2.254 ± 0.150
150	1.167	$0.095 \pm 0.005$	0.019 ± 0.003	1.113 ± 0.225
250	1.946	$0.062 \pm 0.002$	0.009 ± 0.001	0.772 ± 0.087
350	2.724	0.047 ± 0.002	0.008 ± 0.001	0.512 ± 0.049
500	3.891	0.034 ± 0.002	0.000 ± 0.001	0.382 ± 0.053

 Table 3. Model parameters for benzoquinone.