Aquatic photolysis of strobilurin fungicide kresoxim-methyl: kinetics, pathways, and effects of adjuvants†

Xuewei Zhang,a Jing Ye,a Zhigang Ni,b Xuerui Yang,*a Yuefei Ji,a Jean-Marc Chovelon,d Guangli Xiu,e and Lei Zhoua,e

Kresoxim-methyl (KM), an extensively used strobilurin fungicide, displays broad-spectrum fungicidal activity. Despite its prevalent application in agriculture and frequent detection in the environment, specific studies on the photolytic fate of KM in natural surface waters are quite limited. To address this, the present study delves into the photochemical transformation of KM under light irradiation using a high-pressure mercury lamp. Photodegradation of KM followed pseudo-first-order kinetics, with a degradation rate constant of $0.067/\text{h}^{0.005}$, corresponding to a half-life of approximately $10.3 \pm 0.7 \text{h}$, and the quantum yield was estimated to be $6.95 \times 10^{-3}$; transient species identification experiments demonstrated the involvement of singlet oxygen ($\text{O}_2^*$) and singlet ($\text{KM}^*$) and triplet ($\text{KM}^*$) states. Four different photodegradation pathways, i.e., photoisomerization, hydrolysis, hydroxylation, and ether cleavage, were proposed. Toxicity assessments demonstrated that photodegradation effectively reduced the ecotoxicity of KM. Two typical pesticide adjuvants, namely, Tween 20 and sodium dodecylbenzenesulfonate (SDBS), were selected to evaluate their impacts on KM photolysis. While Tween 20 exhibited a remarkable increase in the photodegradation of KM, SDBS showed a concentration dependent behavior, with an inhibitory effect at low concentrations (<200 μM) and promotional effects at higher concentration levels. The present study elucidated the photolytic KM degradation mechanism, as well as its possible inhibition and enhancement, which is of significant importance for evaluating the environmental fate and ecotoxicological risks of KM in sunlit surface waters.

1. Introduction

The use of fungicides is one of the key practices in agriculture and can significantly reduce crop losses.1 They are commonly applied before agricultural production and require a higher spraying frequency than other pesticides, resulting in a longer residence time in the environment and easy bioaccumulation. These factors lead to the development of microbial resistance and ecological imbalances, which could ultimately result in reduced agricultural yields, posing a threat to food security.2 Kresoxim-methyl (KM) is one of the most valuable strobilurin fungicides employed worldwide; its structure is illustrated in Fig. 1. Developed by BASF in 1996, KM possesses various characteristics such as high efficiency in targeting pathogens, broad sterilization spectrum, and low toxicity, which can control a variety of plant diseases caused by fungi such as Basidiomycota and Ascomycetes.3 The widespread application of KM results in high residual concentrations in the environment; for instance, the residual levels of KM varied from 0.05 to
0.6 μg L⁻¹ in different streams.⁴,⁵ The protodrugs of KM was reported to have a high toxicity to *D. magna*, with a 48-h half-maximal concentration (EC₅₀) value of 157.3 μg L⁻¹.⁶ This highlights the significance of studying the environmental behavior and ecological effects of fungicides under various environmental conditions.

Once released into the environment, agricultural pesticides might follow multiple decomposition pathways to achieve self-purification. They can be decomposed through dilution, adsorption on particles and sediments, or bioaccumulation in aquatic organisms.⁷ In addition, biotransformation and photo-adsorption on particles and sediments, or bioaccumulation in purification. They can be decomposed through dilution, might follow multiple decomposition pathways to achieve self-purification. They can be decomposed through dilution, adsorption on particles and sediments, or bioaccumulation in environmental conditions.

**2. Materials and methods**

**2.1 Chemicals and materials**

KM (98%) was purchased from Shanghai Naicheng Biotechnology Co. (China). Phosphoric acid (chromatographic purity), potassium phosphate (98%), p-nitroanisole (98%), rose bengal (95%), sorbic acid (SA, 99.8%), sodium dodecylbenzenesulfonate (SDBS, 98%), and Tween 20 (98%) were obtained from Aladdin (Shanghai, China). Furfuryl alcohol (FFA, 99.9%) was supplied by Energy Chemical (Shanghai, China). Isopropanol (IPA, 99.9%) and pyridine (pyr, 99.8%) were purchased from Thermo Fisher Scientific (Waltham, USA).

**2.2 Photolysis experiments**

Photochemical experiments were performed using a CEL-LAM500 photoreactor (Beijing Zhongjiao Jinyuan Technology Co., Ltd, China) equipped with a 500 W high-pressure mercury lamp and a 290 nm cutoff filter. The light source was placed within a quartz cooling jacket connected to a thermostat, maintaining the temperature at 20 ± 0.1 °C. Prior to the photodegradation experiments, the mercury lamp was powered on for 30 min to stabilize its emission intensity.

Reaction solutions (25 mL) containing KM (10 μM) and phosphate buffer (10 mM) to control and maintain the initial solution pH were used as dark controls and in photodegradation experiments. After the addition of buffer, the initial pH of the solution was maintained at 7.0. When studying KM photolysis under various pH conditions, the pH of the reaction solution was adjusted using a 10 mM phosphate buffer. When investigating the impact of various adjuvants on KM photolysis, the initial pH was also set at 7.0 with the addition of buffer. During photolysis, 0.5 mL of aliquots were extracted in brown vials at predetermined intervals. All samples were temporarily stored at a temperature of 4 °C and subsequently analyzed within 24 h by HPLC. All experiments were performed in triplicate.

**2.3 Analytical methods**

The concentrations of KM were quantified using a Waters high HPLC system, with a 2695 separation module and a 2998 photodiode array detector. Chromatographic separation was performed using an XBridge C18 reverse-phase column (4.6 × 250 mm, 5 μm capillary column). Detailed information is provided in Table S1 (ESI†).

Photoproducts were identified using a HR-MS (Thermo Scientific) coupled with a HPLC separation system (Thermo Scientific) in a positive electrospray ionization mode, in the m/z scan range from 50 to 500. An Acquity UPLC C18 2.1 × 100 mm column with a particle size of 1.7 μm was used for separation.
The mobile phase was a mixture of water (0.5% formic acid) and acetonitrile (ACN) (40:60, v/v) with a flow rate of 0.3 mL min\(^{-1}\). The mass spectrometer was operated at a spray voltage of 3200 V, a capillary temperature of 350 °C, a capillary voltage of 49 V, and aux gas 10 Arb. Concentrated reaction solutions were obtained via solid phase extraction (SPE) using the procedures outlined in Text S1 in the ESI.†

Detailed information on electron paramagnetic resonance spectroscopy analysis (EPR) is provided in Text S2 in the ESI.†

2.4 Quantum yield determination

The apparent quantum yield of KM (\(\Phi_{KM}\)) was determined by using \(p\)-nitroanisole (PNA)/pyr as chemical actinometers.\(^{20}\) The apparent photodegradation rates of KM and PNA (\(k_{KM}\) and \(k_{PNA}\), respectively) were calculated as follows:\(^{21}\)

\[
k_A = -\ln([A]/d[A]/dt) \quad (1)
\]

\[
\Phi_{KM} = \frac{k_{KM}}{k_{PNA}} \times \frac{\sum L_i c_i_{KM}}{\sum L_i c_i_{PNA}} \Phi_{PNA} \quad (2)
\]

\[
\Phi_{PNA} = 0.29[pyr] + 0.00029 \quad (3)
\]

where \([A]\) represents the concentrations of KM or PNA, and \(d[A]/dt\) is the corresponding photodegradation rate, while \(L_i\) and \(c_i\) represent the irradiance of the incident photon and molar absorptivity of KM or PNA at wavelength \(\lambda\), respectively. \(\Phi_{KM}\) and \(\Phi_{PNA}\) represent the quantum yields of KM and PNA, respectively, and [pyr] is the concentration of pyridine.

2.5 Ecotoxicity assessment

The ECOSAR (v. 2.2) model\(^{22}\) is the most extensively used approach to predict toxicity, based on the chemical structure similarity. In the present study, the half-lethal concentration (LC\(_{50}\)), EC\(_{50}\), and chronic toxicity values (ChV) of KM and its photoproducts were assessed for three model aquatic organisms (green algae, daphnia, and fish).

3. Results and discussion

3.1 Absorption spectrum of KM and direct photodegradation

As illustrated in Fig. 2(a), aqueous KM exhibited a broad UV-Vis absorption band ranging from 200 to 310 nm (pH 7), which partially overlapped with the solar spectrum as well as the emission spectrum of the light source. This suggests that direct photodegradation of KM might take place under natural sunlight and play a notable role in its elimination.

Dark control experiments demonstrated the stability of aqueous KM, suggesting that hydrolytic or microbial degradation was negligible for KM degradation (Fig. S1, ESI†). Approximately 20% removal was achieved after 4 h of irradiation, indicating that KM photolysis could take place under simulated irradiation. The direct KM photolysis followed pseudo-first-
order kinetics, with an estimated apparent decay rate constant ($k_{\text{obs}}$) of 0.067 ± 0.005 h$^{-1}$, and a corresponding half-life ($t_{1/2}$) of 10.3 ± 0.7 h (eqn (4) and (5)), which were comparable to the values obtained by Man et al.$^{12}$ The $k_{\text{obs}}$ in the actual water body of Zixia Lake (water quality parameters in Table S2, ESI†) was 0.094 ± 0.003 h$^{-1}$, with a corresponding $t_{1/2}$ of 7.4 ± 0.3 h (Fig. S2, ESI†). This indicates that the photolysis rate in the actual water body is significantly faster than that in ultra-pure water. The reason for this difference may be attributed to the presence of nitrate ions in the lake water, which can directly and indirectly generate peroxynitrite or peroxynitrous acid through photoisomerization, leading to the formation of $^1$NO$_2$ and $^1$OH.$^{23}$ Notably, $^1$OH is a primary reactive oxygen species (ROS) responsible for pollutant degradation in natural water systems,$^{24}$ thereby accelerating the photolysis of KM in Zixia Lake water. The quantum yield is a critical parameter for predicting the direct photodegradation half-life of organic pollutants under irradiation;$^{25}$ in this study, $\Phi_{\text{KM}}$ was determined to be 6.95 × 10$^{-3}$ (Fig. S3, ESI†).

$$\ln([\text{KM}]_t/[\text{KM}]_0) = -k_{\text{obs}}t$$

$$t_{1/2} = \ln 2/k_{\text{obs}}$$

Additionally, the ionization products and reactivities of organic pollutants are commonly influenced by the pH value of natural water.$^{26}$ Therefore, pH effects on the KM's direct photochemical process were also assessed in this section. As displayed in Fig. 2(c), photolysis kinetics exhibited a minimal variation across a broad pH range from 3.2 to 10.6. This observation can be rationalized by considering that the absorption spectrum of KM remained largely unaffected at different pH values (Fig. 2(b), inset). Moreover, it should be noted that KM molecules (Fig. 1) existed predominantly as single species within the pH range investigated in this study ($pK_a = -1.16$) (Fig. 2(c)). Consequently, combined with the absence of significant hydrolysis in our study, we conclude that pH has no significant effect on the photolysis of KM.

### 3.2 Identification of potential reactive intermediates

Previous studies$^{27,28}$ have shown that, upon irradiation, numerous pesticides can generate highly reactive triplet states with relatively longer lifetimes, as well as reactive oxygen species with high oxidation activity, including singlet oxygen ($^1$O$_2$) and hydroxyl radicals ($^1$OH). In turn, these reactive intermediates can interact with the parent pesticides and significantly affect their photochemical fate.

Therefore, to determine the reactive species involved in KM photolysis, EPR tests were conducted along with kinetic quenching experiments. In particular, $^1$O$_2$ was initially identified in the EPR test, where it reacted with the spin-trapping agent 2,2,6,6-tetramethyl-4-piperidine hydrochloride (TEMP),$^{29,30}$ exhibiting a distinct 1:1:1:1 signal (Fig. S4, ESI†). However, in the case of $^1$OH detection using 5,5-diethyl-1-pyrroline-N-oxide (DMPO), the characteristic 1:2:2:1 signal corresponding to the DMPO–OH adduct was not observed, suggesting that $^1$OH was not involved or played a rather minor role in the direct KM photolysis. The kinetic quenching experiments further supported the EPR test results: with the addition of an excess amount (10–40 mM) of IPA, a typical $^1$OH scavenger, the KM degradation rate was barely reduced. The above results indicate a relatively minor role of $^1$OH species in the photolysis process. In addition, FFA was employed as the $^1$O$_2$ scavenger, to differentiate the $^1$O$_2$ produced in the indirect photolysis upon KM sensitization.$^{31}$ The direct KM photolysis rate decreased from 0.067 to 0.049 h$^{-1}$ upon the addition of a 10 mM FFA solution, indicating the involvement of $^1$O$_2$, and its contribution was 46.9% (data not shown). In addition, the bimolecular rate constant between KM and $^1$O$_2$ ($k = 4.34 \times 10^8 \text{L M}^{-1} \text{s}^{-1}$) was estimated using FFA as the probe (Text S3, ESI†); the bimolecular rate constant between FFA and $^1$O$_2$ ($k_{\text{KM}}$) was calculated as $1.2 \times 10^8 \text{L M}^{-1} \text{s}^{-1}$ using eqn (6) (Fig. S5, ESI†):

$$k_{\text{KM}} = \frac{\ln([\text{KM}]_t/[\text{KM}]_0)}{\ln([\text{FFA}]_t/[\text{FFA}]_0)}$$

It is widely acknowledged that $^1$O$_2$ is typically generated via the activation of dissolved oxygen (DO) by excited triplet states; these intermediates also play critical roles in the photolysis of organic contaminants.$^{32}$ Therefore, the potential participation of triplet-state KM ($^3$KM$^*$) was also evaluated in this section. By introducing SA, a known triplet quencher, into the reaction system, the degradation rate of KM decreased from 20.9% to 12.7% within 4 h (Fig. 2(d)), confirming the participation of $^3$KM$^*$ in the direct KM photodegradation, and its contribution was determined as 39.2%. When exposed to sunlight, KM, which contains carbonyl structures, is expected to be excited to its corresponding singlet excited states ($S_n$ where $n \geq 1$).$^{33}$ Subsequently, these intermediates are transformed into the lowest-energy state ($S_1$, $^1$KM$^*$) through processes such as internal conversion or vibrational relaxation.$^{34,35}$

Singlet-state KM is not stable, and can either directly generate its photoproducts or undergo intersystem crossing (ISC) to yield the corresponding $^3$KM$^*$. Similar to $^1$KM$^*$, $^3$KM$^*$ also possesses two conversion paths; the first one is expected to directly generate photoproducts, while in the second one an energy transfer process takes place from $^3$KM$^*$ to DO, ultimately generating $^1$O$_2$,$^{36,37}$ which also exhibits high reactivity toward KM itself (eqn (7)–(12)):

$$\text{KM} \stackrel{h\nu}{\rightarrow} ^1\text{KM}^*$$

$$^1\text{KM}^* \rightarrow \text{Products}$$

$$^1\text{KM}^* \stackrel{\text{ISC}}{\rightarrow} ^3\text{KM}^*$$

$$^3\text{KM}^* \rightarrow \text{Products}$$

$$^3\text{KM}^* + \text{O}_2 \rightarrow ^1\text{O}_2 + \text{KM}$$

$$^1\text{O}_2 + \text{KM} \rightarrow \text{Products}$$

EPR tests and kinetic quenching experiments confirmed the participation of $^3$KM$^*$ and $^1$O$_2$ in the photolysis of KM, while the contribution of $^1$OH was negligible. Interestingly, an excess
amount of SA did not completely inhibit KM decay, indicating that in addition to the two reactive species mentioned above, $^1$KM* might also be involved in KM degradation. However, owing to the relatively short lifetime and the lack of reliable identification strategies, evaluating the contribution of $^1$KM* is challenging, and further analysis is still required.

In addition, we performed theoretical geometry optimizations of $^1$KM* and $^3$KM* using time-dependent density functional theory (TD-DFT) and unrestricted DFT methods, respectively, at the B3LYP-D3(BJ)/6-311G(d,p) level. The values of the two dihedral angles which have a significant impact on the conformations are labelled on the structures. Specifically, the dihedral angles of the main moieties of KM were estimated as $139.7^\circ$ and $62.4^\circ$ (Fig. 3(a)), while in the case of $^1$KM*, the structure twisted, and the corresponding dihedral angles became $66.4^\circ$ and $65.0^\circ$ (Fig. 3(b)). For $^3$KM*, the values were calculated as $168.4^\circ$ and $17.6^\circ$ (Fig. 3(c)). It is that the photoexcitation induced significant variation on the structure, which may result in various photodegradation pathways of KM, such as photoisomerization.

### 3.3 Identification of photoproducts

We conducted a comprehensive investigation of the photoproducts of KM using HR-MS analysis in positive mode following 10 h of irradiation. The total ion chromatogram (TIC) and detailed mass data of the primary photoproducts are shown in Fig. S6 and Table S3 (ESI†), respectively. The parent chemical, KM, was first detected at a retention time (RT) of 3.19 min, with $m/z = 314.1387$ ([M + H]$^+$), as further confirmed for the standard sample (data not shown). A peak at $m/z = 314.1385$ also appeared at 2.05 min, corresponding to one of the KM isomers. As various reports on the photoisomerization of pesticides are available,$^{38-40}$ another five isomers were also detected from the TIC spectrum by a mass searching strategy (Fig. S7, ESI†), with retention times of 1.60, 2.05, 2.17, 2.96, and 6.05 min. TP1 ($C_{13}H_{17}NO_4$, $m/z = 300.1233$, [M + H]$^+$), exhibiting a distinct ion peak at 1.04 min, lacks 1 C and 2 H atoms with respect to KM, implying a cleavage process of the ester bond. TP2 ($m/z = 286.1077$) was detected at 1.55 min, and its molecular formula was estimated to be $C_{18}H_{15}NO_4$. Compared to TP1, the molecular formula of TP2 denoted the loss of a –CH$_2$ group. TP4 was detected at 1.14 min, with $m/z = 346.1290$, matching the molecular formula $C_{14}H_{13}NO_6$. Compared to the KM molecule, TP4 had two additional oxygen atoms, indicating that it might be the dihydroxylation product of KM. The occurrence of TP5 ($m/z = 344.1132$, [M + H]$^+$, RT = 1.30 min), with the molecular formula $C_{14}H_{13}NO_6$, indicated the possible dehydrogenation of TP4. TP6 ($m/z = 346.1288$, [M + H]$^+$, RT = 1.72 min) was labeled as the secondary degradation product of TP5. TP7 ($m/z = 332.1133$, [M + H]$^+$) with a retention time of 0.85 min was generated from TP4 through hydrolysis. Subsequently, TP7 underwent ether bond cleavage to form TP8 ($m/z = 318.0977$, [M + H]$^+$, RT = 0.92 min). Interestingly, TP9 showed a [M + H]$^+$ mass of 332.1497 corresponding to

---

**Fig. 3** DFT-optimized geometries of KM, $^1$KM*, and $^3$KM*.

**Fig. 4** Proposed photodegradation pathways of KM.
C_{16}H_{22}NO_{3} as the molecular formula, suggesting that it lost an O and gained 2 H atoms with respect to the TP4 molecule. TP4 was found to generate TP9 through a reduction reaction. TP10 (RT = 0.58 min) showed a [M + H]^+ mass of 284.1284, with the molecular formula C_{12}H_{17}NO_{3}, suggesting the loss of a CH_{2}O group with respect to the KM molecule. TP11 (m/z = 192.0658, [M + H]^+, RT = 2.43 min) was associated with the break of the benzyl phenyl ether bond. Furthermore, TP3 (m/z = 238.1228, RT = 1.44 min) and TP12 (m/z = 208.0609, RT = 1.27 min) were associated with the oxidation of TP2 and TP11, respectively. In summary, TP1, TP10, TP11, and TP12 have been reported in previous studies.\textsuperscript{12} However, dihydroxylation (TP4) and its subsequent products have not been documented in the literature to date.

### 3.4 Photodegradation pathways

Based on the transformation products (TPs) identified in the experiments, we proposed four potential pathways for the photodegradation of KM (Fig. 4). Pathway I represents the photoisomerization of the target fungicide KM, a significant reaction type frequently observed in the degradation of emerging contaminants.\textsuperscript{41,42} Although the oxime ether remains stable under dark conditions, it becomes active under light irradiation. Similar to the C—C double bond, C=N and C=O bonds of KM can also generate geometric isomers around the double bonds.\textsuperscript{43} It can be concluded that Z-KM was an isomerization product, in agreement with the findings of Chastain et al.\textsuperscript{18} Such result is also supported by the optimized structure in Fig. 3. Due to the existence of the above-mentioned double bonds, KM was considered to be easily photoexcited, leading to large differences between excited (S\textsubscript{1} and T\textsubscript{1}) and ground-state geometries, and consequently forming a series of isomers.

Pathway II starts with the hydrolysis of the ester moiety, leading to the formation of the carboxyl group. KM is expected to be rapidly converted to TP1, the initial product of the hydrolysis process.\textsuperscript{12} The following step is the breaking of the ether bond and oxidation of TP1, generating TP2 and TP3. Pathway III represents a hydroxylation process. KM initially yields a dihydroxylated derivative (TP4).\textsuperscript{44–46} The dehydrogenation and reduction of TP4 leads to the formation of TP5 and TP9, respectively. TP4 can also transfer to TP7 through hydrolysis and subsequently be degraded further to generate TP8 (ether cleavage). Additionally, TP4 can be immediately reduced, producing TP9. Pathway IV directly leads to TP10 through the cleavage of the oxime ether moiety present in the KM structure, for which a hydrogen source is required. After this, TP10 transforms into TP11 via the breaking of benzyl phenyl ether. Subsequently, further degradation of TP11 on the benzyaldehyde moiety would result in the formation of TP12. Therefore, we can conclude that, during photodegradation, KM could undergo isomerization, hydrolysis, hydroxylation, and ether cleavage processes. In this study, we confirm the existence of pathway III for the first time, while pathways I, II, and IV have been previously reported.\textsuperscript{12} This research contributes to the elucidation of previously unreported photodegradation products of KM and provides new insights into its photodegradation pathways.

### 3.5 Toxicity prediction

In the subsequent stage of this work, we employed the ECOSAR software to assess the toxicity of KM and its photoproducts toward aquatic organisms, based on acute (LC\textsubscript{50}, EC\textsubscript{50}) and chronic (ChV) toxicity parameters (Table S4, ESI\textsuperscript{†}), because standard toxicity benchmarks were not available.\textsuperscript{47} The evaluation criteria for both types of toxicity\textsuperscript{48} are presented in Fig. 5 and Table S5, ESI.\textsuperscript{†} For KM, the predicted LC\textsubscript{50} values were 0.170 mg L\textsuperscript{−1} for fish and 0.032 mg L\textsuperscript{−1} for daphnia, while for green algae, an EC\textsubscript{50} value of 0.225 mg L\textsuperscript{−1} was determined. These results indicate that KM exhibits high toxicity toward aquatic species, particularly lower trophic organisms such as daphnia. Furthermore, chronic toxicity appeared to be more significant than acute toxicity across the three species. It is worth noting that almost all photoproducts (except TP12) exhibited lower ecotoxicity than KM. This finding is consistent with both acute and chronic toxicity displayed by the hydroxylation and hydrolysis products to the tested organisms.\textsuperscript{49} Therefore, these results suggest that photodegradation represents a viable approach for mitigating the ecotoxicity of KM in aquatic environments.

![Fig. 5](image-url) Evolution of acute and chronic toxicities of KM and its photoproducts.
3.6 Effect of selected adjuvants

In this study, two commonly used adjuvants, i.e., the Tween 20 emulsifier and the SDBS dispersant, were selected to test their potential impact on the photochemical behavior of KM.

Experiments were conducted using a 10-μM KM solution with varying concentrations of Tween 20 (0, 1, 10, 20, and 40 μM), and the results are presented in Fig. 6(a). Slightly improved performances could be observed in the presence of Tween 20. In particular, the photolysis rate constants at Tween 20 concentrations of 1, 10, 20, and 40 μM were estimated to be 0.067, 0.072, 0.077, and 0.085 h^{-1}. This rate increase could be attributed to several different reasons. First, it was proposed that Tween 20 exhibited photoreactivity, generating hydroxyl radicals under sunlight, which accelerated KM degradation.\(^1\)

Additionally, because no additional hydrogen source was introduced into the reaction system, adjuvants themselves could act as the hydrogen sources responsible for the promoting effect.\(^15\)

Specifically, in the present study, Tween 20 could act as a hydrogen donor to facilitate the ether cleavage process (path IV in Fig. 4).

Further tests were performed with SDBS, a dispersant (anionic surfactant) with a critical micellar concentration (CMC) of 1.24 mM.\(^20\) As shown in Fig. 6(b), before the CMC level was reached, SDBS exhibited a dual effect on the photodegradation of KM. At a concentration of 100 μM, SDBS had an inhibiting effect with a rate constant decrease of 13.7%, which slightly decreased to 4.8% when increasing the SDBS concentration to 200 μM. Subsequently, a promoting effect on the KM photolysis was observed at an SDBS concentration of approximately 500 μM. When continuously increasing the SDBS level to 1000 μM, the rate constant increase reached 37.7%. Within the examined range of SDBS concentrations, the fastest photolysis rate constant of KM was estimated to be 0.089 h^{-1}, 1.3 times faster than in the control group, while the minimum photolysis rate constant was 0.056 h^{-1}. The kinetic investigation indicated that multiple factors might influence the transformation of KM in the presence of SDBS. Specifically, possessing the aromatic chromophore, SDBS exhibited light absorption at wavelengths of simulated sunlight (Fig. S9b, ESI†), for which reason this adjuvant can compete with KM for photons, resulting in a light screening effect to inhibit direct KM photolysis. Similar results were also reported in the case of BDE-28 photolysis.\(^31\) In addition, the light absorption ability of SDBS indicates that it may also act as a photosensitizer to promote the transformation of KM. Moreover, as a surfactant, increasing the SDBS concentration might also increase its hydrophobic core size, resulting in more KM solubilizing and the enhancement of intermolecular KM collisions,\(^32\) finally exhibiting an acceleration impact. Therefore, in this section, we identified the dual roles of SDBS on KM photolysis, and the trade-off among the mentioned effects seemed to vary under different SDBS concentrations, for which reason it is of great value to distinguish the underlying mechanisms of SDBS in further studies.

The results discussed in this section highlight the significant effects of common adjuvants such as Tween 20 and SDBS on the photodegradation rate of KM. However, due to the distinct structures of hydrophilic adjuvants or hydrophobic chains, distinct adjuvant structures likely exhibit different capacities to alter pesticide photolysis rates. Elucidating the photoreactivity of various adjuvants will provide critical insights into their influence on the fate of pesticides in agricultural and natural waters.

4. Conclusions

This contribution systematically investigated the photodegradation process of KM in aqueous solution under simulated sunlight. The direct photolysis rate constant and half-life of KM were estimated to be 0.067 ± 0.005 h^{-1} and 10.3 ± 0.7 h, respectively, indicating its tendency to undergo photochemical reactions under simulated sunlight. Four distinct pathways, including photoisomerization, hydrolysis, hydroxylation, and ether cleavage, were proposed. Among these pathways, the photoisomerization process emerged as the main photolysis route. Both $^3$KM* and $^1$KM* were found to be important intermediates in the photolysis process, and KM could also be oxidized by the $^1$O$_2$ species produced by energy transfer from $^3$KM* to O$_2$. Tween 20 was found to accelerate the degradation
of KM, while SDS initially inhibited and then promoted the photolysis of KM with increasing concentrations. ECOSAR analyses revealed that some of the TPs remained toxic or very toxic to aquatic organisms, despite exhibiting lower aquatic toxicity compared to the parent compound. These findings are crucial for understanding the photolytic behavior of KM in aquatic systems. Further investigations are needed to assess the environmental risks associated with the TPs formed from KM.

**Author contributions**


**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

The authors extend their sincere gratitude for the financial support from the National Natural Science Foundation of China (grant No. 22176059 and 22306064), the National Science Foundation of Shanghai (23ZR1417500), the Fellowship of China (grant No. 22176059 and 22306064), the Natural Science Foundation of China, and the Fundamental Research Funds for the Central Universities.

**References**


