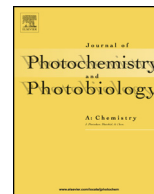




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## A detailed kinetic study of the direct photooxidation of 2,4,6-trichlorophenol



Jose Ángel Pino-Chamorro, Tamás Ditrói, Gábor Lente\*, István Fábán

Department of Inorganic and Analytical Chemistry, University of Debrecen, P.O.B. 21, H-4010, Debrecen, Hungary

### ARTICLE INFO

#### Article history:

Received 26 January 2016

Received in revised form 26 July 2016

Accepted 26 July 2016

Available online 27 July 2016

#### Keywords:

Quantitative photochemistry

Light intensity dependence

Chlorophenols

Temperature dependence

Photochemical mechanism

Kinetics

Photodegradation

2,4,6-trichlorophenol

Polychromatic light

Mechanism of reaction

Quantum yield

### ABSTRACT

The direct photodegradation of 2,4,6-trichlorophenol (TCP) by UV–vis light was studied in aqueous solution in order to analyze the mechanism of the photochemical process and to determine the kinetic parameters including the quantum yield. Based on initial rate studies at different overall volumes and illumination patterns, it was proved that the rate of the process is directly proportional to the intensity of irradiating light. A significant, but moderate acceleration of the reaction rate with increasing temperature was revealed between 5.0 and 35.0 °C, which could be interpreted readily by assuming that the excited state of TCP is involved in two competing processes. High pressure liquid chromatography and mass spectrometry provided us information on the nature of the intermediates and the products formed. 2,6-Dichloro-1,4-benzoquinone, 3,5-dichloro-2-hydroxy-1,4-benzoquinone and 2,6-dichlorohydroxyquinone were detected as products and/or intermediates, and there were also hints of the formation of 3,5-dichlorobenzene-1,2-diol and 3,5-dichloro-1,2-benzoquinone. A possible degradation mechanism is proposed to interpret the kinetic findings.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Chlorophenols are common and persistent environmental pollutants produced in a number of industrial processes. They are not decomposed by usual waste water treatment techniques, and the development of suitable degradation methods has attracted the attention of a large and diverse research community [1–22]. The use of a specifically designed iron complexes for the activation of hydrogen peroxide seems to be a particularly successful strategy [2,7,11]. In these cases, no dioxins are produced among the oxidation products [7], which is a major concern with other waste treatment methods, for example the direct incineration of solid chlorophenols. The use of ozone [5,6], Fenton's reagent [5], peroxidase enzyme [13], electrooxidation [21], or even simple absorption processes [22] are also possible alternatives in the abatement of chlorophenol-containing waste.

Illumination with UV or visible light can also assist such processes. This is typically done using heterogeneous photocatalysts such as TiO<sub>2</sub> [1,15,19], spinels [18,20] and g-C<sub>3</sub>N<sub>4</sub> [17]. Because of the limited light absorption of chlorophenols (which all

form colorless solutions), their direct photolysis was a lot less intensely investigated [3–5]. The iodine-sensitized photooxidation was also considered as a possible alternative [14]. An interesting and unintuitive observation was also made during a kinetic study of the chemical oxidation of chlorophenols: the rate of reaction is influenced by light, even if it is in the visible range [8]. The reason for this phenomenon was understood to be the photochemical transformations of quinones, which form as intermediates in chlorophenol oxidation [8,23,24]. Therefore, an adequate kinetic and mechanistic study of the chemical oxidation of chlorophenols must be done in the dark in order to separate the thermal and photolytic components of the process [9,11,12].

The accelerating effect of light on chlorophenol oxidation also implies that their photochemical properties must be thoroughly investigated together with the known intermediates of the process. Recently, experimental techniques were developed for the online monitoring of photochemical processes using diode array spectrophotometers alone or with external light sources [9,25–29]. These techniques use online monitoring and can yield kinetic data on photoreactions that have very high time resolution and thus be evaluated by up-to-date kinetic analysis methods. They facilitated detailed studies on direct photolytic processes [23,29] and photochemically initiated chain reactions [25]. The

\* Corresponding author.

E-mail address: [lenteg@science.unideb.hu](mailto:lenteg@science.unideb.hu) (G. Lente).

experience gained in a number of different studies was summarized in a review article a few years ago [26].

In this paper, we report a detailed kinetic study on the photochemical reaction of 2,4,6-trichlorophenol, which has the widest industrial applications and is the most important among the chlorophenols [7,11,14]. A new, custom-built photoreactor was used to carry out this quantitative study, which improves the applicability of online monitoring of photochemical reactions compared to the earlier instruments used for this purpose [26].

## 2. Experimental section

### 2.1. Materials

Solid 2,4,6-trichlorophenol (TCP) was purchased from Sigma-Aldrich and used as received. The concentration of TCP in our experiments was typically around  $2.0 \times 10^{-4}$  M. All the experiments were carried out in 0.010 M phosphate and borax buffers at 25.0 °C (except some experiments to study the dependence on temperature). The buffer stock solutions were prepared using sodium phosphate dihydrate (Reanal) and titrated to pH 7.04 with NaOH purchased from VWR, and using disodium tetraborate (Reanal) at pH 9.2. All stock solutions and samples were prepared with double deionized, ultrafiltered and distilled water from a Millipore Q system.

### 2.2. Instruments and software

The excitation light source (AvaLight-LDXE), the detecting light source (AvaLight DHc), the detector (Avaspec-ULS2048L-TEC-RS) and all other optical cables of the photoreactor used in this study were purchased from Avantes, Netherlands. The light source (excitation lamp) has a maximum brightness of 385 mW optical output in the 170–1100 nm range (Fig. S1 in the Supplementary information). A FOS-1-Inline fiber optic switch was used, which allowed us to switch on and off the focused polychromatic light beam that provided the driving source of the photoreaction. Moreover, the halogen and deuterium lamps of the detecting light source can be independently switched on and off. The sample holder used was equipped with a temperature controller Peltier unit configured for absorbance measurement. The cell holder was modified with vertically movable detection ports to avoid scattered or fluorescent light entering the detector. The spectrophotometer (detector) used was AvaSpec-ULS2048L-TEC-RS, which is an internally cooled CCD detector with variable slit size. Standard four-sided quartz cuvettes (optical path length: 1.000 cm) were used in all experiments. The solution in the cuvette was stirred using a 4 mm × 2 mm × 2 mm Teflon-coated stirring rod with the built-in magnetic stirrer of the sample holder to keep the solutions homogeneous at all times. The detailed description and performance characterization of this novel photoreactor was published in a recent technical note [30].

Ferrioxalate actinometry was performed following a published method [28]. A flow of nitrogen gas was circulated through the cell holder to avoid the condensation of water in the walls of the cell during the temperature dependence study. In these experiments, the cuvette was kept in the sample holder during 10 min before starting the experiments to ensure that the solution temperature was homogeneous. Kinetic traces were fitted and other least squares analyses were carried out by the software Scientist [31]. Particularly, initial rates of absorbance change ( $\nu_0$  values) were determined by using a polynomial probe function to fit the experimental kinetic trace. The coefficient of the first order term of the polynomial gives the initial rate in this process. Further details of this method can be found in the literature of chemical kinetics [32].

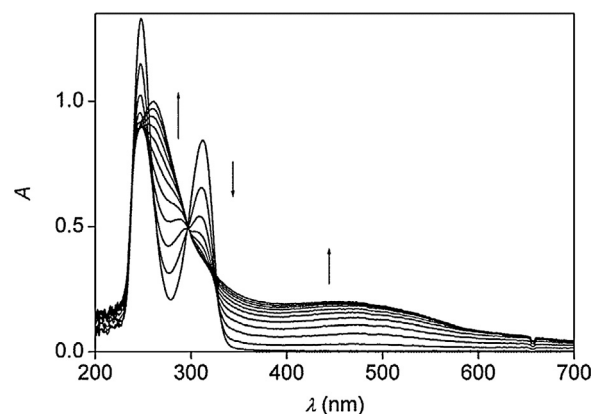
TCP and its degradation products were separated and analyzed by a Shimadzu LC-10AP HPLC system equipped with a Shimadzu SPD-M10A diode array detector, a Luna C18 (2) (3  $\mu$ m) 100 × 4.6 mm reverse phase column and using 7:3 (V/V) mixture of methanol and water as the mobile phase. The flow rate was set at 1.0 mL/min. The intermediates formed from TCP degradation were identified by comparing their retention time and spectrum with the external standards purchased from commercial sources. Under the conditions described, the retention times of the external standards were: TCP: 10.65 min, 2,6-dichloroquinone (DCQ): 2.75 min.

ESI-MS measurements were carried out with a Bruker micrO-TOF<sub>Q</sub> mass spectrometer equipped with a quadrupole and time-of-flight (Q-TOF) analyzer in positive ion mode. The nebulizer pressure was set to 6 psi (0.41 bar), N<sub>2</sub> was used as drying gas at 4 L/min, the temperature was maintained at 160 °C, and the applied capillary voltage was –3.0 kV. The typical error of mass measurement was below 0.005 in the *m/z* range from 80 to 600. Spectra were accumulated and recorded by a digitizer at a rate of 2 GHz.

## 3. Results and discussion

### 3.1. Preliminary observations

In the pH range used in the present study (pH = 7.04–9.2), 2,4,6-trichlorophenol has two UV bands centered at 254 and 312 nm that are characteristic of the dissociated anionic form ( $pK_a = 6.15$ ) [9,12]. The initial observations confirm that the photoreaction can be driven even by a commercial diode array spectrophotometer, the photochemical use of which is now well documented [26]. The photodegradation of TCP was followed in a custom built photoreactor as described in the Experimental section. A cuvette containing a solution of TCP was illuminated and the UV-vis absorption spectrum was scanned repeatedly in the range of 230–700 nm at pH 7.05 and 9.25 using phosphate and borax buffers at 30 s intervals. The photooxidation of TCP at these two pH values had similar rates. An earlier research report found a large difference between the TCP oxidation rates at pH 7.4 and 9.0 [13]. However, that must have been caused by the properties of the peroxidase oxidant used in that study [13] as TCP itself undergoes no major change in this pH region (its  $pK_a$  is 6.15). Figs. S2 and S3 show experiments in the two different media and also confirm an important point: the kinetic observations do not depend on the concentration of the buffer used in any significant way, so the buffers are most probably innocent in this case.



**Fig. 1.** Typical spectral changes in an irradiated aqueous solution of 2,4,6-TCP. [TCP] = 0.2 mM; [phosphate buffer] = 0.010 M; path length 1.000 cm;  $V = 3.00$  cm<sup>3</sup>;  $T = 25.0$  °C; overall reaction time: 300 min).

Download English Version:

<https://daneshyari.com/en/article/6492923>

Download Persian Version:

<https://daneshyari.com/article/6492923>

[Daneshyari.com](https://daneshyari.com)