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Photochemical Degradation of Pesticides: Photocatalytic Effect of Fe(III) Ions on Methylene Blue Sensitized Interaction of 4-Chlorophenoxyacetic Acid with H_2O_2

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In our previous papers (Luňák et al 1987, 1989a) we have described marked photosensitizing effects of methylene blue, as well as the photocatalytic effects of Fe(III) ions, on hydroxylation of some aromatic substrates (i.e., benzoic acid and 2-hydroxybenzoic acid) using hydrogen peroxide. The two effects have been evidenced (Luňák et al 1987) even at very low additions of both the photocatalyst and the photosensitizing agent, of the order of 0.01 µM.

In this work we deal with the problem of the role can be played by the photosensitizing and photocatalytic effects exerted on hydrogen peroxide reactions during pesticide degradation in surface water. In terms of comparatively high hydrogen peroxide concentrations found in surface water (Cooper et al 1989) (between 0.1 µM and 10 µM), it seems probable, that hydrogen peroxide is involved in maintaining high redox potentials of natural waters.

For the purpose of this study the 4-chlorophenoxyacetic acid was singled out, that acts as a replacement of indolylacetic acid, a natural plant hormone. The derivatives of chlorophenoxyacetic acids are employed as selective herbicides (Cremlyn 1978; Angerer 1986). Up to now, the degradation of 4-chlorophenoxyacetic acid has been studied rather in terms of its biological aspects (Shailubhai et al 1983; Sahasrabudhe 1987) than of chemical ones. However, the reaction of the compound with Fenton's reagent was described (Brown et al (1964)). In this paper we study photochemical degradation of 4-chlorophenoxyacetic acid by hydrogen peroxide under the condition of photochemical generation of Fenton's reagent.

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MATERIALS AND METHODS

4-Chlorophenoxyacetic acid (Fluka AG, Switzerland), methylene blue (Merck, Darmstadt, Germany), ferric chloride (Cambrian Chemicals, United Kingdom), hydrogen peroxide (Chemické závody, Sokolov, Czechoslovakia), 4-chloranisole (Fluka AG, Switzerland), 4-chlorophenol (Fluka AG, Switzerland), phenoxyacetic acid (Fluka AG, Switzerland), glycolic acid (Merck, Darmstadt,Germany), glyoxylic acid (Merck, Darmstadt, Germany), phenol (Reactivul, Bucuresti, Rumania) were used as received. Bromopentaamminecobalt(III) bromide was prepared according to Booth (1939). The other chemicals used were of analytical grade (Lachema, Brno, Czechoslovakia).

Redistilled water was purified by employing following procedure: to 4 L water, 40 mL of 30 % hydrogen peroxide was added. The solution was poured into a 5 L three-necked flask, with a thermostatted RVK 500 W arc (Tesla Holešovice, Czechoslovakia). During irradiation (about 10 hr) the photolytic decomposition of hydrogen peroxide added was followed spectrophotometrically. After a complete decomposition of hydrogen peroxide water was rectified on a 1-m column.

Reaction solution (2.5 mL) containing 4-chlorophenoxyacetic acid (0.5 mM), hydrogen peroxide (0.1 M), methylene blue (between 0.01 μM and 10 μM) and catalyst (between 0.1 μM and 10 μM) was irradiated in a 1-cm quartz cell placed in a thermostatted block. The radiation was obtained from a SHC 400 W high-pressure sodium arc (Tesla Holešovice, Czechoslovakia) (λ = 589 nm). The radiation intensity was determined by Reinecke's salt (Wegner et Adamson 1966). UV-VIS spectra was measured by UV-VIS spectrophotomether PU 8720 (Unicam Philips, United Kingdom).

For HPLC analysis, a system equipped with a high pressure pump HPP 5001 with a stop-flow injection valve (Laboratorní přístroje, Praha, Czechoslovakia) and a column (150 x 3.3 mm, packed with Separon SGXC18 7 μm, Tessek, Czechoslovakia) was used. The chromatographic column was connected to the UV detector PU 4025 (Unicam Philips, United Kingdom) operated at 275 nm. The mobile phase consisted of mixture - methanol : water : 1 M phosphoric acid (50.5 : 49.3 : 0.2). The flow rate was 0.5 mL/min (6 MPa) and the sample volume 10 μL. A detection limit was 1 ng CPA at 275 nm.

RESULTS AND DISCUSSION

We have studied the effect of methylene blue addition on the rate of 4-chlorophenoxyacetic acid degradation

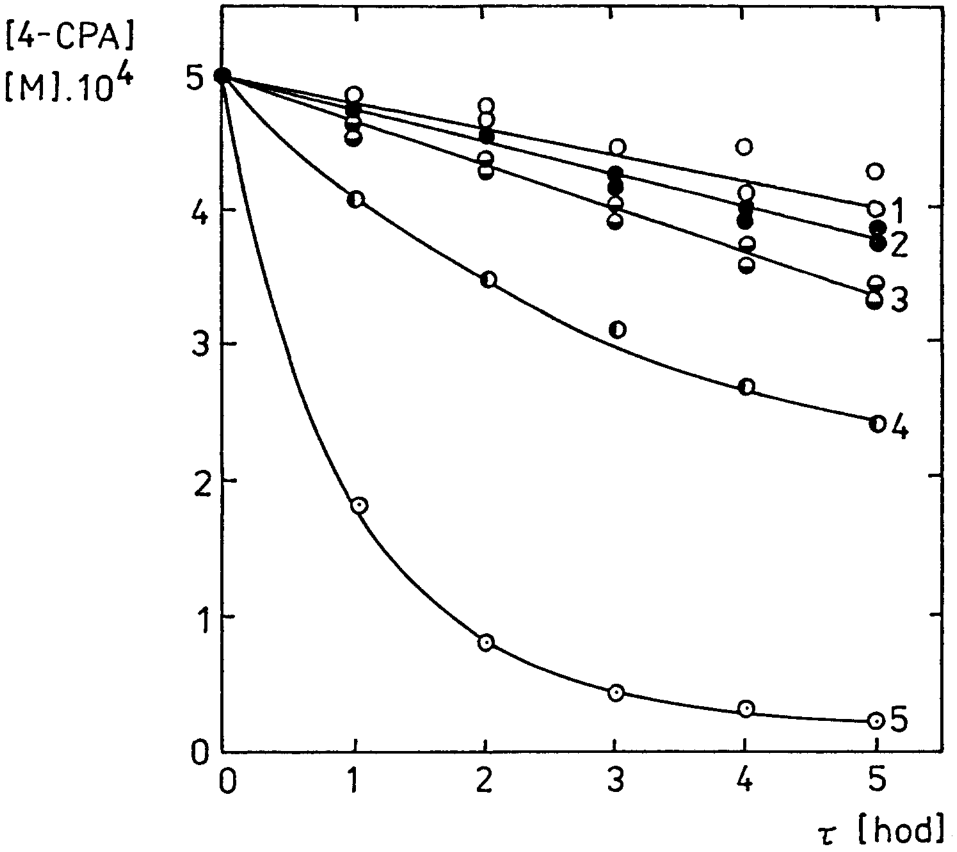

Figure 1. Photochemical degradation of 4-chlorophenoxyacetic acid under various photosensitizer concentrations
[hydrogen peroxide] = 0.1 M; λ = 589 nm; I = 2.19 x x 1E17 quantum/L/s; [methylene blue]: (curve 1) no added photosensitizer; (curve 2) 0.01 μM; (curve 3) 0.3 μM; (curve 4) 1 μM; (curve 5) 10 μM

in solutions containing hydrogen peroxide, under monochromatic irradiation (λ = 589 nm). The products of degradation were analyzed and 4-chlorophenol was determined in levels as high as 20 %, based on initial 4-chlorophenoxyacetic acid molar concentration (0.5 mM). No benzene, phenol, hydroquinone, chlorobenzene, anisole, 4-chloroanisole, or acetic, phenoxyacetic, glycolic and glyoxylic acids were detected.

As shown in Fig. 1, methylene blue acted as a highly efficient photosensitizer; even the levels as low as 0.3 μM exerted measurable effects. As one can see in Table 1, the photosensitization efficiency was enhanced by simultaneous addition of ferric ions. The effect was observable with the concentrations as low

Table 1. Average reaction rates [1E9 x mol/L/s] of thermal ($\bar{v}th$) and photochemical ($\bar{v}ph$) degradation of 4-chlorophenoxyacetic acid.
[hydrogen peroxide] = 0.1 M; λ = 589 nm; I = 2.19 x 1E17 quantum/L/s; τ = 0.5 hr

[meth.blue]	[$FeCl_3$]	[$CuSO_4$]	[Co-complex]	$\bar{v}th$	$\bar{v}ph$
-	-	-	-	0.28	3.67
-	1 μM	-	-	0.28	11.6
0.01 μM	-	-	-	0.22	6.33
0.01 μM	0.1 μM	-	-	1.11	7.44
0.3 μM	-	-	-	0.50	9.22
1 μM	-	-	-	1.22	13.1
1 μM	10 μM	-	-	4.33	20.3
10 μM	-	-	-	2.00	24.8
10 μM	-	1 μM	-	0.66	20.2
10 μM	-	-	1 μM	1.44	5.33

as 0.01 μM and 0.1 μM of methylene blue and ferric chloride, respectively. By analogy with other aromatic systems containing aromatic substrates hydrogen peroxide and ferric ions (Luňák _et al_ 1987; 1989a), it was found that in the system under study, irreversible decoloration of methylene blue occurred, being probably related to the formation of leuco-methylene blue (Sedlák _et al_ in press).

Recently (Sedlák _et al_ 1987) we brought attention to the contradiction between the commonly accepted idea of general involvement of free OH˙ radicals in hydrogen peroxide photochemical reactions and an experimental finding that the photocatalytic effects of individual transition metal ions on hydrogen peroxide photolysis and on its other photoinduced reactions cannot be brought into correlation. Even with the photosensitized destruction of 4-chlorophenoxyacetic acid, it was found that copper(II) ions (that are the best known homogeneous catalyst of hydrogen peroxide photolysis) have rather retarding effect on this reaction. Bromopentaamminecobalt(III) ions, that have been found to have positive catalytic effects on hydrogen peroxide photolysis (Luňák _et al_ 1989b), obviously inhibited the photochemical degradation of 4-chlorophenoxyacetic acid (see Table 1).

One can conclude that both photosensitizing agents (e.g., humic acids or some pigments that can act in this way in nature) and iron compounds, usually occurring at levels of the order of 0.1 mg/L in surface waters, can play a significant role in the kinetics of photooxidative degradation of herbicides.

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