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Studies on reaction mechanisms and distinct chemiluminescence from cyanoimino neonicotinoids triggered by peroxymonosulfate in advanced oxidation processes

Mengdie Cai, Weimin Gan, Zhiqin Ding, Hongping Cai, Lijun Wei*, Xianglei Cheng*

Jiangxi Province Key Laboratory of Preventive Medicine, School of Public Health, Nanchang University, Nanchang *330006, China*

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ABSTRACT

In this study, we proposed a novel method to investigate the advanced oxidation process of neonicotinoids (NNIs) from the perspective of concomitant chemiluminescence (CL) reaction. It was found that in the presence of cobalt ions with cyanoimino NNIs, acetamiprid (ACE) and thiacloprid (THI), could promote peroxymonosulfate and $Ru(bpy)_3^{2+}$ to produce strong CL, but no CL occurred with nitro-involved NNIs as alternatives. Experimental dada from UV absorption spectra and chemiluminescence spectra suggested that new cyclic compounds might be formed during the reaction. Based on the results of free radical scavenging experiment and mass spectra, a new degradation and reaction mechanism of cyanoimino-containing NNIs was proposed. ACE or THI were first attacked by $SO_4^{\bullet-}$ to form benzyl radicals, which in turn reacted with the carbon atoms of cyano group through electrophilic addition reaction in the formation of intramolecular ring. Then a redox reaction between $Ru(bpy)_3^{3+}$ and imino group immediately took place with CL emission (610 nm). The new mechanistic knowledge would be meaningful for other contaminants for their interactions with PMS.

Chemiluminescence (CL) has been widely applied in the field of environment [1,2], food safety [3], clinic diagnostics [4], pharmaceuticals [5] and biology [6]. At present, it is still research focus in CL coupling with various nanomaterials, such as quantum dots [7–9], LDHs [10,11], MOFs [12]. On the other hand, a lot of efforts are made for searching and developing novel CL systems [13] and new CL methods for the determination of emerging contaminants [14].

Neonicotinoids (NNIs) are a class of drugs that act on the nerves of insects. By blocking the transmission between nerve cells, they cause the insects to become overexcited or paralyzed and thus lose control of their behavior [15]. Since the introduction of the first generation of NNIs, Imidacloprid, in the 1990s, more NNIs with different chemical structures have been greatly developed [16,17]. NNIs are widely used in agriculture because of their wide spectrum, high efficiency and low dosage. However, at the same time, the presence of such pollutants has been detected in water bodies of agricultural areas around the world. Additionally, they have been reported in natural water bodies far away from agricultural activities, even in groundwater and drinking water [18,19]. Studies have shown that the global decline in the number of pollinators such as bees is closely related to the presence of NNIs [20,21]. Moreover, through the enrichment of the food chain, NNIs in the aquatic environment can be transferred to mammals, such as birds and rats, resulting in their death [22,23]. It has been reported that NNIs also exist in normal human urine. In addition, it has been reported that the inhalation of high dose of NNIs will affect and change the memory storage, cognition and related behaviors of human beings, further causing human bodies to lose control of its own behavior [24].

Peroxymonosulfate (PMS) and persulfate are a promising oxidant, which has been widely used in advanced oxidation processes (AOPs) to eliminate organic pollutants in water [25]. They can produce $SO_4^{\bullet-}$ through heating, ultraviolet light irradiation or activation by some metal ions [26] or nanomaterials [27,28]. Compared with $^{\bullet}OH$, $SO_4^{\bullet-}$ has higher redox potential, longer survival time, wider pH range. Previous studies such as literatures [29–32] revealed that different degradation method exhibited different performance for the elimination of NNIs and reduction of total organic carbon although with the addition of PMS as oxidants. Meanwhile, various degradation pathways and transformation products were proposed. However, only one kind of NNIs was selected as the model compound to investigate the degradation mechanisms in the previous researches. Although NNIs had a

* Corresponding authors.
E-mail addresses: weilj7681@163.com (L. Wei), chengxlsd@163.com (X. Cheng).

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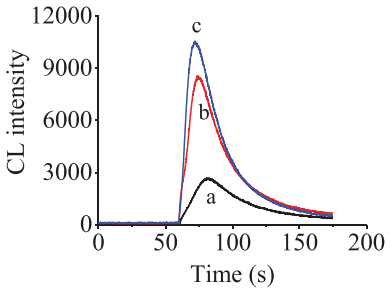


Fig. 1. CL profiles of Co^{2+}/PMS-$Ru(bpy)_3^{2+}$ system: (a) Co^{2+}+$Ru(bpy)_3^{2+}$+PMS; (b) Co^{2+}+$Ru(bpy)_3^{2+}$+THI+PMS; (c) Co^{2+}+$Ru(bpy)_3^{2+}$+ACE+PMS. Condition: 0.5 mmol/L PMS; 0.5 mmol/L Co^{2+}; 10.0 μmol/L $Ru(bpy)_3^{2+}$; 1.0 μmol/L ACE; 1.0 μmol/L THI.

similar chemical structure chloropyridine ring, each NNIs might show quite distinctly active sites (*e.g.*, nitroso or cyanoimino group) when reacting with PMS.

In this work, cobalt ions were employed to active PMS to generate free radical $SO_4^{\bullet-}$ which could degrade NNIs. Then, several frequently used NNIs were studied and compared based on the proposed system. The corresponding CL mechanisms were carried out based on the results of spectral data and mass spectra.

First, kinetic CL profiles of acetamiprid (ACE) and thiacloprid (THI) were investigated in the present Co^{2+}/PMS-$Ru(bpy)_3^{2+}$ system. As shown in Fig. 1 (curve a), when 100 μL PMS solution was injected into the mixture of Co^{2+} and $Ru(bpy)_3^{2+}$, light emission could be measured due to the redox reaction between PMS and $Ru(bpy)_3^{2+}$. Significant CL enhancement could be observed in the presence of trace amount of ACE and THI (Fig. 1, curves b and c). This interesting CL phenomena is in accord with our hypothesis. Moreover, the CL intensity of THI with the same concentration was weaker than that of ACE. This is ascribed to its chemical structure with thiazole ring which influences the CL yield.

Then, the CL spectra of the present Co^{2+}/PMS-$Ru(bpy)_3^{2+}$ system reacting with ACE or THI were recorded (not shown here). An apparent light emission with maximum wavelength locating at 610 nm was obtained using fluorescence spectrophotometer with its exciting light source turning off. It is well known that CL emission at 610 nm belongs to the excited state $[Ru(bpy)_3^{2+}]^*$. What about other CL system including $Ru(bpy)_3^{2+}$ when encountering with NNIs?

CL systems of $Ru(bpy)_3^{2+}$ with permanganate, cerium, lead dioxide as oxidants were studied in the presence of ACE or THI. No CL emission was found in these $Ru(bpy)_3^{2+}$ CL system. Additionally, commonly used NNIs, including imidacloprid, clothianidin, thiamethoxam, dinotefuran and nitenpyram, were examined in the proposed Co^{2+}/PMS-$Ru(bpy)_3^{2+}$ system. Background CL emission was still constant, but remarkable quenching of light emission could be measured when encountering with popular NNIs except ACE and THI. These experimental results indicated that NNIs might generate different products in the presence of PMS with cobalt ions as catalysts, which was not in accord with other researchers. On the other hand, ACE and THI with same cyanoimino group should undergo the same reaction route and form similar products. While other five NNIs mentioned in this study with nitro groups involved did not take place the similar procedure. These clues revealed that other oxidant might include in the proposed system.

Then, the radical scavengers were used to explore the types of free radicals in the reaction process. By introducing methanol (0.01 mol/L) and *tert*–butyl alcohol (0.01 mol/L) as scavengers for $SO_4^{\bullet-}$/$^{\bullet}OH$ and $^{\bullet}OH$, respectively. After adding methanol, the CL intensity of the system was reduced by about 80%, while the CL intensity of the system did not change after adding *tert*–butyl alcohol. It showed that $SO_4^{\bullet-}$ played a key role in this system.

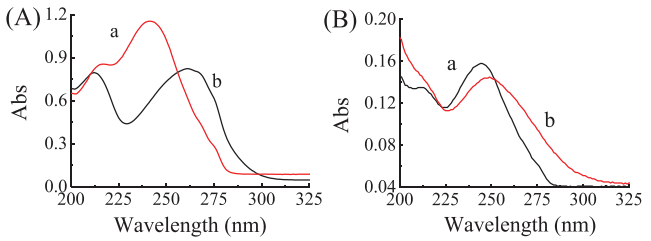


Fig. 2. (A) UV spectra of Co^{2+}/PMS-THI reaction: (a) THI; (b) Co^{2+}+THI+PMS. (B) UV spectra of and Co^{2+}/PMS-ACE reaction: (a) ACE; (b) Co^{2+}+ACE+PMS. Condition: 0.5 mmol/L PMS; 0.5 mmol/L Co^{2+}; 50.0 μmol/L THI; 5.0 μmol/L ACE.

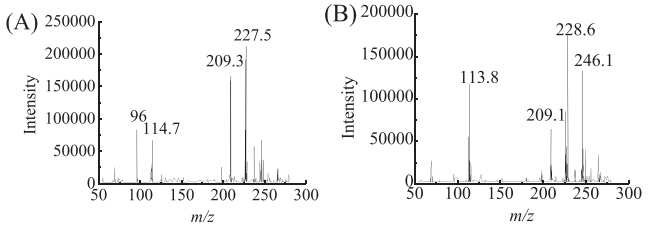
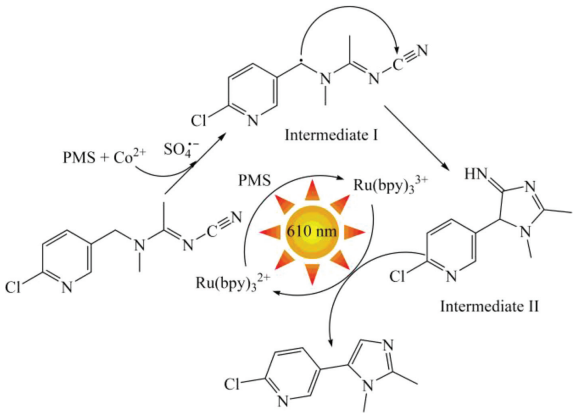


Fig. 3. Mass spectra of products generated from the reaction Co^{2+}/PMS-$Ru(bpy)_3^{2+}$-ACE (A) and Co^{2+}/PMS-$Ru(bpy)_3^{2+}$-THI (B).

In order to further clarify the mechanism of present CL system, UV spectra of the substances were recorded before and after reaction. The results were shown in Fig. 2. The UV absorbance of THI (Fig. 2A) locating at 245 nm was produced by the pyridine ring. With the addition of Co^{2+}/PMS, the UV absorbance at 245 nm disappeared and a new peak occurred with the maximum absorption locating at 264 nm, which indicated that the pyridine ring of THI might be damaged or a new ring was recombined and stronger conjugation effect was formed. As for ACE (Fig. 2B), the UV spectra changed a little differently. The UV absorbance at 245 nm decreased when the solutions of Co^{2+} and PMS were mixed with ACE. Then the absorbance of Co^{2+}/PMS-ACE in the range of 260 nm to 300 nm increased but not as dominantly as that of Co^{2+}/PMS-THI. It is speculated that it is associated with conjugation. Due to the existence of thiazole ring, the conjugation effect from products of Co^{2+}/PMS-THI is stronger than that of Co^{2+}/PMS-ACE.

Mass spectrometry has been widely used as a powerful technology for the identification of degradation products [33,34]. In this work, mass spectra of products derived from the present CL system was shown in Fig. 3A in the presence of ACE or THI. The corresponding peak of ACE molecules with *m/z* 223.7 disappeared. The characteristic peak with *m/z* 209.3 (compound **A**) and 227.5 merged. It is further speculated that the cyanoimino group were the main reaction sites [31]. An ACE molecule after reducing a nitrogen atom was regarded as the peak with *m/z* 209.3, while *m/z* 227.5 was the addition products between H_2O and compound **A**. Thus, a compound, cimetidine, also possessing cyanoimino group was selected to investigate the CL behavior under the same condition. The results indicated that cimetidine did not have any influence on the light emission. In addition, careful evaluation of mass spectra led us to confirm that there were not any hydroxylated or demethylated products reported in prior literatures [35–37]. The unusual results could be ascribed to not hydroxyl radical but sulfate radicals taking part in AOPs of cyanoimino NNIs. This coincided with the radical scavenging experiments and hydroxylated reaction pathway was less likely in the present condition. These evidences proved that there might be other factors in the present CL system. Compared to cimetidine, benzyl group existing in ACE and THI should be the target of $SO_4^{\bullet-}$, which triggered the initial step of the present CL system and was consistent with the report of Zare's group [38]. Results from our experiments led us to pro-



Scheme 1. Proposed CL mechanism of Co^{2+}/PMS-$Ru(bpy)_3{}^{2+}$-NNIs system.

pose that benzylic hydrogen abstraction of ACE and THI attacked by $SO_4^{\bullet-}$ afforded a carbon radical intermediate. The mass spectra of products generated from the reaction Co^{2+}/PMS-$Ru(bpy)_3{}^{2+}$-THI had similar results with that of Co^{2+}/PMS-$Ru(bpy)_3{}^{2+}$-ACE as shown in Fig. 3B. The peak with *m/z* 228.6 came from the THI molecules after the subtraction of both a sulfur atom and a nitrogen atom, while the peak with *m/z* 246.1 was products of water addition to *m/z* 228.6.

According to the above-mentioned data, a possible reaction mechanism of the Co^{2+}/PMS-$Ru(bpy)_3{}^{2+}$-NNIs CL system was established as shown in Scheme 1, with ACE as an example. First, a part of PMS could be activated by Co^{2+} to generate $SO_4^{\bullet-}$ radicals, which acted on the benzyl group of ACE and caught an electron. The resulted intermediate **I** with cyano group attacked benzyl group and a pentacyclic structure (intermediate **II**) was formed with imino group as a branched chain. On the other hand, the rest part of PMS could oxidize $Ru(bpy)_3{}^{2+}$ to produce $Ru(bpy)_3{}^{3+}$. The imino groups could react with $Ru(bpy)_3{}^{3+}$ to generate $[Ru(bpy)_3{}^{2+}]^*$, which returned to the ground state and CL emission occurred.

The present work is carried out due to the findings of CL generated by ACE and THI in the Co^{2+}/PMS-$Ru(bpy)_3{}^{2+}$ system. Based on the results of chemiluminescence spectroscopy, ultraviolet absorption spectroscopy, mass spectrometry and radicals quenching experiments, the reaction mechanisms of the advanced oxidation process of cyanoimino-containing NNIs was proposed. To the best of our knowledge, this is the first report on annulation reaction occurring in AOPs of NNIs by PMS.

Declaration of competing interest

The authors report no competing interest.

Acknowledgments

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