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Photodecomposition of Chlorophenols in Aqueous Medium in Presence of Hydrogen Peroxide

P. N. Moza,[1] K. Fytianos,[2] V. Samanidou,[2] and F. Korte[1,3]

[1]Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, D-8050 Freising-Attaching, F.R.G.; [2]University of Thessaloniki, Environmental Pollution Control Laboratory, Thessaloniki, Greece, and [3]Technische Universität München, Institut für Chemie, D-8050 Freising-Weihenstephan, F.R.G.

Chlorophenols have been studied for their influence on the natural environment because of their importance in the manufacture of fungicides and herbicides. Their presence in natural waters (Burttschelt et al. 1959) is not only because they are industrial effluents but also they are formed by the chlorination of waste waters containing phenolic compounds. Their fate in waste waters depends besides biotic processes also on photochemical processes. Abiotic processes in aqueous phase may proceed via direct photolysis as well as via secondary reactions with oxygen species like hydroxy and peroxy radicals (Mill et al. 1980).

Direct photolysis of mono and dichlorophenols in aqueous solution have been reported in the literature (Boule et al. 1982; Krijgsheld and Gen 1986). But very little is known about the indirect processes initiated by naturally occurring active species of oxygen on the fate of higher chlorinated phenols. The objective of our work was to obtain information about the reactivity and degradation products of monochlorophenol (2-chlorophenol), dichlorophenol (2,4-dichlorophenol) and trichlorophenol (2,4,6-trichlorophenol) with hydroxy radicals generated in aqueous solutions by photolysis of hydrogen peroxide at wavelength $\lambda \geqslant 290$ nm.

MATERIALS AND METHODS

2-chlorophenol (98 % purity), 2,4-dichlorophenol (98 % purity) and 2,4,6-trichlorophenol (99 % purity) were obtained from E. Merck, Darmstadt, F.R.G. and hydrogenperoxide (30 %) was obtained from Fluka, Neu-Ulm, F.R.G. Experiments with 2-chlorophenol (12.6 ppm), 2,4-dichlorophenol (11.3 ppm) and 2,4,6-trichlorophenol (10.0 ppm) were carried out in deaerated distilled water. The aqueous solutions of respective phenols were irradiated in presence of H_2O_2 by a HPK 125 W mercury medium pressure lamp (Philips). The lamp was jacketed with a water cooled pyrex filter.

Rate of disappearance of the chemicals under investigation at various intervals of time was directly measured with a high per-

Send reprint requests to P.N. Moza at the above address.

formance liquid chromatography (HPLC), Hewlett Packard model 1090, with a diode-array-detector, fixed at 220 nm. The column used was a Shandon reverse phased column (RP 18, 25 cm long); mobile phase methanol:water (1:1) for mono and dichlorophenol and methanol:water (4:1) for 2,4,6-trichlorophenol, flow 1 ml/min. After 3 hours of irradiation at $\lambda \geqslant 290$ nm the reaction mixtures were extracted with diethylether. The diethylether extracts were concentrated in a rotary evaporator at room temperature. Product analysis of the concentrated extracts was performed with GC/MS combination supplied by Hewlett Packard (HP) model 59928. A capillary HP column 25 m x 0.35 mm i.d. coated with 5 % phenylmethylsilicon was used for chromatographic separation. The column was programmed from 70° to 250°C at a rate of 5°C/min. and helium was used as a carrier gas. The mass spectra were recorded at 70 eV.

Dark reactions were carried for a period of 4 hours using hydrogenperoxide (55 ppm), monochlorophenol (12.6 ppm), dichlorophenol (11.3 ppm) and trichlorophenol (10.0 ppm) in distilled water which was purged with nitrogen.

RESULTS AND DISCUSSIONS

Fig. 1 and Fig. 2 show the results of photodegradation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in presence and in absence of H_2O_2 respectively. The degradation curve demonstrates that the photolysis of chlorophenols was strongly enhanced by H_2O_2. 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol disappears nearly 80 %, 95 % and 100 % respectively in presence of 55 ppm H_2O_2 in 2.5 to 3 hours. Disappearance of these chemicals by direct photolysis is reasonably less 13 %, 2 % and 15 % respectively which is in accordance with the reported work (Omura, Matsuura 1971). The reason for the quantitative disappearance of these chlorophenols is due to the powerful oxidative action of the hydroxyl radical which is formed from hydrogen peroxide by photolysis.

It is reported in the literature (Yasuhara et al. 1977) that high concentration of H_2O_2 are required to decompose 2-chlorophenol. We, in our experiments observed that 55 ppm of H_2O_2 are enough to photolyse 2-chlorophenol by 50 % in 1 hour. Fig. 1 shows a nonlinear relationship between the residual chlorophenols and the irradiation time. Our results show that these reactions are not first order kinetics because plots of lnc of residual phenols as function of time are also nonlinear. Graphic representation of the reciprocal of the concentration as a function of time shows a fair linear relationship consistant with the kinetics of the second order reaction. The rate constants were calculated using the equation

$$K'' = \frac{\frac{1}{C_1} - \frac{1}{C_0}}{t_1 - t_0} \qquad \begin{array}{l} C_0 = \text{concentration at time } t_0 \\ C_1 = \text{concentration at time } t_1 \end{array}$$

and the values calculated are $0.33 \times 10^{-4} \mathrm{sec}^{-1}$, $1.1 \times 10^{-4}\ \mathrm{sec}^{-1}$

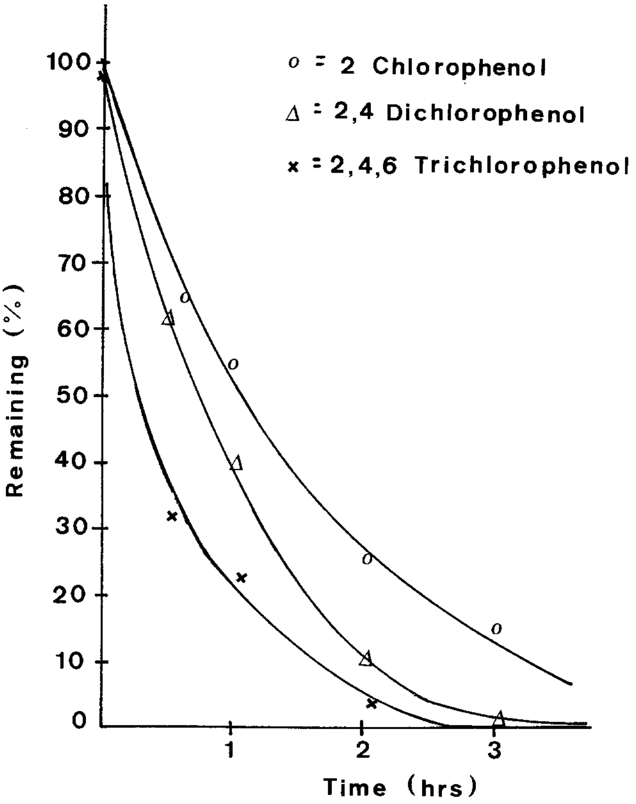

Figure 1: Change of 2-chloro, 2,4-dichloro and 2,4,6-trichlorophenol content in water after irradiation with UV-light at 290 nm in presence of H_2O_2

and 3.3 x 10^{-4} sec^{-1} for 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol respectively. From this data, it is seen that 2,4,6-trichlorophenol photolyses faster than 2-chloro and 2,4-dichlorophenols in presence of H_2O_2. Here the position of the chlorine on the ring strongly influences the transformation which is also the case by direct photolysis (Krijgsheld and Gen 1986). 2-chlorophenol in presence of H_2O_2 at 290 nm degrades into catechol (I) and dihydroxy chlorobenzol (II), Fig. 3.

Formation of catechol (I) from 2-chlorophenol proceeds via C-Cl scission and the attack with OH radical. However, in another study (Boule et al. 1982) pyrocatechol was reported as a main product by direct photolysis of 2-chlorophenol in aqueous solution at 296 nm. Many investigators have intimated that the OH radical resembles electrophillic reagents in many of its reactions and it consequently shows preference for attach at positions of high electron density in aromatic rings (Volkert and Schulte-Frohlinde 1968). Thus in phenols, owing to the strong +M-effect of the OH-group, the major points of attack are expected at the ortho and para positions. Therefore formation of compound II is explained by the attack of OH radical on the para position of the

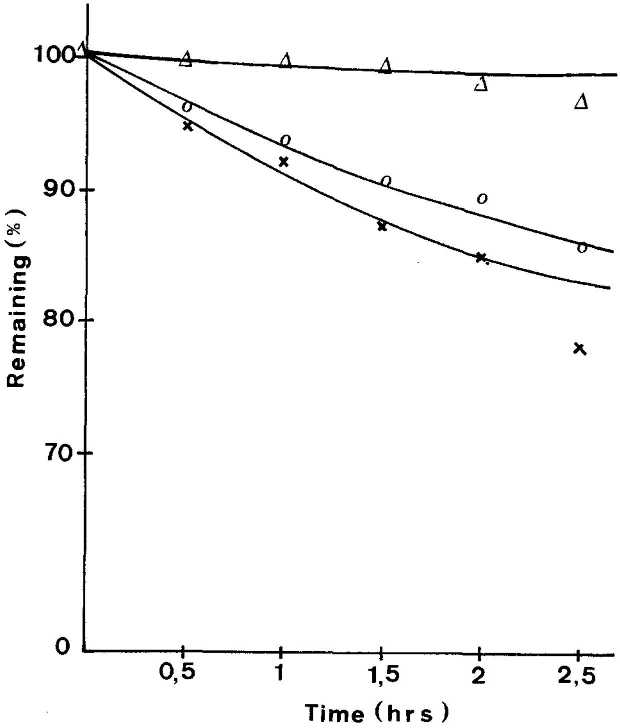

Figure 2: Change of 2-chloro, 2,4-dichloro and 2,4,6-trichlorophenol content in water when irradiated with UV-light 290 nm in absence of H_2O_2

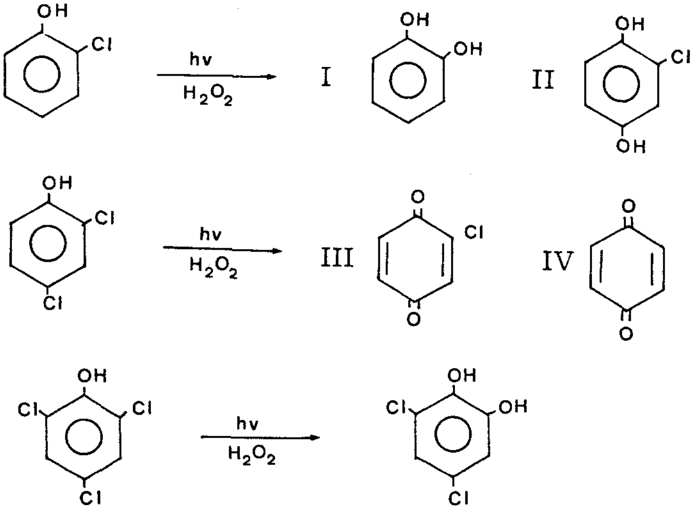

Figure 3: Degradation products of 2-chloro, 2,4-dichloro and 2,4,6-trichlorophenol identified after irradiation with UV-light in presence of H_2O_2

benzene ring due to high electron density at this position caused by +M-effect of phenolic OH on the ring.

Upon irradiation of 2,4-dichlorophenol at 290 nm in presence of H_2O_2 formation of 1,4-hydroquinone (IV) and chlorohydroquinone (III), Fig. 3, have been observed, and no 4-chlorocatechol and/or 2 chlorohydroquinone have been detected. Here besides homolytic C-Cl scission and oxidation also dechlorination take place. In the case of 2,4,6-trichlorophenol we obtained 4,6-dichlorocatechol, compound V, Fig. 3. Here again homolytic C-Cl scission and attack with OH radical leads to the formation of compound V. Quantification of one or more of the photooxidation end products of 2-chloro, 2,4-dichloro and 2,4,6-trichlorophenol posed problems due to small amounts of these compounds.

No further oxidation or dehalogenation of 2,4,6-trichlorophenol molecule was observed. Experiments with mono, di- and trichlorophenols in aqueous solution with H_2O_2 in dark for a period of 4 hours upon analysis showed neither any change in the original concentrations of the chemicals nor any other product. From these experiments it should be concluded that indirect processes initiated by OH radicals play an important role in the photolysis of chlorinated phenols leading to polyhydroxy, carbonyl and dehalogenated products which might bear some relevance to toxic effects to aquatic life.

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