



Reactivity of neonicotinoid pesticides with singlet oxygen

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ABSTRACT

The reaction kinetics and mechanisms of three neonicotinoid insecticides, imidacloprid (IMD), thiacloprid (THIA) and acetamiprid (ACT), with singlet oxygen and Rose Bengal excited triplet state is reported. The rate constants $(5.5 \pm 0.5) \times 10^6$, $(3.9 \pm 1) \times 10^7$, and $(1.3 \pm 1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ were determined for the chemical reaction of singlet oxygen, and the values $(4.8 \pm 1) \times 10^7$, $(1.5 \pm 1) \times 10^8$, and $(3.6 \pm 1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the reactions with Rose Bengal triplet state for IMD, THIA, and ACT, respectively. The most important primary degradation product identified was 6-chloronicotinic acid. The results support a reaction mechanism involving a charge transfer reaction between the insecticides and singlet oxygen or Rose Bengal triplet state. The toxicity of the solutions towards *Vibrio fischeri* seems not to decrease during the early stages of the reactions. Depletion of the insecticides by singlet oxygen and naturally occurring excited states might be important abiotic pathways involved in natural waters.

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1. Introduction

Neonicotinoid insecticides are agonists at nicotinic acetylcholine receptors and therefore show selective toxicity for insects over vertebrates [1]. In particular, acetamiprid (ACT, (E)-N-(6-chloro-3-pyridylmethyl)-N'-cyano-N-methylacetamidine) and thiacloprid (THIA, 3-(6-chloro-3-pyridylmethyl)-2-thiazolidinylidene-cyanamide) have been demonstrated to be less toxic towards beneficial insects such as honey bees [2] than the widely employed imidacloprid (IMD, 1-(6-chloro-3-pyridylmethyl)-2-nitroimino-imidazolidine), and therefore, they are increasingly used. Large amounts of these insecticides reach the natural aqueous systems where they may be degraded by biotic and abiotic pathways. Several naturally occurring oxidizing species, such as hydroxyl radicals ($\cdot\text{OH}$), singlet oxygen ($^1\text{O}_2$), and carbonate radicals ($\cdot\text{CO}_3^-$) are found in natural aqueous ecosystems at very low concentrations. Therefore, despite these reactive intermediates are capable of initiating the abiotic oxidation of the pesticides, mineralization or strong oxidation of organic matter is not expected to occur. As a consequence, safe self-cleaning of rivers or lakes could only be possible if the primary oxidation products formed are less toxic than the parent compounds [3]. In fact, the reactions of

imidacloprid, thiacloprid and acetamiprid with hydroxyl radicals have been recently studied and no significant detoxification was measured at the early stages of the process [4].

Since singlet oxygen, formed from the photosensitization of humic substances [5], is present in concentrations below 10^{-12} M [6], its reaction with the neonicotinoid pesticides might have unexpected consequences on the self-cleaning of natural waters. Therefore, the aim of this paper is to study the kinetics and mechanisms of the primary steps in the singlet oxygen-driven oxidation of imidacloprid, thiacloprid and acetamiprid.

2. Experimental

2.1. Reagents

Imidacloprid, acetamiprid, thiacloprid and Rose Bengal (RB) were obtained from Aldrich and used as received. Distilled water was Millipore grade. The pH of the solutions was controlled by addition of either HClO_4 or NaOH as required. Lyophilised bioluminescent bacteria (*Vibrio fischeri*, NRRL B-11177) were purchased from Macherey-Nagel and kept at -18°C until use.

2.2. Chemical analyses

Product detection and toxicity assays were performed for aqueous solutions of the pesticide (80 mg/L) containing 10 mg/L of RB. A volume of 250 mL of the samples was irradiated with a solar

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simulator (Oriol Instruments, Model 81160 equipped with a 300W xenon lamp) in an open glass vessel with magnetic stirring.

The insecticides concentration was determined by liquid chromatography (Perkin Elmer Autosystem XL). A LiChrosphere 100 RP-18 column was employed with an isocratic mixture of acetonitrile (35%) and H₂SO₄ 1 mM (65%) as eluent (1 mL/min flow). IMD was detected by its absorption at 270 nm, and THIA and ACT at 240 nm.

By-products identification was performed by GC–MS analysis (GCMS-QP2010S, Shimadzu, equipped with a quadrupole mass analyser). A Meta X5 Teknokroma column was used and the oven temperature was increased from 60 to 250 °C with a 5 °C/min rate. Samples were previously concentrated by solid phase extraction (100 mL of the aqueous solution were flown through a LiChrolut EN 200 mg cartridge (Merck)) and the organics recovered with 3 mL of methanol.

Luminescent assays were carried out according to the standardised ISO 11348-3 norm, using lyophilised *V. fischeri*. A salty solution (Macherey-Nagel) was used for the reconstitution of the bacteria. The luminescence was measured by a Lumiflex-Bio-10 Luminometer from Macherey-Nagel. The toxicity of 500 µL solution containing a given amount of insecticide was determined after 15 min incubation with 500 µL solution of reconstituted bacteria. Distilled water and zinc sulphate were used in control samples. A blank sample consisting of bacterial suspension in 2% NaCl is included along with the test sample. All samples were neutralised before analysis.

2.3. Time-resolved kinetic measurements

The overall rate constants for O₂ (¹Δ_g) quenching k_t , were determined by time-resolved phosphorescence detection (TRPD) emitted by O₂ (¹Δ_g) at 1270 nm. The lifetimes were evaluated in the absence ($\tau_{\Delta 0}$) and presence (τ_{Δ}) of the insecticide (I). These lifetimes were plotted according to the Stern–Volmer equation: $1/\tau_{\Delta} = 1/\tau_{\Delta 0} + k_t \times [I]$.

The doubled frequency of 532 nm from a Nd:YAG (Surelite) laser (2 ns pulse width and 5 mJ per pulse) was used to excite RB. The emitted radiation was detected at right angle (using an amplified Judson J16/8Sp germanium detector) after passing through appropriate filters. The output of the detector was coupled to a digital oscilloscope (500 MHz Tektronix TDS 520A) and stored. The solutions were prepared with D₂O and pD values were calculated by adding 0.4 units to the known pH values [7,8].

The rate constant of the reaction between the triplet state of RB and the insecticides, k_T , was determined from the absorption traces of RB triplet state at 620 nm in the presence and absence of the insecticides in Ar-bubbled solutions. The apparent rate constants of the decay of the triplet absorbance at 620 nm (k_{app}) linearly depend on the concentration of the insecticide (I), $k_{app} = k_0 + k_T \times [I]$, with k_0 the decay rate constant of RB triplet in the absence of the insecticide. Therefore, k_T values were determined from the slopes of the plots of k_{app} vs. [I]. On the other hand, plots of the ratio of the initial singlet oxygen emission in the absence (P_0) and the presence (P) of a known concentration of insecticide vs. [I], also yield information on k_T , $P_0/P = 1 + k_T \times \tau_0 \times [I]$, where τ_0 is the lifetime of RB triplet in air-saturated solutions in the absence of insecticide.

2.4. Steady-state kinetic experiments

The consumption of oxygen and the insecticide were measured during irradiation of initially air-saturated aqueous solutions containing RB and the insecticides. A 150 W quartz-halogen lamp passed through a 480 nm cut-off filter was used to irradiate preferentially the sensitizer. Dissolved oxygen concentrations

were measured with a selective oxygen electrode Orion 97-08-99, connected to a Consort C-832 pH-meter and data digitalized into a computer. Furfuryl alcohol was used as a specific probe for singlet oxygen [8]. Solutions containing RB (0.5–0.6 absorbance at 532 nm) and either furfuryl alcohol or the insecticide, were introduced in a sealed vessel containing the electrode and were continuously stirred. The ratio between the oxygen and insecticide consumption was also determined.

The slopes of the linear plots of $[O_2]_t/[O_2]_0$ vs. $[I]_t/[I]_0$ yield the number of O₂ molecules consumed per molecule of the insecticide. Apparent rate constants involving the steady-state concentration of singlet oxygen, $k_{app} = k_r \times [^1O_2]_{ss}$, can be obtained from plots of $[I]_t/[I]_0$ vs. the photolysis time. To determine the absolute rate constant k_r of the reaction between the insecticides and singlet oxygen, $[^1O_2]_{ss}$ is evaluated from experiments performed under identical experimental conditions but in the presence of furfuryl alcohol, whose reaction rate constant with singlet oxygen, $k_r^F = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, is well reported in the literature [9].

3. Results and discussion

3.1. Kinetic measurements

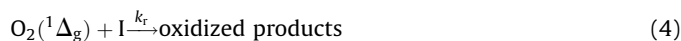
Removal of all three insecticides by means of singlet oxygen was investigated. To generate this species, RB was irradiated with visible light to generate an electronically excited triplet state (³RB). An energy transfer from ³RB to the ground triplet state of molecular oxygen, O₂ (³Σ_g[−]), yields singlet oxygen, O₂ (¹Δ_g) with rate constant k_{O_2} , reaction (1):



Singlet oxygen decays by interaction with the solvent with a rate constant k_D , reaction (2):



Scavenging of O₂ (¹Δ_g) by the insecticides may take place by two main pathways: a physical interaction with quenching constant k_q , reaction (3), and a chemical reaction with rate constant k_r leading to the oxidation of the insecticides, reaction (4). The bimolecular rate constant for the overall process, $k_t = k_r + k_q$, includes the contribution of both reaction channels.



The k_T values depicted in Table 1 are obtained from the slope of the linear plot of $1/\tau_{\Delta}$ vs. [I], *vide supra* (see Fig. 1). The value $\tau_{\Delta 0} = 66 \mu\text{s}$ in D₂O obtained from the intercepts of the plots are in agreement with reported values [10].

The phosphorescence traces of singlet oxygen show decreasing initial emission values with increasing insecticide concentration (see Fig. 1 inset), which indicates that RB triplet, the precursor for

Table 1

Absolute rate constants obtained for the overall reaction of the insecticides with singlet oxygen (k_t) and for the reaction between RB triplet state and the insecticides (k_T).

| Insecticide | $k_t \text{ (M}^{-1} \text{ s}^{-1}\text{)}$ | $k_T \text{ (M}^{-1} \text{ s}^{-1}\text{)}$ |
|--------------|--|--|
| Imidacloprid | $(5.5 \pm 0.5) \times 10^6$ | $(4.8 \pm 1) \times 10^7$ |
| Thiacloprid | $(3.9 \pm 1) \times 10^7$ | $(1.5 \pm 1) \times 10^8$ |
| Acetamiprid | $(1.3 \pm 1) \times 10^6$ | $(3.6 \pm 1) \times 10^7$ |

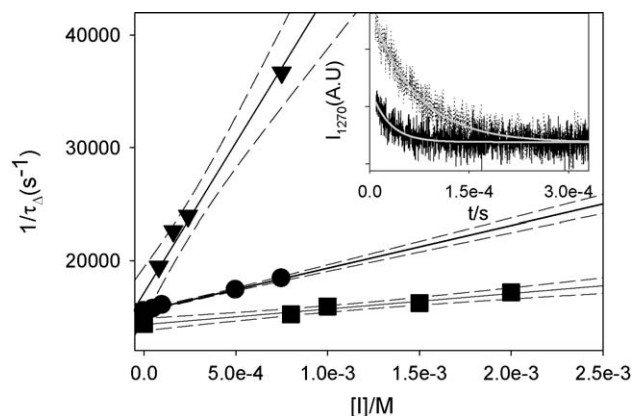


Fig. 1. Plot of $1/\tau_{\Delta}$ vs. $[I]$ obtained for THIA (▼), IMD (●), and ACT (■) in deuterated aqueous solutions at 25 °C. *Inset:* phosphorescence intensity emitted at 1270 nm, I_{1270} , obtained from experiments of the main figure with solutions in the absence and presence of 7.5×10^{-4} M of THIA (upper and lower trace, respectively).

singlet oxygen, is capable of reacting with the insecticides, reaction (5).



To investigate the reaction of the triplet state of RB with the insecticides, laser photolysis experiments were performed with oxygen-free solutions of RB and the insecticides as described in Section 2. Fig. 2 shows the plots of k_{app} vs. $[I]$ for the three insecticides. From the slopes of these straight lines, the rate constants for the reaction of RB triplet state and the insecticides (k_T) are obtained, as shown in Table 1. Values of k_T calculated from P_0/P vs. $[I]$ plots agree, within the experimental error, with those shown in Table 1. The initial absorbance of ^3RB observed in the different experiments does not depend, within the experimental error, on the concentration of the insecticide; therefore, any reaction of the insecticide with the excited singlet state of RB (^1RB) may be neglected. This conclusion is in agreement with the <1 ns lifetime reported for ^1RB [11].

The values of k_T for the chemical reaction of singlet oxygen with the insecticides may be determined in steady-state experiments following the insecticide consumption during irradiation of air-saturated aqueous solutions containing RB and the insecticides. Despite the experimental conditions were optimized to minimize photolysis of the insecticides during RB irradiation, control experiments in the absence of RB were performed. Fig. 3 depicts

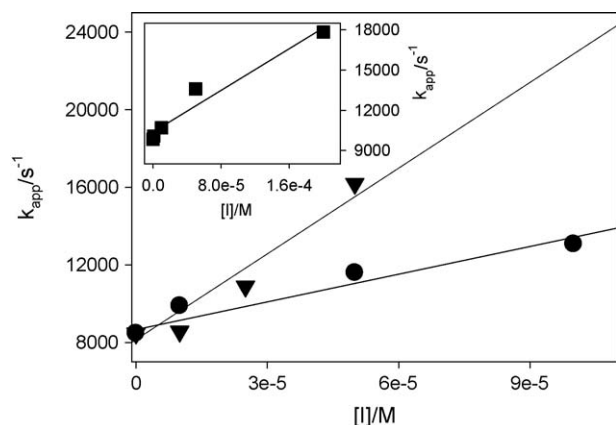


Fig. 2. Plots of the apparent rate constant, k_{app} , vs. $[I]$ for argon-saturated aqueous solutions containing 10 mg/L of RB and variable concentrations of the insecticides: THIA (▼), IMD (●), and ACT (■).

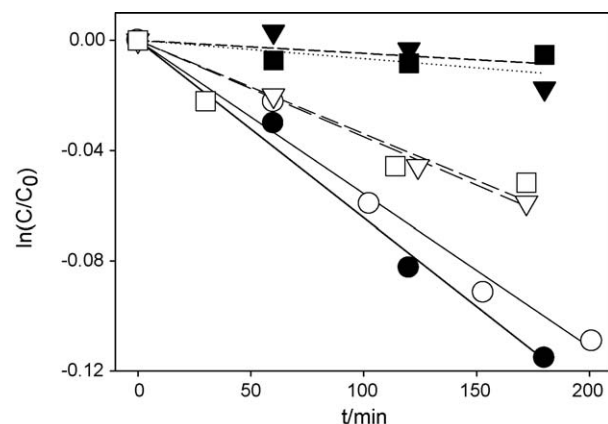


Fig. 3. Semilogarithmic plots of the relative concentration of the insecticide vs. time for initially air-saturated aqueous solutions containing 3.3×10^{-4} M of IMD (●), THIA (▼) and ACT (■) irradiated with light of $\lambda > 480$ nm in the absence (full symbols) and presence (empty symbols) of 10 mg/L of RB.

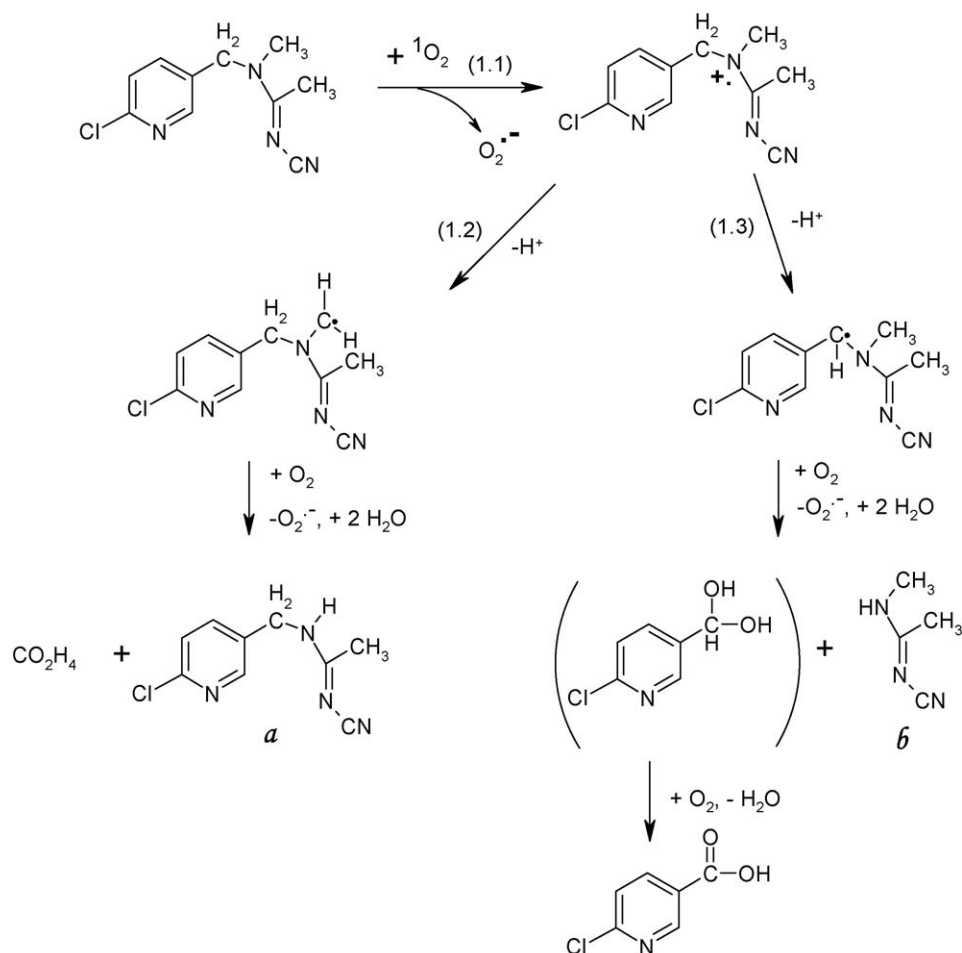
the semilogarithmic plots of the insecticide consumption against time for experiments in the presence and absence of RB. Depletion of THIA and ACT is significant only in the presence of RB, which therefore indicates that the contribution of the insecticide photolysis under these experimental conditions is negligible; hence, reliable information on their rate constants k_T can be obtained from their respective decays. However, the faster depletion observed for IMD in the absence of RB indicates that IMD photolysis is still the main reaction path under the experimental conditions used, as expected from its stronger absorption in the visible range compared to THIA and ACT [12].

The pseudo first-order slope for the consumption of the insecticide is proportional to k_T if the reaction of O_2 ($^1\Delta_g$) with the insecticide is the main substrate consumption pathway; however, this is not the case for the insecticides herein studied due to the occurrence of reaction (5). An expression for the ratio $k_{\text{app}}^{\text{I}}/k_{\text{app}}^{\text{R}}$ may be obtained from the solution of the differential mass equations for reactions (2)–(5) in experiments with the insecticides and with the reference, respectively. Eq. (6) is obtained considering that under our experimental conditions $k_D > k_T^{\text{R}} \times [\text{R}]$, $k_D > k_T \times [\text{I}]$, and $k_{\text{O}_2} \times [\text{O}_2] > k_T \times [\text{I}]$.

$$\frac{k_{\text{app}}^{\text{I}}}{k_{\text{app}}^{\text{R}}} = \left(\frac{k_T}{k_T^{\text{R}}} + \frac{k_T \times k_D}{k_{\text{O}_2} \times [\text{O}_2] \times k_T^{\text{R}}} \right) \quad (6)$$

The k_T values obtained from Eq. (6) taking the reported values for $k_{\text{O}_2} = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [13], $k_D = 2.5 \times 10^5 \text{ s}^{-1}$ [10], and $k_T^{\text{R}} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [9] and those measured for k_T (depicted in Table 1) are $(4 \pm 1) \times 10^7$ and $(9 \pm 6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for THIA and ACT, respectively. The latter values indicate that the quenching of singlet oxygen by the insecticides is almost entirely due to the insecticide oxidation reaction (4), and $k_t \cong k_T$. Therefore, as k_t values were measured with higher precision than k_T , we recommend the use of the k_t values as a measure of k_T .

The values of k_T are approximately three orders of magnitude lower than those measured for the reaction with the hydroxyl radical [4]. However, the steady concentration of O_2 ($^1\Delta_g$) in natural waters is several orders of magnitude higher than that of hydroxyl radicals, and therefore the reaction of the insecticides with this reactive species might be of importance in the natural systems. In sunlight-exposed shallow waters, the steady-state concentration of singlet oxygen is on the order of 10^{-12} to 10^{-13} M [6]. The values of k_T herein reported indicate that the half life of ACT, IMD, and THIA, due to their reaction with singlet oxygen in natural aquatic reservoirs is around 7 h to 21 days. Despite the low rate constants observed for the reactions between singlet oxygen



Scheme 1. Mechanism for ACT reaction with singlet molecular oxygen. Stable compounds in brackets are proposed, but not detected.

and the insecticides, the insecticides lifetimes in natural waters due to these reactions are on the same order than those of the more reactive hydroxyl radicals [4] and are therefore a significant abiotic route in the natural systems.

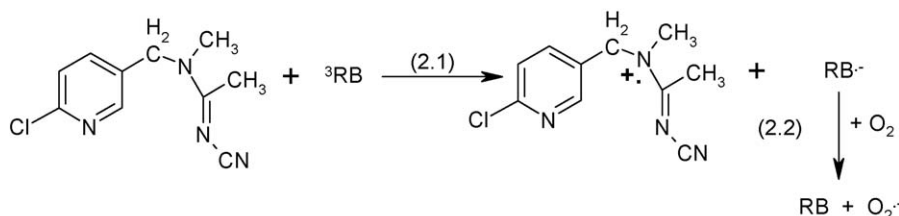
3.2. Reaction pathways

Formation of 6-chloronicotinic acid and 6-chloronicotinamide were observed by GC–MS in irradiation experiments of air-saturated aqueous solutions of each of the three insecticides in the presence of RB. For ACT, also N-[(6-chloro-3-pyridyl)methyl]-N'-cyanoacetamide was detected. The number of 1.9, 1.5 and 1.5, oxygen molecules consumed per molecule of IMD, THIA, and ACT, respectively, indicate a complex reaction mechanism.

Based on the detected intermediates, a pathway for the primary steps of the $^1\text{O}_2$ oxidation of ACT is proposed in Scheme 1. Singlet oxygen reaction with ACT may be explained by a charge transfer pathway leading to the formation of superoxide radical anions,

$\text{O}_2^{\bullet-}$, and the radical cation of ACT (reaction (1.1)) in agreement with the reported mechanism for the reaction of $^1\text{O}_2$ with substituted amines [14]. Elimination of H^+ leads an α -aminoalkyl radical, either in the amine methyl group (reaction path (1.2)) or in the methylene bridge (reaction path (1.3)). The α -aminoalkyl radicals ($-\text{HC}^\bullet-\text{N}<$) are known by their reducing properties [15] and may further reduce molecular oxygen to superoxide radical [16] being themselves oxidized to hydroxymethylamine after water addition [4]. Further hydrolysis of the latter compounds leads to the formation of secondary amines **a** and **b** in Scheme 1, and to aldehyde hydrates (formaldehyde and chloronicotinaldehyde, not detected). Under oxidizing conditions, the aldehyde hydrates readily oxidize to the corresponding acids (carbonic and chloronicotinic acids). Strong oxidation of compound **a** may yield to 6-chloronicotinamide formation.

The nature of the products formed is in agreement with those observed for the reaction of singlet oxygen with benzyldimethylamine [17]. Singlet oxygen attack to ACT takes place mainly at the



Scheme 2. Reaction mechanism of ACT and Rose Bengal triplet state (^3RB).

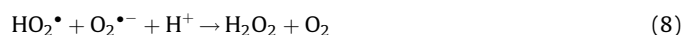
Table 2

INH% values for 80 mg/L insecticide solutions in the presence of 10 mg/L of RB before and after 3 h irradiation.

| Substrate | EC ₅₀ (mg/L) | Toxicity before irradiation (%) | Toxicity after 3 h irradiation (%) |
|-----------|-------------------------|---------------------------------|------------------------------------|
| IMD | 101 | 32 | 67 |
| THIA | 79 | 51 | 67 |
| ACT | 129 | 28 | 67 |
| RB | – | 23 | 16 |

amine group of the molecule and does not at the pyridine ring, as expected from the reported low reactivity of ¹O₂ with substituted pyridines [18].

Superoxide radicals formed recombine to yield molecular oxygen and H₂O₂, according to reactions (7) and (8) [19].



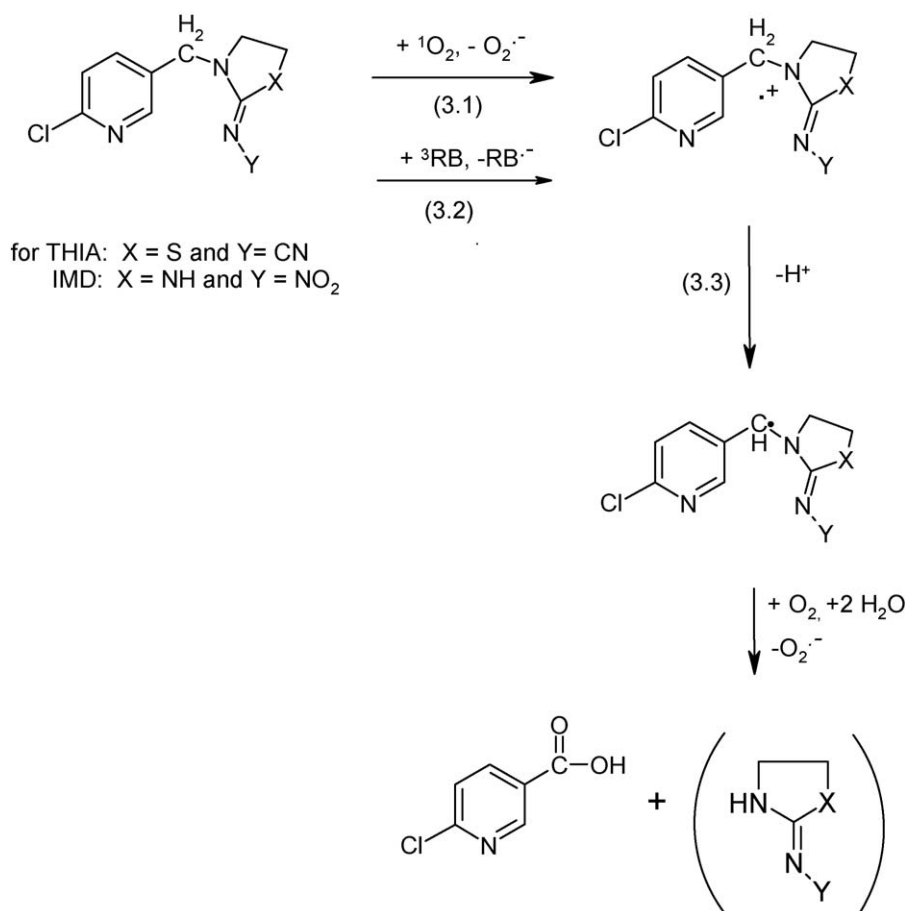
However, as already discussed, the insecticide quenching of ³RB is also an important reaction in air-saturated solutions, and therefore, the observed products may also arise from reaction (5). RB triplet state is known to undergo charge transfer processes, acting either as electron donor or electron acceptor [11]. Since amines are excellent electron donors [14], a charge transfer from the amine to ³RB also yields the radical cation of ACT (reaction (2.1) in Scheme 2). RB radical anion may react with the dissolved

molecular oxygen to yield superoxide, reaction (2.2). Further reactions of the radical cation of ACT in the presence of dissolved molecular oxygen are those shown in Scheme 1.

Since the reactions of IMD and THIA with singlet oxygen and ³RB also leads to the formation of 6-chloronicotinic acid and 6-chloronicotinamide, similar reaction paths as those observed for ACT are expected. Scheme 3 shows the charge transfer pathways leading to the formation of the radical cation of IMD and THIA either after reaction with singlet oxygen or ³RB (reactions (3.1) and (3.2), respectively). Further elimination of H⁺ leads an α-aminoalkyl radical in the methylene bridge (reaction path (3.3)), which upon subsequent reaction with molecular oxygen and water forms 6-chloronicotinic acid. Formation of an α-aminoalkyl radical at the methylene group of the heterocycle may be a possible reaction path leading to the final generation of 6-chloronicotinamide after oxidation of the partially oxidized intermediate products. However, as no other intermediates could be observed with our analytical equipment, these reaction pathways are not shown in Scheme 3.

The variation in the standard free energy ΔG° for an electron transfer reaction involving an excited triplet state such as reactions (2.1) and (3.2), in Schemes 2 and 3, respectively, can be expressed by Eq. (9), which relates the redox potentials E° of the acceptor (RB) and the donor (I), and RB triplet energy, ΔE₀₀ in J mol⁻¹ [20]. The electrostatic work term w accounts for the coulombic attraction in the products (RB^{•-}/I^{•+}). The symbols: e and N_A stand for the electron charge and the Avogadro constant.

$$\Delta_{\text{ET}}G^\circ = N_A \times (e \times E^\circ(\text{I}^{\bullet+}/\text{I}) - e \times E^\circ(\text{RB}/\text{RB}^{\bullet-}) + w(\text{I}^{\bullet+}\text{RB}^{\bullet-})) - \Delta E_{00} \quad (9)$$



Scheme 3. Reaction mechanism of IMD and THIA with either singlet oxygen or ³RB. Stable compounds in brackets are proposed, but not detected.

Since the one-electron reduction potential for RB is $E^\circ(\text{RB}/\text{RB}^{\bullet-}) = -0.54 \text{ V}$ vs. NHE and that its triplet state energy is $168.56 \text{ kJ mol}^{-1}$ [11], then any ^3RB quencher with a reduction potential lower than 1.23 V vs. NHE may undergo an electron transfer from the quencher to ^3RB . The reported reduction potentials for IMD and ACT are -0.96 and -1.26 V , respectively [21,22], and therefore $\Delta_{\text{ET}}G^\circ - w \cong -213 \text{ kJ mol}^{-1}$ is obtained for IMD and -242 kJ mol^{-1} for ACT. Due to the nature of the charges in the pair $\text{I}^{\bullet+} \text{RB}^{\bullet-}$, the term w contributes to the exergonicity of $\Delta_{\text{ET}}G^\circ$, which shows that the reaction of the insecticides with ^3RB is thermodynamically allowed.

3.3. Toxicity of the insecticides and their oxidation products

The toxicity of the mixture of RB and the insecticides was determined before and after 3 h irradiation. The trend observed for the initial toxicities are in agreement with those of the EC_{50} values determined in a previous work [4]: $\text{ACT} < \text{IMD} < \text{THIA}$ (see Table 2). Data measured after 3 h irradiation were higher than the initial ones: 67% in all cases. However, the latter solutions contain $\sim 10 \text{ mg/L}$ of the highly colored RB which may interfere the toxicity assays. Therefore, the inhibition of *V. fischeri* luminescence by a 10 mg/L solution of RB was determined before and after 3 h photolysis. Although the obtained toxicity values were significant (see Table 2), not all the toxicity observed for the treated insecticide solutions should be attributed to RB. The detoxification of the insecticide solutions by singlet oxygen is not observed, in agreement with previous investigations on the oxidation of the insecticides initiated by hydroxyl radicals [4]. This is an expectable behavior as almost the same intermediates were observed in both cases. A more detailed discussion on the toxicity of the primary oxidation products of the insecticides can be found in Ref. [4].

4. Conclusions

The insecticides IMD, ACT, and THIA chemically react with singlet oxygen and Rose Bengal triplet state with rate constants in the range from 1×10^6 to $4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $^1\text{O}_2$ and of 4×10^7 to $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for ^3RB . Both reactions involve a charge transfer from the insecticide to either $^1\text{O}_2$ or ^3RB , characteristic for tertiary amines. The reaction of the insecticides with triplet states have important environmental consequences, as the absorption of 355 nm light by DOM leads to the generation of triplet states with energies of $\sim 160 \text{ kJ mol}^{-1}$ [23,24]. The latter triplets may therefore efficiently initiate the insecticides degradation in heavily contaminated waters with severely depleted concentrations of dissolved molecular oxygen.

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