

Kinetics of Acid-Assisted Hydrolysis of Pentachlorophenol in Aqueous Media¹

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Abstract—The rate of acid catalyzed hydrolysis of pentachlorophenol (PCP) can be described by the general equation $-d[\text{PCP}]/dt = k_{\text{exp}}[\text{PCP}]$. The experimental pseudo-first order rate constant generally increases with increase of the H^+ concentration, but this dependence has a complex character. A kinetic model, which takes into account the $\text{p}K_{\text{a}}$ of PCP and a combination of catalyzed and uncatalyzed reactions, was suggested. This model is consistent with experimental results in the whole range of pH studied.

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INTRODUCTION

Pentachlorophenol (PCP) is a chlorinated hydrocarbon insecticide and fungicide. It is primarily used to protect timber from fungal rot, but may also be used as a preharvest defoliant, as a general preemergence herbicide, and as a biocide in industrial water systems [1]. PCP is a restricted use pesticide; it is categorized as toxicity class II—moderately toxic with respect to humans and animals [2, 3]. However, PCP may be highly to very highly toxic to aquatic organisms [4]. Some species of fish and algae can accumulate PCP up to 10000 times compared to the concentration of PCP in the surrounding water [5]. In the aqueous environment, PCP biodegrades mainly at the surface, with a half-life ranging from hours to days [6]. However, low concentrations of PCP are commonly found in natural aqueous environments [7, 8]. According to [8] 88.9% of samples taken from the urban watershed contained PCP. It is believed that, when released into water, it will be partly absorbed by sediments and particulate matter with consequent biodegradation. However, the fate of dissolved PCP in the main water body remains unknown. Although the solubility of PCP reported in different sources differs significantly, from as low as 8 mg/l [9] to as high as 80 mg/l [9, 10], it is clear that at least a portion of PCP can exist in water in its pure dissolved state. Taking into account the high toxicity of PCP to aquatic life, stability of water-dissolved PCP is of great interest. In this study the kinetics of PCP hydrolysis in water have been studied at elevated temperatures and low pH level, with consequent extrapolation of data into moderate pH and temperature conditions.

EXPERIMENTAL

The reaction kinetics was monitored by following the decay of PCP during the course of reaction. The concentration of PCP was measured by Gas Chromatograph-Mass Spectrometer (GC-MS). The GC-MS used was Fisons Instrument, GC 8000 series, Mass Detector MD 800, 70 eV, capillary column SPB 608, 30 m, ID 0.25 mm, carrier gas He, injector 250°C, column 178°C. Hydrolysis rates were studied in aqueous solution over a wide range of pH, ionic strength, and temperature conditions. Reactions were carried out in a 250 ml glass reaction vessel with a water-cooled condenser at 100°C (boiling), unless stated otherwise. Into the reaction vessel was placed 150 ml of PCP solution with the initial concentration 10 mg/l; during the course of the reaction, aliquots of solution (25 ml) were taken, fast cooled with an ice-water mixture, acidified if necessary to pH 2 (0.5 to 3 ml of 1 M HCl), and extracted with 2 ml of dichloromethane. Experiment times varied from 3 h (0.5 M HCl, 100°C) to 32 days (various pH, 30°C). For analysis of possible intermediates and final products, 100 ml of the reaction mixture was extracted (after acidification) with 1 ml of benzene or n-hexane and analyzed by GC-MS with the programmed temperature of the column being 80°C for 10 min, 9 K/min until 178°C, then 60 min at 178°C. All chemicals used were of analytical grade (>99%), except PCP (98%, Aldrich), benzene (crystallizable, BDH Laboratory Chemicals), and sulfuric acid (98%, Fisher Scientific). All solutions were prepared with bidistilled water. The stock solution of PCP in methanol (2.497 g/l) was kept in the dark, and 1 ml of this solution was used to prepare 250 ml of the reaction mixtures. Constant ionic strength (0.1 mol/l) was adjusted by adding corresponding quantities of NaCl. Experiments in 0.5 M HCl, 0.01 M NaOH, 0.01 M HCl, 0.001 M HCl, and

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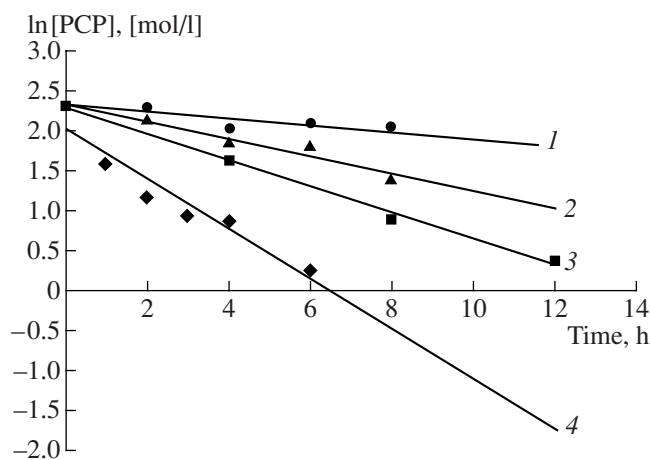


Fig. 1. Hydrolysis of PCP at different HCl concentrations at 100°C and ionic strength 0.1 mol/l. ((1) 0.1 M NaCl, (2) 0.001 M HCl, (3) 0.01 M HCl, (4) 0.1 M HCl).

pure water were also carried out without ionic strength adjustment.

RESULTS AND DISCUSSION

Neutral and Basic Media

The concentration of PCP in pure water, 0.01 M HCl, and 0.01 M NaOH aqueous solutions did not change at room temperature after 32 days in the darkness. Even after 15 h of boiling, neutral and basic aqueous solutions of PCP did not show any significant traces of decomposition. Therefore, it was impossible to study the stability of PCP to hydrolysis at conditions close to environmental (neutral solutions, reasonable temperature). However, the concentration of PCP in 0.01 M HCl decreased at elevated temperature, showing that acid catalyzed reaction kinetics could be studied, at least at elevated temperature, with consequent extrapolation of results to normal temperature and neutral pH.

Decomposition in Acidic Solutions

Experimental data show that the reaction of PCP disappearance is first order with respect to the concentration of PCP

Table 1. Rate constants and half-lives for the destruction of PCP in solutions of varying $[H^+]$ at 100°C

[HCl], mol/l	k_{exp} , h^{-1}	Half-life, h
—	0.050 ± 0.008	13.8
0.001	0.11 ± 0.01	6.3
0.01	0.16 ± 0.02	4.3
0.1	0.31 ± 0.03	2.2
0.5	1.13 ± 0.05	0.61

$$-d[\text{PCP}]/dt = k_{\text{exp}}[\text{PCP}]. \quad (1)$$

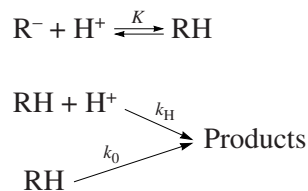
At constant HCl concentration, pseudo-first order rate constant k_{exp} can be calculated from the integrated rate equation

$$\ln[\text{PCP}] = -k_{\text{exp}}t + \text{const.} \quad (2)$$

Data in Fig. 1 illustrate that Eq. (2) describes the kinetics of disappearance of PCP in the whole range of concentrations studied. Experimental rate constants and half-lives at 100°C are presented in Table 1.

The reaction shows a very small influence of ionic strength. The rate constant at 0.1 M NaCl concentration was exactly the same as the rate constant in pure water (not shown), although the ionic strength was very different for those two points. Differences of the rate constants measured in 0.001 and 0.01 M HCl without adjustment of ionic strength and at 0.1 M ionic strength were within the experimental error border. It means that there is no necessity to keep ionic strength constant and that extrapolation to higher pH can be done from the data obtained at high ionic strength. Data presented in Fig. 1 and in Table 1 illustrate a definite increase of the experimental rate constant at increasing concentrations of HCl. However, the rate constant measured at a concentration of HCl equal to 0.0001 M (not shown) was indistinguishable from the rate constant obtained at 0.001 M of HCl. At the same time, any lower concentration of HCl (less than 10^{-4} M, not shown) did not differ from the rate constant obtained in pure water (or 0.1 M NaCl solution). To explain these results, the acidic properties of PCP should be taken into account. According to [11] pK_a of PCP is 4.75. Simple calculations show that at an initial concentration of PCP 10 mg/l (3.76×10^{-5} M) without any addition of acid, the concentration of H^+ in solution is 1.84×10^{-5} M. Addition of HCl in the concentration range 10^{-6} – 10^{-5} M does not influence this already relatively high H^+ concentration very much.

Taking into account the relatively weak influence of the HCl concentration on the experimental rate constant (Table 1), it is perfectly clear that only after addition of at least 10^{-4} M of HCl (in which the proton concentration is about 5 times larger than in the solution of PCP in pure water) are we expected to see an increase in the k_{exp} . This however does not explain the strange, nonlinear increase of the experimental rate constant at higher concentrations of HCl added. To explain this we suggest a kinetic scheme, which takes into account catalytic and noncatalytic pathways and the equilibrium between ionic and molecular forms of PCP.



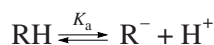
Scheme 1.

$$\frac{-d[\text{RH}]}{dt} = (k_0 + k_{\text{H}}[\text{H}^+])[\text{RH}] = \frac{d[\text{Products}]}{dt}. \quad (3)$$

In Eq. (3) [RH] is the concentration of PCP in water in molecular form. However, in kinetic experiments, the total concentration of PCP was measured

$$[\text{RH}]_{\Sigma} = [\text{RH}] + \text{R}^-.$$

To compare the experimental rate constant with the rate constant in Eq. (3), we need to make some rearrangements which relate the total concentration of PCP $[\text{RH}]_{\Sigma}$ and the concentration of PCP in solution in molecular form [RH] (see Scheme 2). Combined solution of material balance and acidity constant equations gives this relation (Scheme 2) and leads to Eq. (4).



$$[\text{RH}]_{\Sigma} = [\text{RH}] + [\text{R}^-] \quad \text{Material balance}$$

$$K_a = \frac{[\text{R}^-][\text{H}^+]}{[\text{RH}]} \quad \text{Acidity constant}$$

$$[\text{RH}]_{\Sigma} = \frac{K_a + [\text{H}^+]}{[\text{H}^+]}[\text{RH}].$$

Scheme 2.

$$\begin{aligned} \frac{-d[\text{RH}]_{\Sigma}}{dt} &= k_{\text{exp}}[\text{RH}]_{\Sigma} \\ &= k_{\text{exp}} \left(\frac{K_a + [\text{H}^+]}{[\text{H}^+]} \right) [\text{RH}] = \frac{d[\text{Products}]}{dt}. \end{aligned} \quad (4)$$

Comparison of Eqs. (3) and (4) gives the relation between experimental pseudo-first order rate constant k_{exp} and theoretical rate constants k_0 and k_{H}

$$k_{\text{exp}} \frac{K_a + [\text{H}^+]}{[\text{H}^+]} = k_0 + k_{\text{H}}[\text{H}^+]. \quad (5)$$

From this equation it is possible to determine the theoretical rate constants k_0 and k_{H} graphically and then calculate the expected experimental rate constant for any concentration of $[\text{H}^+]$. Figure 2 shows that our experimental data can be described quite well by Eq. (5) and gives $k_0 = 0.12 \text{ h}^{-1}$ and $k_{\text{H}} = 2.02 \text{ L mol}^{-1} \text{ h}^{-1}$.

The rate constants k_0 and k_{H} obtained from the graph in Fig. 2 were used to calculate the expected rate constant (k_{Σ}) at 100°C at different $[\text{H}^+]$ using Eq. (6).

$$k_{\Sigma} = \frac{k_0[\text{H}^+]}{K_a + [\text{H}^+]} + \frac{k_{\text{H}}[\text{H}^+]^2}{K_a + [\text{H}^+]}. \quad (6)$$

Comparison of these k_{Σ} with k_{exp} (Table 2) shows remarkably good results and allows us to conclude that the scheme considered above can be used to predict the rate constant for PCP disappearance.

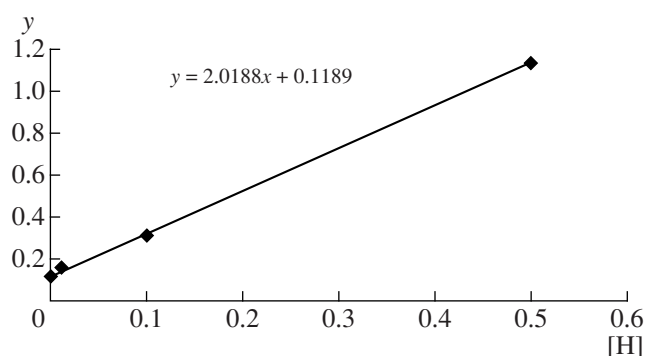


Fig. 2. Equation (5) presented in graphical form $\left(y = k_{\text{exp}} \frac{K_a + [\text{H}^+]}{[\text{H}^+]} \right)$ (denoted on the graph as y) versus $[\text{H}^+]$.

Equation (6) makes it possible to predict the rate constants at any desirable pH at 100°C. Table 2 illustrates the quite reasonable accuracy of such calculations. In Table 3 calculated rate constants are given for neutral solutions at 100°C. They are too small to be measured accurately experimentally; however, taking into account the good agreement of calculated and experimental data in Table 2, we can conclude that they are correct at least in the order of magnitude.

It should be taken into account that pH 6 and higher can be reached only for very low concentrations of PCP, less than 0.1 mg/l.

The temperature dependence of the rate constants is presented in Table 4.

Apparently, the Arrhenius equation cannot be applied in our case, probably because the experimental rate constant is a combination of three different constants (Eq. (5)). Indeed, the Arrhenius plot based on data in Table 4 was not a straight line. The activation energy calculated from the data obtained at 100 and 90°C gives 300 kJ/mol. For the points 90 and 80°C, it is 190 kJ/mol. This is an unusually high activation energy

Table 2. Experimental pseudo-first order rate constants (k_{exp}), and predicted rate constant (k_{Σ}) Eq. (6)

[HCl], mol/l	$k_{\text{exp}}, \text{h}^{-1}$	$k_{\Sigma}, \text{h}^{-1}$
—	0.050 ± 0.008	0.057 ± 0.004
0.0001	0.11 ± 0.01	0.104
0.001	0.11 ± 0.01	0.12
0.01	0.16 ± 0.02	0.14
0.1	0.31 ± 0.03	0.32
0.5	1.13 ± 0.05	1.13

* When HCl was not added into the system at all, the concentration of protons $(1.6 \pm 0.2) \times 10^{-5} \text{ M}$ was used in calculations. This corresponds to a concentration of PCP $(3.3 \pm 0.5) \times 10^{-5} \text{ M}$.

Table 3. Calculated rate constant and half-lives for the disappearance of PCP in water at 100°C and neutral conditions

pH	k , (h^{-1}) at 100°C	Half-life at 100°C (days)
6	6.4×10^{-3}	5
7	6.7×10^{-4}	43
8	6.7×10^{-5}	430

Table 4. Pseudo-first order rate constants and half-lives for the disappearance of PCP in 0.01 M HCl at different temperatures with no adjustment of ionic strength

T , °C	k_{exp} , h^{-1}	Half-life, h
100	0.16 ± 0.02	4.3
90	0.012 ± 0.002	58
80	0.0019 ± 0.0002	365

for the reaction in solution. According to [12] for the reaction in solution, 90% of reported E_a lie between 40 and 120 kJ/mol; the highest reported activation energy was 180 kJ/mol [12]. The enormously high increase in the rate constant between 90 and 100°C can be explained, at least qualitatively, by the transition from nonboiling to boiling conditions. This makes exact extrapolation to the region of moderate temperatures not possible. Rough estimation (assuming a common value for the activation energy in water of about 100 kJ/mol) gives a half-live time for PCP in water at 25°C and pH 7 equal to 300 years. This is in agreement with data [7, 8] obtained in field studies, where low concentrations of PCP were found in water in the majority of the samples.

Of course, this estimation does not take into account the possible sorption mechanism of removal [11] or possible influence of oxidation and/or reduction reactions. However, although these ways of pesticide removal are important, they can work reasonably well in water with large concentrations of undissolved particles, humus substances, or at the surface or the bottom of a water pond. Truly dissolved PCP at moderate pH and temperature will not be decomposed for many years.

No significant quantities of either intermediate or final products have been found with use of GC-MS. We did identify small quantities (less than 1% compared to the chromatographic peak of PCP) of all three possible isomers of tetrachlorophenol in the benzene extract at small conversion of the substrate, but those were impurities in the PCP itself. During the course of the reaction, tetrachlorophenols disappeared together with PCP. This allows us to suggest that in acidic media PCP couples to produce heavier, polymerlike products, which either precipitate or are too heavy to be analyzed by GC-MS. This is a rather common situation in the study of the degradation polychlorinated phenols [13–

17]. In many cases both enzyme-assisted and electrochemical oxidative destruction lead to free radical polymerization, either with or without release of free chlorine. Di-, tri-, and tetra-coupled products were considered as the most probable products of one-electron oxidative coupling. The growth of the polymer is terminated with the formation of tetramers and pentamers; these are insoluble in water and precipitate from the aqueous phase [14]. High molecular products were discovered at mild electrochemical oxidation [15–17]. Catalytic degradation of PCP by the Photo-Fenton system also gives dimers and polymers as the main products of radical oxidative coupling [18]. In our case cationic polymerization is a possible reaction pathway for the proton-catalyzed reaction. In the case of an uncatalyzed reaction, we cannot totally exclude the radical mechanism described in [14, 18], but it seems less probable than cationic polymerization. Radical activation of PCP would not depend very much on the pH of the solution; as a matter of fact, it can even be faster in basic solutions [14]. In our case the reaction was not going in basic solutions at all. According to Scheme 1, only the molecular form of PCP (RH) should give rise to the reaction. At pH greater than 7, more than 99% of PCP is in ionized form (R^-), which, according to our scheme, should not react, and we do not see any reaction. Thus, we can assume that in the acid-assisted pathway the first step is proton addition with carbocation formation, which couples either to oxygen in the next molecule, or to the carbon in the ring; the chain grows to an unidentified number of molecules in the oligomer, and terminates by the release of H^+ . In the uncatalyzed reaction, carbon atoms in the benzene ring have a strong deficit of electrons, because of 5 Cl atoms attached. Coupling is more probable in this case to the oxygen group in the neighboring PCP molecule.

Results of this study show that the stability of PCP dissolved in water can be much larger than expected from the literature data [1].

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