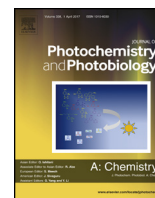




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Mechanistic study on thiacloprid transformation: Free radical reactions



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ABSTRACT

Free radical induced oxidation/reduction mechanisms of the hazardous water contaminant thiacloprid have been unravelled using pulse radiolysis techniques involving transient spectral analysis and redox titration experiments. The $\cdot\text{OH}$ -induced oxidation of thiacloprid proceeds with appreciable rate, the reaction rate constant has been determined to be $k_{\text{OH}} = 4.8 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$. The $\cdot\text{OH}$ attack leaves behind a rather complex free radical system consisting of $\sim 9\%$ α -aminoalkyl radicals, $\sim 31\%$ aminyl + aminium nitrogen centred radicals, $\sim 46\%$ radicals at the sulfur and $\sim 14\%$ hydroxycyclohexadienyl radical of the pyridyl moiety. Since $\sim 86\%$ of radicals are formed on the key cyanoiminothiazolidine pharmacophore, $\cdot\text{OH}$ is anticipated to be an appropriate candidate for inactivation of this biologically active pollutant. The one-electron reduction exerted by e_{aq}^- occurs at a diffusion controlled rate. As a result of the e_{aq}^- attack pyridinyl radical forms that takes part in subsequent protonation and dechlorination processes. The course of events is anticipated to lead to the destruction of another important part of the molecule in respect to insecticidal activity.

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1. Introduction

The gradual contamination of surface and ground waters is an unfortunate consequence of the increasing industrial and agricultural production, resulting in new slowly degradable pollutants in the environment. Traditional waste water treatment processes are not efficient enough in the removal of these compounds from the effluent. A family of new technologies based on free radical reactions, called Advanced Oxidation Processes (AOPs) are under development to solve this problem. High energy ionizing radiation treatment, investigated here, also belongs to the AOP family [1]. The reactive radical intermediates that induce solute degradation are produced in water radiolysis: hydroxyl radical ($\cdot\text{OH}$), hydrated electron (e_{aq}^-), hydrogen atom ($\text{H}\cdot$), and hydroperoxyl radical/superoxide radical anion pair ($\text{HO}_2\cdot/\text{O}_2^{\cdot-}$) [2].

A special advantage of the irradiation technique is that it has its own method, the pulse radiolysis, for examining the mechanism of the ongoing processes and for the observation of intermediates. Since the same or similar intermediates form in case of practically all AOPs, the radiolysis investigations can provide details for mechanisms of other AOPs.

The target compound in this study is thiacloprid, a low dose, long-acting chloronicotinyl insecticide with high biological activity, which is used against sucking and chewing pests. It has high stability and good water solubility (184 mg L^{-1} at 20°C), thus it can accumulate in the environment and have harmful effects on the biosphere [3]. The cyanoiminothiazolidine substructure of the molecule (Fig. 1) plays a key role in insecticidal activity [4–6]. It is of our prime interest to destroy the pharmacophore of the molecule via free radical reactions. To rationalize the applicability of these processes for elimination of the insecticidal activity of thiacloprid the mechanism of the oxidation/reduction needs to be placed under scrutiny.

Based on previous studies thiacloprid has three sensitive sites for $\cdot\text{OH}$ -induced oxidation: 2-chloropyridine, thiazolidine and the cyanoimino part (Fig. 1) [7]. During pulse radiolysis, pyridine reacts with $\cdot\text{OH}$, e_{aq}^- and $\text{H}\cdot$ with rate constants of $3.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, $7.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and $4.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively [8,9].

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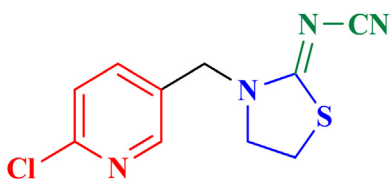


Fig. 1. Thiacloprid having 2-chloropyridine (red), thiazolidine (blue) and cyanoimino (green) substructures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Kosno et al. [10] reported that $\bullet\text{OH}$ reacts with nicotine by preferentially attacking the pyrrolidine moiety. They found that the rate of $\bullet\text{OH}$ scavenging by the nicotine molecule depends on the protonation of the pyrrolidine moiety and decreases from $6.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ in its basic form to $1 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ in its protonated form. Due to the electron-withdrawing Cl substituent, the rate constant of 2-chloropyridine with $\bullet\text{OH}$ is expected to be smaller than that of pyridine ($3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$): it was reported to be $1.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [8,11]. $\bullet\text{OH}$ generally also attacks thioether groups with rate constants on the diffusion controlled level ($\sim 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) [12]. The double bond in the cyanoimino group of the molecule may also be involved in reaction with this radical. In case of thiazolidine no data is available about the reactions with these primary radicals. Nevertheless, the mechanism of the $\bullet\text{OH}$ -induced reaction of thiaprine, which is a carboxylated thiazolidine derivative, has been unravelled [13]. The $\bullet\text{OH}$ rate constant for pyrrolidine was determined directly by pulse radiolysis, and was found to be $(2.43 \pm 0.05) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [1].

Dell'Arciprete et al. [14] reported that thiacloprid (and generally the chloronicotinoid insecticides) shows low reactivity towards carbonate radicals. Their reaction rate constants ($k_{(\text{THIA}^+ \bullet\text{OH})} = 7.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{(\text{THIA}^+ \text{CO}_3^{\bullet-})} = 2.8 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$) were obtained using flash photolysis, however, the former rate constant seems to be unrealistic, since it is half of an order of magnitude higher than the diffusion limited value [14,15].

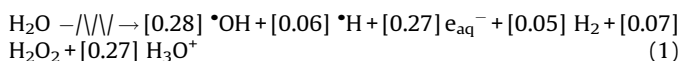
The $\bullet\text{OH}$ -induced oxidation of nicotine from pH 1 to 13.6 was studied using pulse radiolysis techniques by Kosno et al. [10]. They reported that the spectra exhibit two absorption bands: a strong band near 350 nm and a much weaker, broader band in the spectral region around 460 nm. In their study the kinetic behaviour of these bands suggested that both absorption bands belonged to the same species. To our best knowledge no results have been published yet on the pulse radiolysis with time-resolved transient spectroscopic techniques of thiacloprid.

In this paper the kinetics and mechanism of hydroxyl radical and hydrated electron reactions of thiacloprid are studied using pulse radiolysis with time-resolved transient spectroscopic techniques including also redox titration experiments.

2. Materials and methods

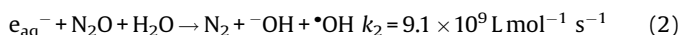
2.1. Radicals under different experimental conditions

The radiolysis of water gives a distribution of transient and stable products according to Eq. (1) [16]:

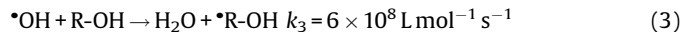


where the numbers in brackets are the G-values (yields) in $\mu\text{mol J}^{-1}$.

The hydroxyl radical reactions were examined in nitrous oxide saturated solutions, in order to convert e_{aq}^- to $\bullet\text{OH}$ in Eq. (2) [2].



The reaction of the organic molecules was with e_{aq}^- were studied in the presence of *tert*-butanol in N_2 -saturated solutions [16]. *tert*-Butanol (R-OH) reacts with $\bullet\text{OH}$ according to Eq. (3) generating less reactive radicals ($\bullet\text{CH}_2(\text{CH}_3)_2\text{COH}$).



The role of $\bullet\text{H}$ in the reaction mechanism was examined in acidic N_2 -saturated solutions (set with HClO_4) in the presence of *tert*-butanol.

We have also studied the effects of ferricyanide [$\text{K}_3\text{Fe}(\text{CN})_6$] on the absorption spectra (have to mention that we did not find similar study in the literature in which hydroxycyclohexadienyl radicals with heterocyclic ring were identified by this method). Hexacyanoferrate (III) is well-known for its oxidizing property; it oxidizes the hydroxycyclohexadienyl radical at a fast rate eliminating this transient from the system [17].

Hydroxycyclohexadienyl-type radicals have characteristic absorption bands in the UV range with maximum between 310 and 340 nm. These radicals are produced when an $\bullet\text{OH}$ reacts with the aromatic ring. As $\bullet\text{OH}$ can attack the ring in several sites, several isomers of hydroxycyclohexadienyl radicals may form. When the hydroxycyclohexadienyl radical reacts with ferricyanide its absorption band disappears from the spectrum, giving a possibility for spectral identification.

2.2. Kinetic curves

The transient changes of the optical absorption are followed by kinetic spectrophotometry. Kinetic systems that are described by the following differential equation [18] were used:

$$d[\text{R}^*]/dt = -k \times [\text{M}] [\text{R}^*] = -k' [\text{R}^*] \quad (4)$$

where k = rate coefficient, M = molar concentration of substance [mol L^{-1}], $[\text{R}^*]$ = the radical concentrations, $k' = k \times [\text{M}]$ and t is time.

Integrating the equation and using the Lambert-Beer law, according to which the concentration of intermediate is proportional to the absorbance (A), the following relationship is obtained:

$$\ln A^* = \ln A_0^* - k't \quad (5)$$

where A_0^* = absorbance measured at time t_0 , A = absorbance measured at time t . This equation is used to calculate the rate coefficient when the absorbance of the reacting radical is measured (e_{aq}^-). When the reacting radical does not have absorbance in the readily accessible wavelength region ($\bullet\text{OH}$, H^*) the absorbance of the product radical is utilized for rate coefficient determination. In this case the equation used for fitting has the form:

$$\ln(A^*_{\infty} - A) = \ln A^*_{\infty} - k't \quad (6)$$

where A and A^*_{∞} are the product radical absorbance at time t and after the build-up.

Plotting the linearized values against time, and applying linear regression fitting, the resulting slope gives the value of k' . For a pseudo-first-order reaction, the reaction rate coefficient is directly proportional to the concentration of one of the reactants.

2.3. Materials, equipment and experimental setup

Thiacloprid (99.9% purity), hydroquinone (H_2Q), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), methyl viologen dichloride hydrate (MV^{2+}), and $\text{Fe}(\text{CN})_6^{3-}$ were provided by Sigma-Aldrich. *tert*-butanol was obtained from Spectrum 3D. Purified water was prepared using an Adrona B30 system, the specific conductivity was $0.055 \mu\text{S cm}^{-1}$ and a total organic carbon content < 2 ppb. The pH was adjusted using HClO_4

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