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Mechanistic study on thiacloprid transformation: free radical reactions

Georgina Rózsa[a,b*], László Szabó[b,c], Krisztina Schrantz[a], Erzsébet Takács[b], László Wojnárovits[b]

[a]Department of Inorganic and Analytical Chemistry, University of Szeged
Dóm tér 7, H-6720 Szeged, Hungary

rozsa.georgina@chem.u-szeged.hu

sranc@chem.u-szeged.hu

[b]Institute for Energy Security and Environmental Safety, Centre for Energy Research, Hungarian Academy of Sciences, Konkoly-Thege Miklós út 29-33, H-1121 Budapest, Hungary

erzsebet.takacs@energia.mta.hu

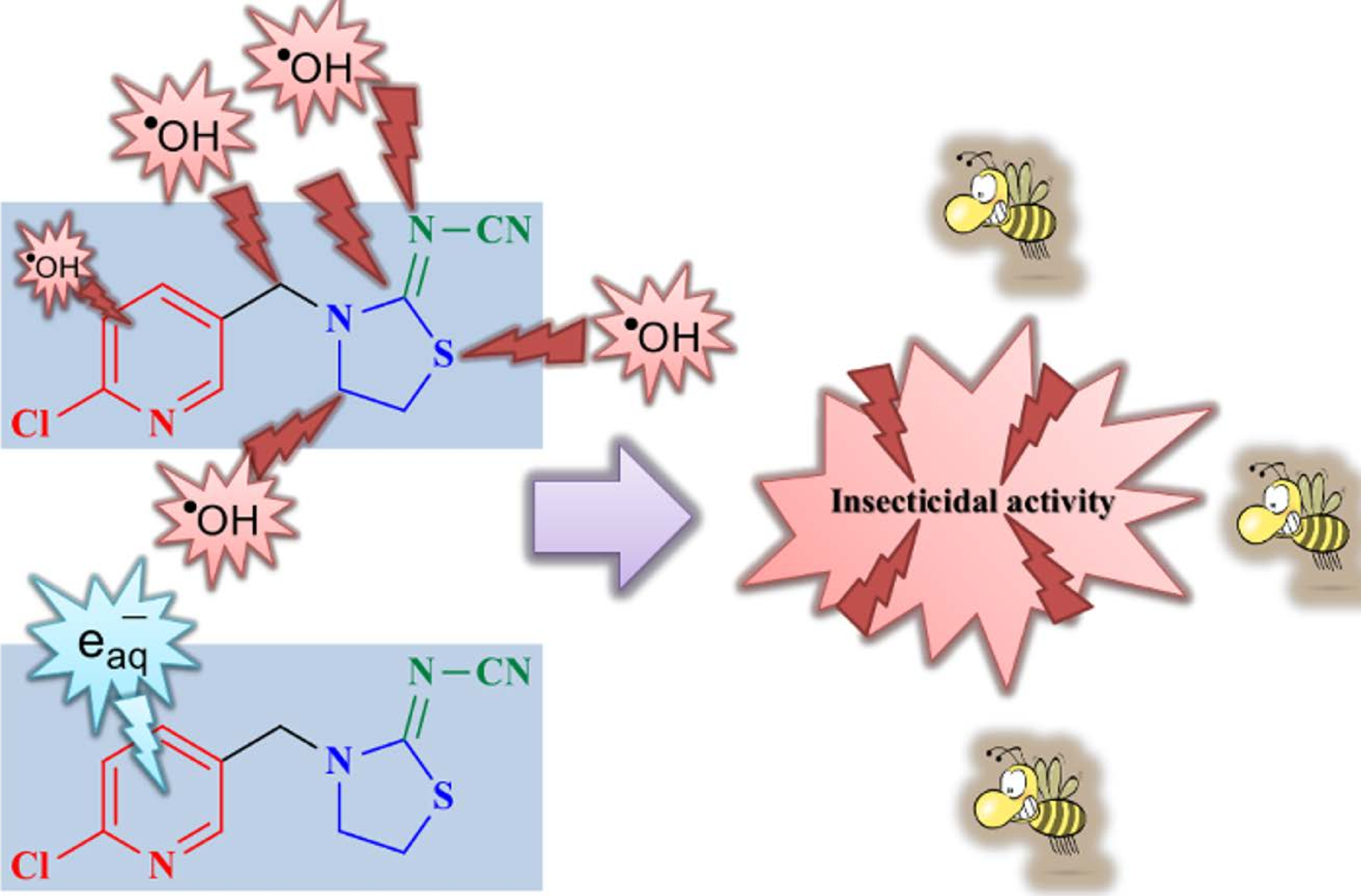
wojnarovits.laszlo@energia.mta.hu

[c]Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Szent Gellért tér 4, H-1111 Budapest, Hungary

szabo.laszlo@energia.mta.hu

*Corresponding author: tel.: +36-62/54 4285, e-mail: rozsa.georgina@chem.u-szeged.hu

Address: Department of Inorganic and Analytical Chemistry, University of Szeged
Dóm tér 7, H-6720 Szeged, Hungary


•OH
•OH
•OH
N–CN
•OH
N
S
•OH
Cl
N
•OH
e^-_{aq}
N–CN
N
S
Cl
N
Insecticidal activity

Highlights

- ${}^{\bullet}OH/e_{aq}^{-}$ exhibits appreciable reactivity towards the insecticide thiacloprid
- The majority of ${}^{\bullet}OH$ attack the key cyanoiminothiazolidine pharmacophore
- α-aminoalkyl, N-centred, α-(alkylthio)alkyl and $>S^{\bullet}$-OH radicals form on this moiety
- One-electron reduction occurs at the pyridyl function yielding pyridinyl radicals
- Destruction of pharmacologically important substructures is anticipated

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 ${}^{\bullet}OH$-induced oxidation of thiacloprid proceeds with appreciable rate, the reaction rate constant has been determined to be $k_{OH} = 4.8 \times 10^9$ mol^{-1} L s^{-1}. The ${}^{\bullet}OH$ attack leaves behind a rather complex free radical system consisting of ~9% α-aminoalkyl radicals, ~31% aminyl + aminium nitrogen centred radicals, ~46% radicals at the sulfur and ~14% hydroxycyclohexadienyl radical of the pyridyl moiety. Since ~86% of radicals are formed on the key cyanoiminothiazolidine pharmacophore, ${}^{\bullet}OH$ 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.

Keywords: thiacloprid; hydroxyl radical; pulse radiolysis; transient spectroscopy; radical kinetics

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 ($^{\bullet}OH$), hydrated electron (e_{aq}^{-}), hydrogen atom ($H^{\bullet}$), and hydroperoxyl radical/superoxide radical anion pair ($HO_2^{\bullet}/O_2^{\bullet-}$) [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 (Figure 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 $^{\bullet}OH$-induced oxidation: 2-chloropyridine, thiazolidine and the cyanoimino part (Figure 1) [7]. During pulse radiolysis, pyridine reacts with $^{\bullet}OH$, e_{aq}^{-} and $H^{\bullet}$ with rate constants of 3.0×10^9 L mol^{-1} s^{-1}, 7.7×10^9 L mol^{-1} s^{-1} and 4.0×10^8 L mol^{-1} s^{-1}, respectively [8, 9]. Kosno et al. [10] reported that $^{\bullet}OH$ reacts with nicotine by preferentially attacking the pyrrolidine moiety. They found that the rate of $^{\bullet}OH$ scavenging by the nicotine molecule depends on the protonation of the pyrrolidine moiety and decreases from 6.7×10^9 L mol^{-1} s^{-1} in its basic form to 1×10^9 L mol^{-1} s^{-1} in its protonated form. Due to the electron-withdrawing Cl substituent, the rate constant of 2-cloropyridine with $^{\bullet}OH$ is expected to be smaller than that of pyridine (3×10^9 L mol^{-1} s^{-1}): it was reported to be 1.8×10^9 L mol^{-1} s^{-1} [8, 11]. $^{\bullet}OH$ generally also attacks thioether groups with rate constants on the diffusion controlled level (~10^{10} L mol^{-1} 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 $^{\bullet}OH$-induced reaction of thiaproline, which is a carboxylated thiazolidine derivative, has been unravelled [13]. The $^{\bullet}OH$ rate constant for pyrrolidine was determined directly by pulse radiolysis, and was found to be $(2.43 \pm 0.05) \times 10^9$ L mol^{-1} 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 ($k_{(\mathrm{THIA}\,+\,{}^{\bullet}\mathrm{OH})}$ = 7.5 × 10^{10} L mol^{-1} s^{-1} and $k_{(\mathrm{THIA}\,+\,\mathrm{CO}_3^{\bullet-})}$ = 2.8 × 10^{5} L mol^{-1} 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 ${}^{\bullet}$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 equation (1) [16]:

$$H_2O \text{ -/\!\backslash\!/\!\backslash\!/}\!\!\rightarrow [0.28]\,{}^{\bullet}OH + [0.06]\,{}^{\bullet}H + [0.27]\,e_{aq}^{-} + [0.05]\,H_2 + [0.07]\,H_2O_2 + [0.27]\,H_3O^{+} \qquad (1)$$

where the numbers in brackets are the *G*-values (yields) in μmol J^{-1}.

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

$$e_{aq}^{-} + N_2O + H_2O \rightarrow N_2 + {}^{-}OH + {}^{\bullet}OH \qquad k_2 = 9.1 \times 10^{9}\ \mathrm{L\ mol^{-1}\ s^{-1}} \qquad (2)$$

The reaction of the organic molecules with e_{aq}^{-} were studied in the presence of *tert*-butanol in N_2-saturated solutions [16]. *Tert*-Butanol (R-OH) reacts with ${}^{\bullet}$OH according to equation (3) generating less reactive radicals (${}^{\bullet}CH_2(CH_3)_2COH$).

$${}^{\bullet}OH + R\text{-}OH \rightarrow H_2O + {}^{\bullet}R\text{-}OH \qquad k_3 = 6 \times 10^{8}\ \mathrm{L\ mol^{-1}\ s^{-1}} \qquad (3)$$

The role of $^{\bullet}$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 [$K_3Fe(CN)_6$] 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 to 340 nm. These radicals are produced when an $^{\bullet}$OH reacts with the aromatic ring. As $^{\bullet}$OH can attack the ring in several sites, several isomers of hydroxycyclohexadienyl radicals may form. When the hydroxycyclohexadienyl radical reacts with ferricyanide its adsorption 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:

$$d[R^{\bullet}]/dt = -k \times [M]\,[R^{\bullet}] = -k'\,[R^{\bullet}] \qquad (4)$$

where k = rate coefficient, M = molar concentration of substance [mol L^{-1}], [R$^{\bullet}$] = the radical concentrations, $k' = k \times [M]$ 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:

$$\ln A^{\bullet} = \ln A_0^{\bullet} - k't \qquad (5)$$

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 ($^{\bullet}$OH, H$^{\bullet}$) the absorbance of the product radical is utilized for rate coefficient determination. In this case the equation used for fitting has the form:

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

where A and $A^{\bullet}_{\infty}$ 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 $Fe(CN)_6^{3-}$ 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 $\mu S\ cm^{-1}$ and a total organic carbon content < 2 ppb. The pH was adjusted using $HClO_4$ obtained from Reanal. The solutions were bubbled with O_2, N_2 or N_2O (Messer, > 99.5%).

The measurements were executed using a 4 MeV linear electron accelerator (LINAC) attached to a kinetic spectrophotometric system. The sample cell is located beneath the window of the electron accelerator, and the electrons reach the optical cell vertically. The path of the analyzing light and the accelerated electrons intersects at the sample holder, the optical rail is horizontal. During the measurement, the lens system focuses the analyzing light first to the sample, then to the glass fiber optic’s entry window.

The dose/pulse values were determined before each measurement with thiocyanate (KSCN) dosimetry (1.0×10^{-2} mol L^{-1}) taking a molar absorption coefficient of 7580 $M^{-1}\ cm^{-1}$ for $SCN_2^{\bullet-}$ at 480 nm [19, 20]. Samples were irradiated in a 1 cm flow-through cell. Absorbed doses were in the order of 20-30 Gy/pulse.

The investigated solutions were purged with N_2 or N_2O for 30 minutes before the measurements. In some cases *tert*-butanol was added to the solution to scavenge $^{\bullet}OH$.

2.4 Redox titration

In redox titration measurements different redox indicators were used to observe one-electron transfer and thus identify free radicals (e.g. aminyl and aminium radicals) with different reduction potentials. These experiments were performed as described in a previous study [21].

Methyl viologen ($E°(MV^{2+}/MV^{\bullet+})$ = - 0.448 V vs NHE [22]) was applied to detect reducing α-aminoalkyl radicals [23], the forming $MV^{\bullet+}$ was followed at 600 nm (ε_{600} = 11 850 $mol^{-1}\ L\ cm^{-1}$ [24]). Oxidizing radicals were trapped using ABTS ($E°(ABTS^{\bullet+}/ABTS)$ = 0.680 V [25]), the kinetic trace that represents the formation of $ABTS^{\bullet+}$ was recorded at 415 nm (ε_{415} = 36 000 $mol^{-1}\ L\ cm^{-1}$ [26]). In addition, hydroquinone ($E°(Q^{\bullet-}/Q^{2-})$ = 0.459 V at pH 7

[22]) was also employed to further confirm the yield of oxidizing species, generation of $Q^{\bullet-}$ was monitored at 430 nm (ε_{430} = 7200 mol^{-1} L cm^{-1} [27]). Since the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple has a one-electron reduction potential of 0.361 V [28], it is able to oxidize a wide range of free radicals including α-aminoalkyl radicals [29], benzyl radicals [30], carbon centred alkyl radicals [31], hydroxycyclohexadienyl radicals [17] and cyclohexadienyl radicals [32]. The total yield of these species can therefore be obtained from the bleaching of the absorbance at 420 nm (ε_{420} = 1027 mol^{-1} L cm^{-1}) [33]. The pH of 4.0×10^{-4} mol L^{-1} thiacloprid solution is 5.23.

In redox titration experiments the redox indicator also reacts with the initially forming free radicals from water radiolysis thereby consuming these agents in competition with thiacloprid. Furthermore, the transient thus generated can either be the same as the one forming in the one-electron transfer event or it can contribute to the absorbance at the wavelength of interest. These effects were taken into account when calculating the corrected yield of oxidizing/reducing species. The standard deviation calculated at the plateau of the kinetic curve is used to derive the accuracy of the transient product yield (*G*-value) during the spectral analysis. The treatment of a similar complex system has been described in details previously [21].

3. Results and discussion

Pulse radiolysis measurements were performed within 250-600 nm wavelength interval, and the aqueous solution in some cases contained 0.025 mol L^{-1} *tert*-butanol and was saturated with either N_2O or N_2. The transient absorption spectra were obtained from the kinetic curves recorded in pulse-irradiated thiacloprid solutions at different wavelengths. When the intermediate build-up was examined, the measured points were taken with high resolution and short time interval, the produced intermediates were studied on a longer time scale.

3.1 $^{\bullet}$OH-induced oxidation of thiacloprid

3.1.1 Kinetics of the ongoing reactions

Three major bands were observed in the absorption spectra of thiacloprid intermediates formed in the reaction with $^{\bullet}$OH in N_2O-saturated solutions (Figure 2A). The pseudo-first order rate constant (*k*’) of the $^{\bullet}$OH + thiacloprid reaction was determined following the build-up of absorbance at 335 nm. The concentration-dependence of *k*’ (Figure 2A inset) yielded a value of $k_{OH} = 4.8 \times 10^9$ mol^{-1} L s^{-1}. Thiacloprid exists in neutral form in aqueous solutions.

Kosno et al. [10] argued that $^{\bullet}$OH reacts mainly by attacking the pyrrolidine moiety of the nicotine molecule, which is a structurally close molecule. If this applies to the $^{\bullet}$OH-induced oxidation of thiacloprid a higher reaction rate constant (compared to the reaction rate constant of the neutral form of nicotine being 6.7×10^{9} L mol^{-1} s^{-1}) would be expected on account of the presence of additional reaction sites e.g. the thiother group of the thiazolidine ring. In fact, this is not the case here since a lower value is derived from our fitting. It is apparent at the same time that the chlorine substituent exerts its electron-withdrawing effect, which is nicely reflected on the lower reaction rate constant for the electrophilic $^{\bullet}$OH reported herein. The reaction rate constant for 2-chloropyridine, which is the aromatic sub-structure of thiacloprid, has been reported to be $k_{\mathrm{OH}} = 1.8 \times 10^{9}$ mol^{-1} L s^{-1} [11]. The somewhat higher k_{OH} for thiacloprid further indicates the reactions at other sites of the molecule besides the aromatic ring. This is also undoubtedly revealed by the kinetics of the ongoing reactions in the system.

Our spectrum obtained for thiacloprid (two absorption bands at 335 nm and 525 nm) is similar to the spectrum obtained for nicotine reported by Kosno et al [10], the only difference being the appearance of a small band at around 280 nm (Figure 2A). Nevertheless, the kinetics in our system is markedly different from the kinetics observed in the study of Kosno et al. [10] indicating the presence of at least three absorbing intermediates. The decay of the absorption band at 285 nm (Figure 2B) after an initial drop follows pseudo-first order kinetics with a rate constant of $k = 119$ s^{-1} implying a unimolecular transformation process of the intermediate. Furthermore, the decay of the absorption band at 335 nm also obeys first order kinetics, however, with dependence on the thiacloprid concentration. Thus a second-order rate constant of $k = 3.1 \times 10^{7}$ mol^{-1} L s^{-1} was derived from the k' *vs.* concentration plot. This type of kinetics indicates the reaction of the forming intermediate with the thiacloprid molecule. After 600 μs a long-living absorption remains that can be assigned to the forming stable species (Figure 2C). In addition, the decay process at 525 nm can be described by second-order kinetics showing no dependence of the rate constant on radical concentration (no dose-dependence observed) with $2k/\varepsilon = 1.4 \times 10^{6}$ cm s^{-1}. This kind of kinetics is characteristic for radical-radical disproportionation/combination reactions.

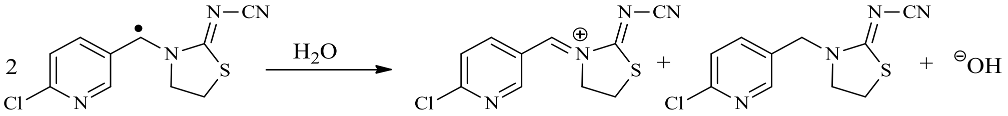
3.1.2 Spectral analysis

While evidence for the reaction of $^{\bullet}$OH at the aromatic system of thiacloprid and at several other sites came from kinetics investigations, to establish a reaction mechanism the transient absorption spectra need to be placed under scrutiny taking the characteristic absorption of certain type of radical species into account. $^{\bullet}OH$ can exert a wide range of reactions: addition to electron-rich sites, $^{\bullet}H$ abstraction and one-electron oxidation [34]. Attack at the aromatic pyridyl moiety leads to a mixture of isomeric hydroxycyclohexadienyl type radicals (one is shown in Scheme 1 as **a**). This type of radicals show characteristic absorption band in the UV range. Since the corresponding cyclohexadienyl type radicals forming in the reaction of the aromatic system with $^{\bullet}H$ have an absorption band very close to that of hydroxycyclohexadienyl type radicals, we also obtained the transient absorption spectra when the reactions of $^{\bullet}H$ predominate (Figure 3A) [35]. $^{\bullet}H$ reacts with thiacloprid with appreciable reaction rate, the concentration-dependence of the build-up of the absorbance at 340 nm yields a reaction rate constant of 2.3×10^9 mol^{-1} L s^{-1} (Figure 3A inset). Based on the spectra of cyclohexadienyl type radicals generated in the reaction of $^{\bullet}H$, the band centred at 335 nm in Figure 2A can be partly (*vide infra*) assigned to the absorbance of hydroxycyclohexadienyl type radicals forming in the reaction of $^{\bullet}OH$ (species **a** and its isomers).

$^{\bullet}OH$ also exhibits considerable reactivity towards organic sulfides [12]. Initially hydroxyl radical adds to the sulfur forming intermediate **b** (Scheme 1), which presumably exists as a three-electron bonded species [36]. Such radical is usually unstable ($\tau_{1/2} < 1$ μs), however, it can be stabilized by intramolecular H-bond formation with an appropriate H-bond acceptor heteroatom [37, 38]. Otherwise it quickly converts to sulfur radical cation (**c**) via proton catalyzed H_2O- or unimolecular ^{-}OH-elimination [39]. The sulfur radical cation can also be engaged in intramolecular reaction with closely located heteroatom (e.g. the nitrogen of the cyano group) leading to three-electron-bonded $>S\therefore N$ complexes [40-42]. In the absence of this reaction path proton elimination occurs from the α-carbon giving rise to α-(alkylthio)alkyl radicals being described by resonance structure **d**/**e** [12]. The presence of **d**/**e** is apparent in our system on account of the characteristic absorbance of these species at 285 nm (Figure 2A) [43]. To find out the existence of other absorbing intermediates of sulfur oxidation some of the species were eliminated from the system (*vide infra*) using $Fe(CN)_6^{3-}$ as oxidizing agent.

$^{\bullet}OH$ can also add to the double bond of the cyanoimino part of the thiacloprid molecule. In the reaction species **f** might form. Due to the strong electron-withdrawing cyano group the radical attack is expected at the carbon atom and the unpaired electron is proposed to be localized on the nitrogen. Thus aminyl type radical forms, which usually does not show absorption in the UV range [44] and therefore, directly cannot be identified from the transient spectra. To rationalize this reaction path redox titration needs to be performed (*vide infra*).

Furthermore, $^{\bullet}$OH can take part in $^{\bullet}$H abstraction giving rise to carbon centred radicals. This type of reaction proceeds when there is a driving force that is the resonance stabilization of the forming radical centre. Benzyl radicals, α-aminoalkyl radicals and α-(alkylthio)alkyl radicals can form in this way. In α-aminoalkyl radicals the unpaired electron and the non-bonding electron pair of the nitrogen establish a two-centred three-electron interaction exerting a stabilizing effect. In general, this type of species has an absorption band with $\lambda_{max} < 300$ nm exhibiting low molar absorption coefficient and decaying absorbance towards longer wavelength [45, 46]. α-Aminoalkyl radicals of thiacloprid are species **g** and **h**. While the absorption at shorter wavelength can be assigned to radical **h**, species **g** is expected to have markedly different absorption characteristics. In fact, species **g** is not only resonance-stabilized by the adjacent nitrogen, but also by the aromatic system. Benzyl type radicals show characteristic absorption in the UV range with high molar absorption coefficient [47]. The extended resonance-stabilization of species **g** suggests a red-shift of the absorption band of simple benzyl radicals. We propose that the band at 525 nm belongs to species **g**. This assignment is in line with the second-order kinetics observed at 525 nm, since α-aminoalkyl radicals usually take part in disproportionation reactions forming iminium cations (7) that do not absorb significantly at this wavelength [10, 46].



(7)

In fact, >S∴S< three-electron bonded species absorb at longer wavelength with broad absorption band [48], therefore, the peak at 525 nm could also be assigned to them. To probe the presence of these complexes the transient spectra were also recorded in 4.0×10^{-4} mol L^{-1} thiacloprid solution (4-times higher concentration compared to the previous investigation). Since >S∴S< species are in equilibrium with the sulfur radical cation (**c**) and the thiacloprid molecule, a higher concentration of thiacloprid would imply a shift towards the formation of the complex. Our expectation - increasing absorbance at 525 nm - is based on our previous study on a structurally similar analogue containing the thiazolidine ring, namely 6-aminopenicillanic acid [49] . Assuming that the equilibrium constants do not differ much, a rise in absorbance is anticipated since the corresponding species could be observed for 6-aminopenicillanic acid at a concentration of 1.0×10^{-3} mol L^{-1} while at 1.0×10^{-4} mol L^{-1} no spectral change occurred. However, there was no absorbance increase observed at 525 nm in the transient spectrum (Figure 3B inset) that was normalized to the absorption maximum at 335 nm (due to the higher thiacloprid concentration slightly more $^{\bullet}$OH is scavenged [33]).

$^{\bullet}$OH is also able to be engaged in direct electron transfer on account of its high one-electron reduction potential ($E°(^{\bullet}OH/^{-}OH) = 1.9$ V [22]). Since $E°$ for the $R_1R_2NH^{\bullet+}/R_1R_2NH$ couple falls significantly below this value in case of methylamine (1.25 V) and dimethylamine (0.8 V) [50], electron transfer from the nitrogens of thiacloprid might also occur. This type of electron transfer from thiacloprid and from its mesomeric form **i** (Scheme 1) was observed by Dell'Arciprete et al. [51] in the $SO_4^{\bullet-}$-induced ($E°(SO_4^{\bullet-}/SO_4^{2-}) = 2.43$ V [22]) oxidation yielding species **j** and **k** (mesomeric structures). Therefore, the one-electron reduction for the corresponding couple in case of thiacloprid should fall below 2.43 V. As it was mentioned before, the forming aminyl (**j**) and aminium (**k**) radicals are practically invisible in the transient spectrum and redox titration is needed to detect and quantify these transients that will be the focus of the forthcoming section.

In an attempt to reveal the presence of further absorbing species, e.g. from the reaction path of sulfur oxidation, $Fe(CN)_6^{3-}$ was applied to oxidize and eliminate some of the intermediates from the system. $Fe(CN)_6^{3-}$ oxidizes α-aminoalkyl radicals [29], benzyl radicals [30], carbon centred radicals not activated at α-position [31], hydroxycyclohexadienyl radicals [17] and cyclohexadienyl radicals [32]. Although α-(alkylthio)alkyl radicals are reducing agents [52], they do not react with $Fe(CN)_6^{3-}$ based on our previous study [53]. Hence it is expected that by adding this oxidizing agent at appropriate amount to the thiacloprid solution the only absorbing species remaining in the system are those resulting from the oxidation of the thioether moiety (blue color in Scheme 1). Figure 3B shows the transient spectra recorded in the presence of $Fe(CN)_6^{3-}$. Indeed, the absorption belonging to the aforementioned transients of thiacloprid, i.e. species **a**, **g** and **h** yielding products **l**, **m** and **n**, respectively, are firmly eliminated. Furthermore, it is apparent that α-(alkylthio)alkyl radicals are still present as it is expected (absorption at ~285 nm). Interestingly, an absorption band appears with λ_{max} at ~330 nm that has not yet been accounted for due to the overlapping bands of the hydroxycyclohexadienyl type radicals (**a**). Based on previous studies [38, 43] the $^{\bullet}$OH adduct to the sulfur exhibits typically a band around this wavelength. It follows that species **b** is also present in our system. This is quite surprising because at the same time the transformation product **d**/**e** also appears. The phenomenon has already been experienced previously [49], where similarly to thiacloprid there was an H-bond acceptor in close vicinity to the sulfur centre (-CN here) stabilizing intermediate **b**. On account of the stereochemistry (two stereoisomers of **b** can form at the sulfur) at the sulfur only a part of the adducts is ready to be stabilized (the stereoisomer being in appropriate position for the formation of an H-bond) whereas some of them transform to α-(alkylthio)alkyl radicals (**d**/**e**). This phenomenon also gives explanation for the kinetics at 285 nm that was characterized by an initial drop followed by slow decrease in absorbance (Figure 2B). The slow decrease can proceed due to parallel build-up and decay processes of species **d**/**e**.

3.1.3 Free radical reactions in quantitative terms – redox titration experiments

In an attempt to quantify the contribution of different free radical reactions in our system, redox titration experiments were performed. By harnessing the characteristic redox behaviour of different free radicals electron acceptors/donors are added to the solution that transform to intermediates with well-known molar absorption coefficients. Kinetic traces that represent the formation of the corresponding radicals generated from the redox indicators are shown in Figure 4. The plateaus of these kinetic traces are used to calculate the radiation chemical yield of species previously reacting with the redox indicator.

α-Aminoalkyl radicals are strong reducing agents $E°(H_2N^+{=}CH_2/H_2NC^{\bullet}H_2)$ = -1.5 V has been calculated for methylamine [50]) that can readily donate an electron to MV leading to $MV^{\bullet+}$. The kinetic trace in Figure 4A indicates that α-aminoalkyl radicals of thiaclorpid, species **h** and **g** form with a radiation chemical yield of (0.051±0.001) µmol J^{-1} (corrected with direct reduction of MV by hydrated electron [21]). It follows that ~9% of the initially available $^{\bullet}OH$ (the $^{\bullet}OH$ yield was corrected according to the reaction of hydrated electron with MV) generates species **h** and **g**.

ABTS and H_2Q are applied to quantify free radicals with one-electron reduction potential above 0.680 and 0.459 V, respectively [22, 25]. N-centred radicals are strong oxidizing agents, $E°(CH_3NH^{\bullet}, H^+/CH_3NH_2)$ = 1.96 V and $E°((CH_3)_2N^{\bullet}, H^+/(CH_3)_2NH)$ = 1.57 V have been calculated for the aminyl and aminium radicals of methylamine, respectively [50]. The dialkyl sulfide radical cation is also a powerful oxidant ($E°((CH_3)_2S/(CH_3)_2S^{\bullet+})$ = 1.66 V [54]), however, this characteristically absorbing species [23, 49] has not been observed in the spectral analysis (*vide supra*). Therefore, it is anticipated that species **c** rapidly converts to other transients making its identification with a redox indicator impossible. Hence ABTS and H_2Q are appropriate redox indicators to quantify N-centred radicals in our system. ABTS and H_2Q show considerable reactivity towards $^{\bullet}OH$ [21], scavenging ~30% of the initially available amount. The evolution of the kinetic trace in pure N_2O-saturated solution containing 7.0×10^{-5} mol L^{-1} ABTS and H_2Q is shown in Figure 4B and C insets, respectively, which was used to correct the result derived from the kinetic trace obtained in redox titration experiments (Figure 4B and C). Radiation chemical yields of (0.122±0.001) µmol J^{-1} and (0.133±0.001) µmol J^{-1} were calculated in case of ABTS and H_2Q, respectively. Thus ~31-34% of $^{\bullet}OH$ takes part in reactions leading to species **k** and **f**.

$Fe(CN)_6^{3-}$ is expected to react with α-aminoalkyl (species **g** and **h**) and cyclohexadienyl type radicals (species **a** and its isomers) of thiacloprid. However, the kinetic trace in Figure 4D allows only approximation yielding $G \approx 0.13$ µmol J^{-1} being ~23% of the initially available $^{\bullet}OH$. By tentatively subtracting the contribution of α-aminoalkyl radicals (9%) we obtain ~14% contribution of hydroxycyclohexadienyl type radicals (species **a** and its isomers) to the total amount of free radicals in the system.

α-(Alkylthio)alkyl radicals are reducing agents that do not react with $Fe(CN)_6^{3-}$, this fact being substantiated with the remaining peak at 285 nm in Figure 3B, where these intermediates usually absorb. They do not react with MV either due to their mild reducing nature based on previous studies [23, 53]. A prediction can, however, be made taking the molar absorption coefficient of similar α-(alkylthio)alkyl radicals as $\varepsilon = 3000$ L cm^{-1} at the maximum [55]. The calculation yields $G = 0.194$ µmol J^{-1} that is equal to ~35% of the initially available hydroxyl radical. By summarizing the yields of radicals in the system ~11% gap remains which could be explained by the overlap of spectra of various intermediates and errors in the molar absorption coefficients. We propose that it represents the stabilized $^{\bullet}OH$ adduct to the sulfur giving species **b**.

3.2 One-electron reduction of thiacloprid – reactions initiated by e_{aq}^{-}

The free radical processes initiated by e_{aq}^{-} were studied in N_2-saturated solutions containing 1.0×10^{-4} mol L^{-1} thiacloprid and 0.025 mol L^{-1} *tert*-butanol. The reaction rate constant of the e_{aq}^{-} + thiacloprid reaction was determined by monitoring the decay of e_{aq}^{-} (at 600 nm due to practical reasons), which has a strong absorption band peaking at 720 nm with $\varepsilon = 22\,700$ mol^{-1} L cm^{-1} [56]. The concentration-dependence of the pseudo-first order rate constant (Figure 5A inset) yielded $k_{eaq} = 1 \times 10^{10}$ mol^{-1} L s^{-1}, implying a practically diffusion-controlled reaction. This value is somewhat higher than that for pyridine (7.7×10^{9} mol^{-1} L s^{-1} [8]), which is attributed to the chlorine substituent that activates the aromatic system for the nucleophilic attack of e_{aq}^{-}. In case of picolinic acid containing an electron-withdrawing carboxyl group adjacent to the nitrogen also diffusion-controlled rate constant has been reported [57].

The transient absorption is characterized by one absorption band centred at 285 nm (Figure 5A). This band resembles that determined for methylated pyridine derivatives with λ_{max} at ~270 nm [8]. The transient absorption spectrum in case of pyridine and its methylated derivatives has been attributed to pyridinyl radicals [8]. The slight red-shift of this band in case of thiacloprid is presumably the net result of the opposed inductive (-I) and mesomeric (+M) effect of the chlorine substituent along with the probably electron-withdrawing nature of the side chain thiazolidine structure (due to the cyanoimino function).

The time evolution of the absorbance at 285 nm exhibits quite interesting feature with subsequent build-up and decay processes being compatible with the reaction mechanism proposed in Scheme 2. Analogously to pyridine the radical anion **o** is expected to form in the initial step, which is expected to undergo protonation at the nitrogen leading to species **p** [58]. The initial build-up, which is assigned to the formation of species **o**, is followed by a fast first-order decay with $k = 2.4 \times 10^4$ s^{-1} that represents the transformation process into species **p** (Figure 5B). Decrease in absorbance upon protonation has already been observed in our previous study [59] and it is a frequently observed phenomenon in the literature. Assuming that the absorption band at 285 nm represents the only transient in the system molar absorption coefficients of 1360 mol^{-1} L cm^{-1} and 684 mol^{-1} L cm^{-1} are calculated for species **o** and **p**, respectively. These are much lower values than that reported for pyridinyl radical (ε_{255} = 3050 mol^{-1} L cm^{-1} [8]), however, comparable to the molar absorption coefficient of monofluorocyclohexadienyl radicals ($\varepsilon_{300} \approx 1500$ mol^{-1} L cm^{-1} [60]) indicating similar electronic properties to these species.

Subsequently, another build-up process was observed on the kinetic trace obeying first-order kinetics with 1.4×10^4 s^{-1} (Figure 5C). We propose that this phenomenon is due to a dechlorination event leading to the radical cation **q** since dehalogenation of aromatic compounds by hydrated electron is a well-established reaction path [60, 61]. In addition, elimination of this substituent might eventually lead to a transient with higher molar absorption coefficient that was calculated to be 1150 mol^{-1} L cm^{-1} for **q**. Finally, the absorbance disappears following first-order kinetics with $k = 36$ s^{-1} ($\tau \approx 28$ ms).

It should also be noted that the structures in Scheme 2 have several mesomeric forms. Nevertheless, a reverse reaction sequence, i.e. dechlorination followed by protonation, is rather ambiguous since the excess charge is expected to be located on the nitrogen in the initial step facilitating a protonation process whereas the chlorine substituent can only exert its effect through the carbon atom.

4. Conclusions

The free radical chemistry lying behind the one-electron oxidation/reduction of the hazardous water contaminant thiacloprid has been comprehensively deciphered herein. These mechanistic details are essential for rationalizing the applicability of an advanced oxidation process for destroying the biological warhead of the insecticide.

Hydrated electron reacts with thiacloprid at a diffusion controlled rate forming free radicals of the pyridyl substructure. $^{\bullet}OH$ exhibits also appreciable reactivity towards thiacloprid, the reaction rate constant was found to be 4.8×10^9 mol^{-1} L s^{-1}. The reactions mostly affect the key cyanoiminothiazolidine pharmacophore essential for biological activity as ~86% of $^{\bullet}OH$ attacks this part of the molecule generating free radicals of the thioether moiety, and also α-aminoalkyl and nitrogen centred species. This finding is promising in respect to the implementation of advanced oxidation technologies for removing the insecticidal activity of thiacloprid.

Acknowledgements

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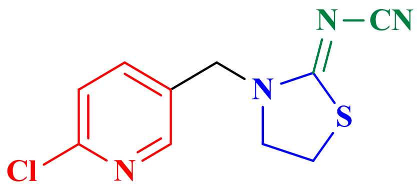


Figure 1. Thiacloprid having 2-chloropyridine (red), thiazolidine (blue) and cyanoimino (green) substructures

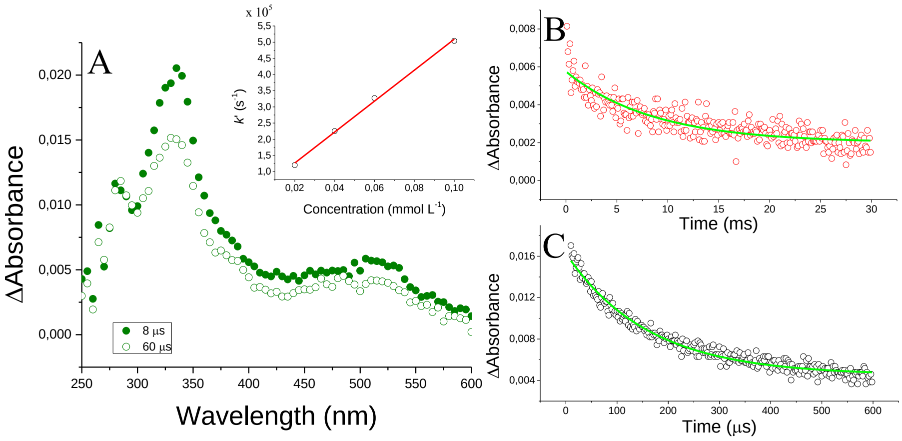


Figure 2. (A) Transient absorption spectra recorded 8 µs and 60 µs after the electron pulse in 1.0×10^{-4} mol L^{-1} thiacloprid solution at pH 5.23 saturated with N_2O, inset shows the concentration dependence of the pseudo-first order rate constant determined at 335 nm. First-order decay at 285 (B) and 335 nm (C) observed in the same solution.

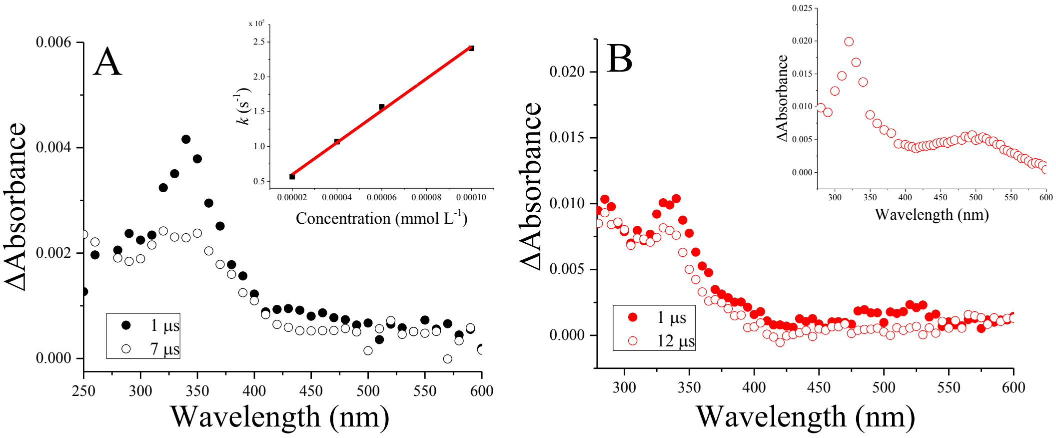


Figure 3. (A) Transient absorption spectra observed after pulse irradiation of 1.0×10^{-4} mol L^{-1} thiacloprid solution at pH 2 saturated with N_2 with inset showing the concentration-dependence of the pseudo-first order rate constant obtained at 340 nm, (B) containing also 1.0 $\times 10^{-4}$ mol L^{-1} $K_3[Fe(CN)_6]$ and saturated with N_2O. (B) inset shows the transient absorption spectra 3 µs after the electron pulse in N_2O-saturated 4.0×10^{-4} mol L^{-1} thiacloprid solution.

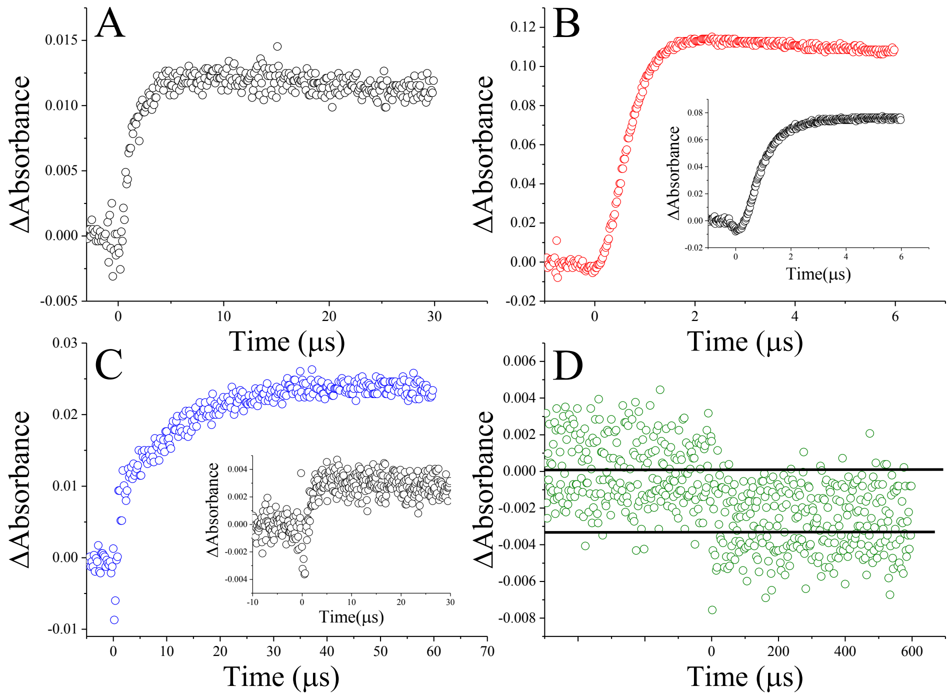


Figure 4. Kinetic trace recorded in N_2O-saturated solution containing 4.0 × 10^{-4} mol L^{-1} thiacloprid and 1.0 × 10^{-4} mol L^{-1} MV at 600 nm with ε = 11850 mol L^{-1} cm^{-1} (A), 7.0 × 10^{-5} mol L^{-1} ABTS at 415 nm with ε = 36000 mol L^{-1} cm^{-1} (B), 7.0 × 10^{-5} mol L^{-1} H_2Q at 430 nm with ε = 7200 mol L^{-1} cm^{-1} (C) and 1.0 × 10^{-4} mol L^{-1} $Fe(CN)_6^{3-}$ at 420 nm with ε = 1027 mol L^{-1} cm^{-1} (D). Inset of (B) and (C) displays a kinetic trace recorded in solution of the redox indicator at 7.0 × 10^{-5} mol L^{-1} concentration without thiacloprid.

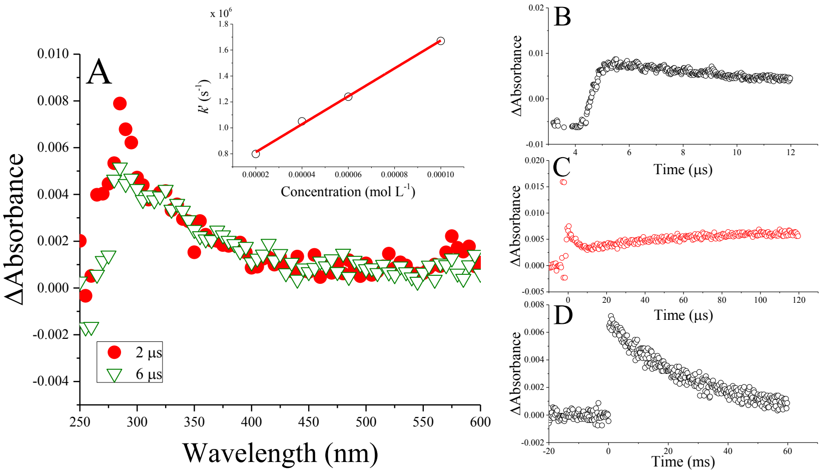
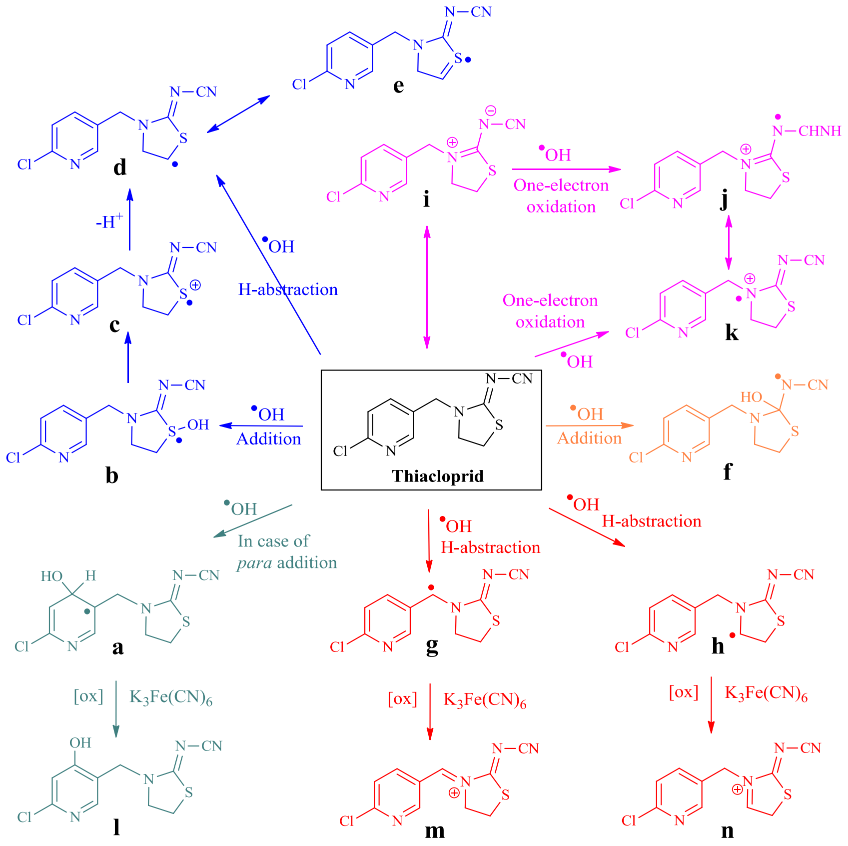
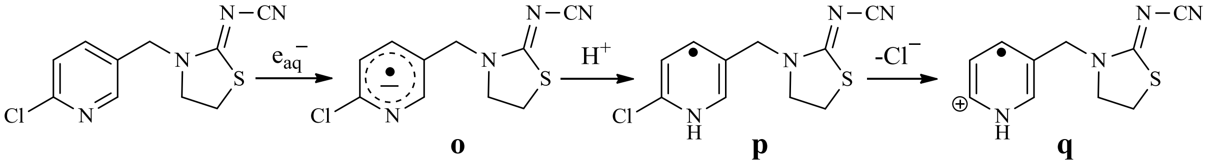


Figure 5. (A) Transient absorption spectra recorded in N_2-saturated 1.0 × 10^{-4} mol L^{-1} thiacloprid solution containing 0.025 mol L^{-1} *tert*-butanol at pH 5.23, inset shows the concentration-dependence of *k*' determined from the decay kinetics at 600 nm. (B), (C) and (D) display kinetic curves recorded in the same solution at 285 nm with different time resolution.



Scheme 1. $^{\bullet}$OH-induced free radical reactions of thiacloprid.



Scheme 2. Proposed one-electron reduction mechanism of thiacloprid.