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Reaction behaviors of decomposition of monocrotophos in aqueous solution by UV and UV/O₃ processes

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Abstract

The decomposition of monocrotophos (*cis*-3-dimethoxyphosphinyloxy-*N*-methyl-crotonamide) in aqueous solution by UV and UV/O₃ processes was studied. The experiments were carried out under various solution pH values to investigate the decomposition efficiencies of the reactant and organic intermediates in order to determine the completeness of decomposition. The photolytic decomposition rate of monocrotophos was increased with increasing solution pH because the solution pH affects the distribution and light absorbance of monocrotophos species. The combination of O₃ with UV light apparently promoted the decomposition and mineralization of monocrotophos in aqueous solution. For the UV/O₃ process, the breakage of the >C=C< bond of monocrotophos by ozone molecules was found to occur first, followed by mineralization by hydroxyl radicals to generate CO₃²⁻, PO₄³⁻, and NO₃⁻ anions in sequence. The quasi-global kinetics based on a simplified consecutive-parallel reaction scheme was developed to describe the temporal behavior of monocrotophos decomposition in aqueous solution by the UV/O₃ process. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many pesticides in the aquatic environment are potentially toxic and are hard to be decomposed by conventional treatment processes. Organic phosphates, such as ethyl-

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parathion, malathion, and monocrotophos, are widely used as pesticides because of their rapid rate of decomposition and therefore are not likely to be bioaccumulated. Despite their benefits, organic phosphates are still of great concern because they are more acutely toxic to birds and mammals than chlorinated hydrocarbons, and are also more likely to contaminate surface and ground waters because they are more soluble in water than chlorinated hydrocarbons. Advanced oxidation processes (AOP) have already found a widespread application in the treatment of industrial wastewater, groundwater, and landfill leachate [15,18,20–22,24]. In recent years, the ozone-related processes such as O_3/OH^- , H_2O_2/O_3 , UV/O_3 have attracted attention as potential treatments for various organic compounds including pesticides in waters and as part of advanced wastewater treatment processes. Gunther et al. [7] observed the formation of sulfate ion during ozonation of parathion and proposed that the detach of the sulphur group from the aromatic ring to form paraxon as a major organic intermediate. Laplanche et al. [13] reported ozonation of parathion to form phosphate and nitrophenols. Although the treatment of organic phosphates by ozone-related processes has been discussed phenomenologically by previous investigators, detailed information on the reaction kinetics by other ozone-related processes is scarce.

Monocrotophos, a popular foliar insecticide mainly used for cotton, is effective against a wide range of insects and mites, and has contact, systemic and residual activities. By the literature investigation [5,11,14], the bio- and photocatalytic-decomposition of monocrotophos seem not to be feasible due to the slow decomposition rate. The monocrotophos was chosen as the target contaminant in this study mainly because a more effective alternative for the removal of organophosphates by ozone-related processes was sought but not found. Our previous work has investigated the effect of various reaction parameters on the decomposition of monocrotophos in aqueous solutions by ozonation [18]. The objective of this study was extended to compare the kinetic behavior for the decomposition of monocrotophos in aqueous solution by UV, ozonation and UV/O_3 processes. The reaction rates and temporal behavior of monocrotophos and intermediate reacting species by UV and UV/O_3 processes were characterized using an empirical kinetic model.

2. Experimental

The photoreaction system used in this research contained a capped batch annular photoreactor made entirely of Pyrex glass with an effective volume of 2.5 l and was water-jacketed to maintain a solution temperature of 25°C for all experiments. The photoreactor consisted of one 25-cm i.d. quartz tube housing a 254 nm low pressure UV lamp with approximately 5.3 W maximum output. The light intensity of the UV lamp was adjusted by a variable voltage transformer and detected by a Spectroline model DRC-100X digital radiometer combined with a DIX-254 radiation sensor. The solution pH value was kept constant at desired levels by the addition of NaOH and HCl solutions using a Kyoto APB-118-20B autotitrator. Ozone content of the feed gas was controlled by adjusting the power input to a Fischer model 500 ozone generator at an inlet oxygen

gas flowrate of 33.6 l/h. The monocrotophos and other chemicals used for analysis were reagent grade and all experimental solutions were prepared with deionized water. Two liters of monocrotophos solution were initially charged to the reactor and the ozone-containing gas was continuously fed into the reactor through a 100-mesh diffuser during the course of the reaction. At desired time intervals, aliquots of 15 ml solution were withdrawn from the sampling port which was located at the bottom of the reactor. Monocrotophos was analyzed by a Spectra-Physics P1000 HPLC equipped with an UV detector and a Spherisorb ODS2 5 μ column. The total organic carbon (TOC) was analyzed by an O.I.C model 700 TOC analyzer. The anion concentrations, including nitrite, nitrate, sulfate, and phosphate, were analyzed by a Dionex model DX-100 ion chromatograph. The concentration of ozone in the aqueous and gaseous phases was determined by the Indigo blue method [10] and the Seki SQZ-6000 ozone analyzer, respectively. For several experiments, the reaction intermediates were determined using a HPG1800A GCD equipped with an electron ionization detector (EID).

3. Results and discussion

Because most of the experiments carried out in this research were performed in a semibatch reactor with ozone-containing feed gas flowing into the reactor, the volatilization and the hydrolysis of monocrotophos in aqueous solution was examined at various pH levels and were found to be negligible.

3.1. Photolysis of monocrotophos by UV irradiation

The absorbance ($\lambda = 254$ nm) of monocrotophos solution at various pH conditions was determined as shown in Table 1. The absorbance of monocrotophos was found to increase with increasing solution pH indicating that the possible presence of various monocrotophos species (protonated and unprotonated) at different solution pH. Similar observations were reported [4,19,20] previously for treating other organic compounds at various pH conditions with ozone-related processes. However, the organic compounds studied by previous researchers usually contain $-\text{OH}$ or $-\text{COOH}$ functional groups. Depending on the solution pH, the neutral molecules might dissociate to release protons and become negatively-charged species.

Table 1
The absorbance of monocrotophos solution at various pH conditions ($\lambda = 254$ nm)

pH	Absorbance
2	0.859
3	0.861
7	1.221
9	1.240

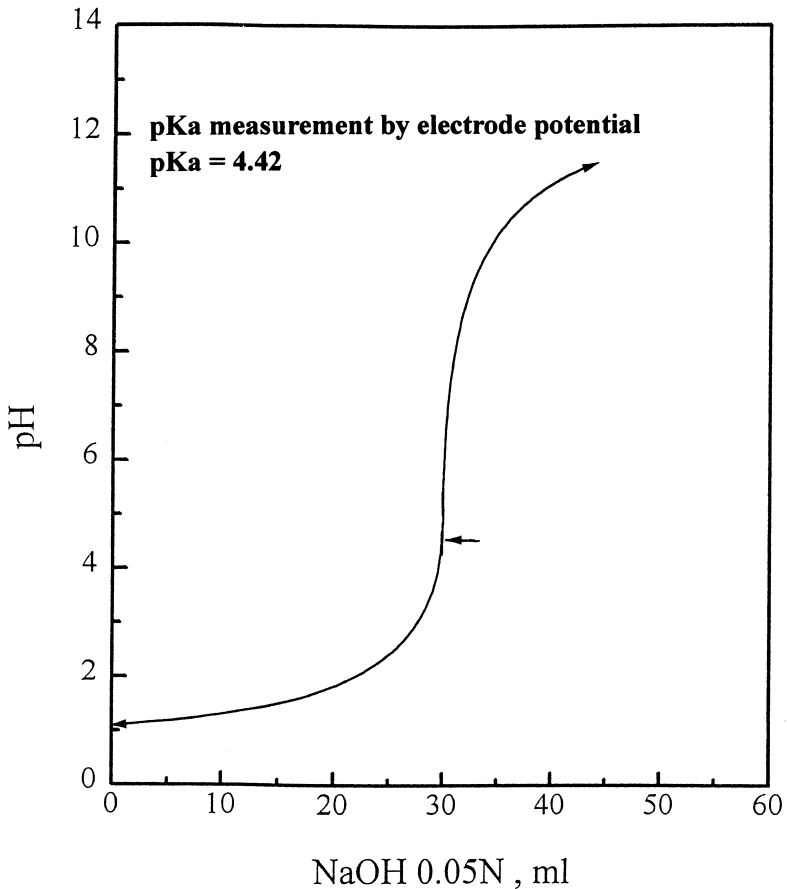
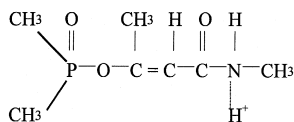


Fig. 1. The potential titration curve of monocrotophos in aqueous solution.

The potential titration curve of monocrotophos shown in Fig. 1 also indicates that the monocrotophos is a conjugative compound. Even though the exact structures of protonated and deprotonated species have not been determined, but with reference to the molecular structure of monocrotophos indicate that the protonation of monocrotophos occurs by adding a proton to the nitrogen atom on the neutral monocrotophos molecules and might be presented as:



The pK_a of monocrotophos in aqueous solution can be approximated to be 4.42 by simultaneously solving the Nerst Equation combined with the definition of pK_a :

$$E = E_0 + 0.0591 \times \log \frac{[\text{monocrotophos}]}{[\text{monocrotophos-H}^+]} \quad (1)$$

$$pK_a = \log \frac{a_{H,x} \times [\text{monocrotophos}] \times f_{\text{mono}}}{[\text{monocrotophos-H}^+] \times f_{\text{mono-H}^+}} \quad (2)$$

where $a_{H,x}$: activity of monocrotophos molecules in aqueous solution, mM; f_{mono} : activity coefficient of monocrotophos molecules in aqueous solution; $f_{\text{mono-H}^+}$: activity of monocrotophos-H⁺ molecules in aqueous solution of monocrotophos molecules in aqueous solution.

Fig. 2 illustrates the calculated species distribution of monocrotophos in aqueous solution as a function of solution pH values based on the pK_a value determined in this

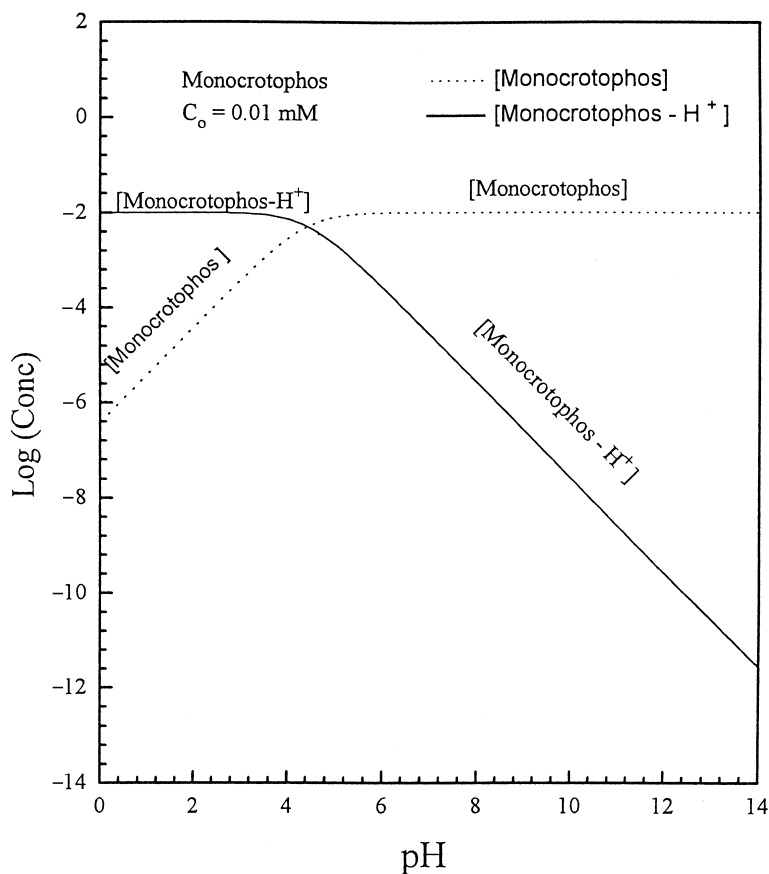


Fig. 2. The calculated species distribution of monocrotophos in aqueous solution as a function of solution pH values.

study. In acidic solutions, the protonated species is the predominant species while the unprotonated species predominates at neutral and alkaline solutions.

The pH effect on the decomposition of organic pollutants in aqueous solutions by UV photolysis had been studied by some previous researchers [16,20,23]), but the reported results did not display consistent conclusion. The photolytic decomposition rate of monocrotophos was studied under various pH conditions in this research as shown in Fig. 3. The decomposition rate of monocrotophos by photolysis was apparently decreased for acidic solutions, consistent with the effect of solution pH on the light absorbance of monocrotophos. The experimental results shown in Fig. 3 can be adequately described by a first-order rate equation, and the rate constants are shown in Table 2.

3.2. Decomposition of monocrotophos by UV/O₃ process

The temporal distribution of the reaction species during the decomposition of monocrotophos in aqueous solution by UV/O₃ process at pH 9 was shown in Fig. 4.

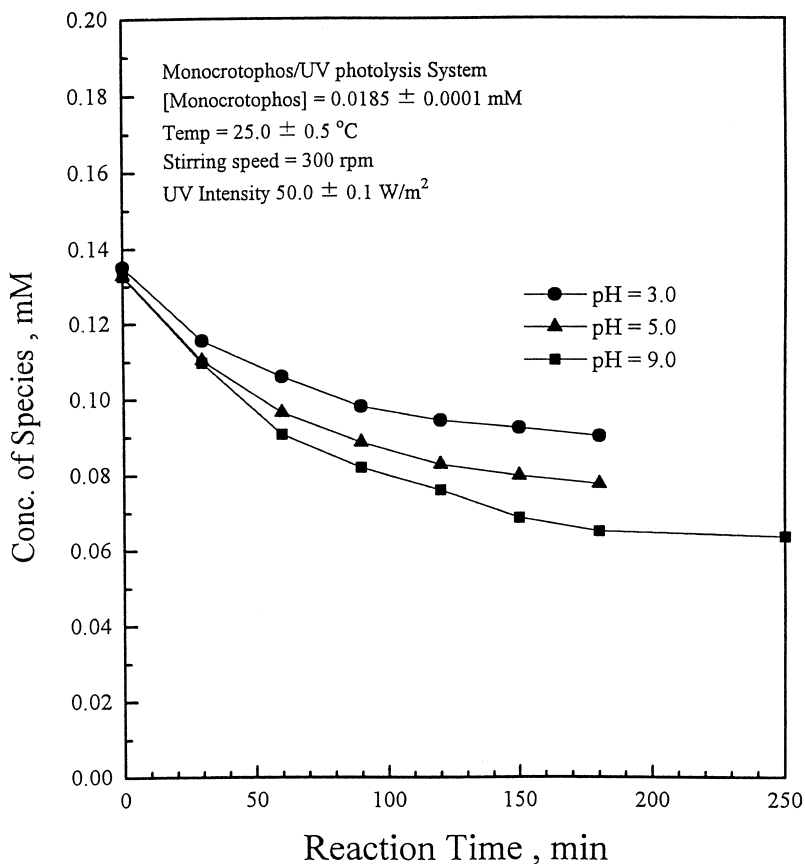


Fig. 3. The decomposition of monocrotophos under UV irradiation and various pH conditions.

Table 2

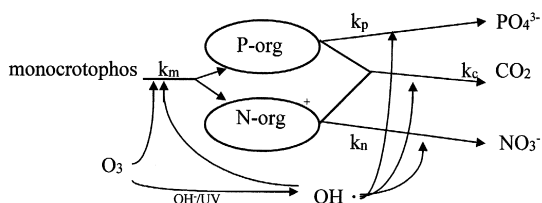
The pseudo-first order rate constant of monocrotophos and anions in aqueous solution by UV irradiation and UV/O₃ processes at various solution pH values

Rate constant, min ⁻¹	Removal rate constant of monocrotophos k_m , min ⁻¹	Formation rate constants of PO ₄ ³⁻ k_p , min ⁻¹	Formation rate constants of NO ₃ ⁻ k_n , min ⁻¹	Formation rate constants of CO ₂ k_c , min ⁻¹	
Process	pH				
UV irradiation ^a	3	0.0013	–	–	–
	5	0.0022	–	–	–
	9	0.0028	–	–	–
UV/O ₃ ^b	3	0.6902	0.0891	0.0000	0.0020
	5	0.5404	0.0383	0.0001	0.0081
	9	0.4953	0.0182	0.0004	0.0122

^aUV light intensity = 50 ± 0.1 W/m².

^bOzone mass flow rate = 3.54 ± 0.05 mg/min, UV light intensity = 50 W/m².

Monocrotophos could be almost completely (> 95%) decomposed within 15 min. No indication of any anions was formed during the early stage of the decomposition of monocrotophos. Formation of carbonate and phosphate ions was observed after about 10 min of reaction time, followed subsequently by the formation of nitrate after about 70 min. Similar experiments were conducted at various solution pH, and the results are shown in Fig. 5. The reaction rates were found to be decreased with increasing solution pH. These findings can be explained by observing the structure of monocrotophos that the C=C double bond of the monocrotophos molecule is supposed to be easily detached by ozone attack to form phosphorus- and nitrogen-containing organic intermediates. The organophosphates were converted almost entirely to phosphate indicating the CH₃O–P bond was effectively destroyed. The formation of nitrate was much slower than that of phosphate indicating the nitrogen-containing organic intermediates were more resistant to OH· attack, possibly because the sequential oxidation of amine group on the molecular structure to form nitrate is a slow process. Similar findings that ammonia is refractory to ozonation were reported by previous researchers [9,10,21]. The simplified decomposition pathway of monocrotophos by UV/O₃ process in aqueous solution are suggested as follows:



Based on the simplified pathway described above, each step of the reaction was assumed to be irreversible and first order with respect to the organic species, consistent

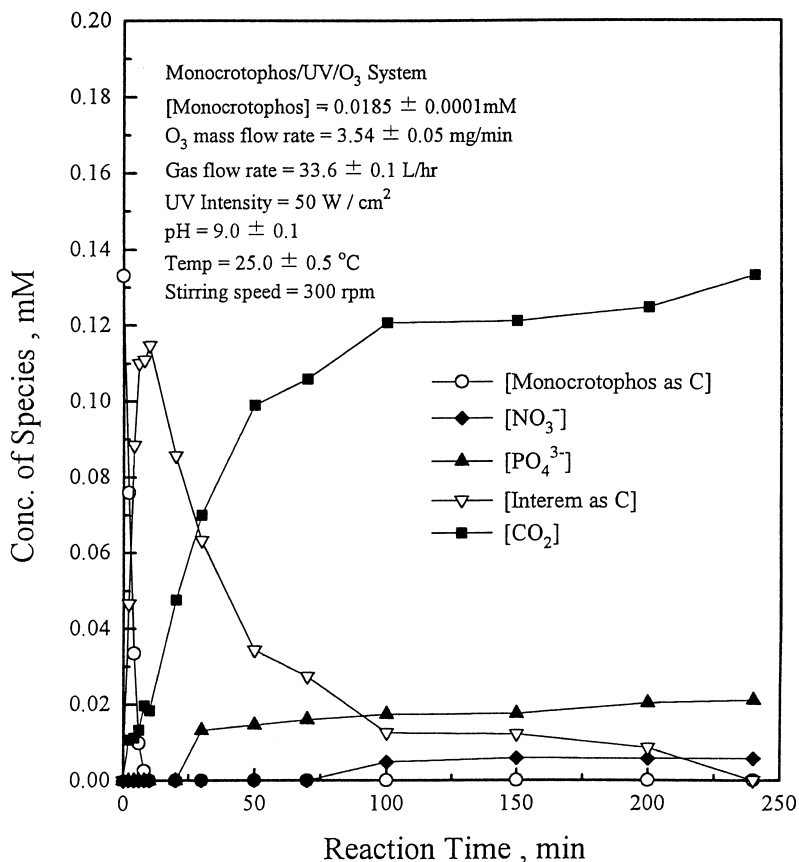


Fig. 4. The temporal distribution of reaction species during the decomposition of monocrotophos in aqueous solution by UV/O₃ process at pH 9.

with other studies of ozonation of various organic compounds [2,6,8,20]. The reaction rate equations for various species can be derived based on elemental mass balances of carbon, phosphorus and nitrogen:

$$[M] = [M]_o e^{-k_m t} \quad (3)$$

$$[\text{Interme}]_p = [M]_o k_m (e^{-k_m t} - e^{-k_p t}) / (k_p - k_m) \quad (4)$$

$$[\text{Interme}]_n = [M]_o k_m (e^{-k_m t} - e^{-k_n t}) / (k_n - k_m) \quad (5)$$

$$[\text{Interme}]_c = [M]_o k_m (e^{-k_m t} - e^{-k_c t}) / (k_c - k_m) \quad (6)$$

$$[\text{PO}_4^{3-}]_p = [M]_{o,p} - [M]_p - [\text{Interme}]_p \quad (7)$$

$$[\text{NO}_3^-]_n = [M]_{o,n} - [M]_n - [\text{Interme}]_n \quad (8)$$

$$[\text{CO}_2]_c = [M]_{o,c} - [M]_c - [\text{Interme}]_c \quad (9)$$

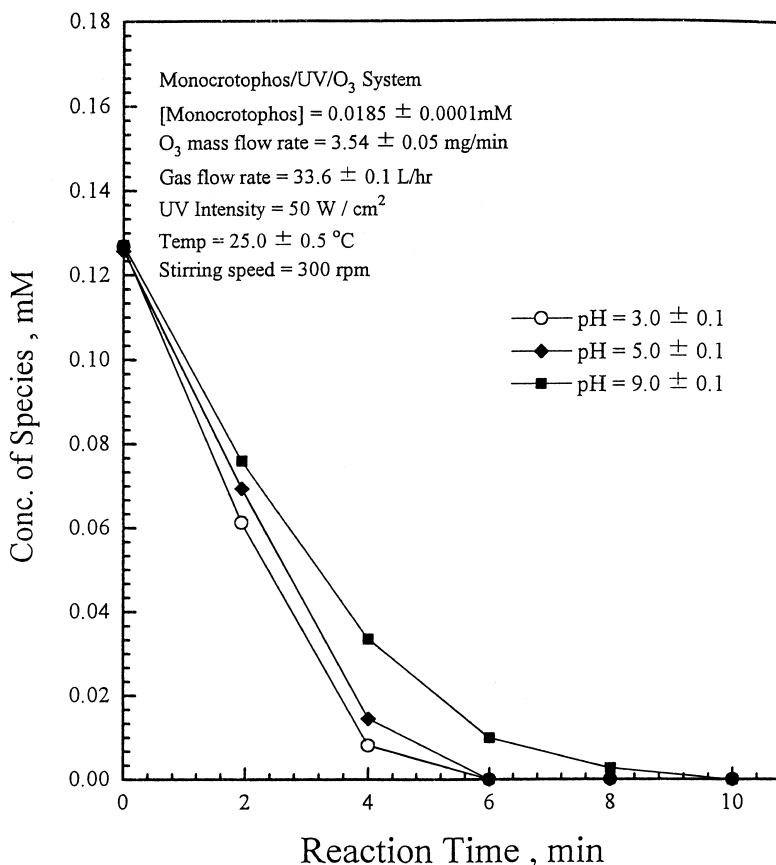


Fig. 5. The effect of solution pH on the decomposition of monocrotophos in aqueous solution by UV/O₃ process.

where M , the concentration of monocrotophos, mM; M_0 , the initial concentration of monocrotophos, mM; $[\text{Interme}]_p$, the concentration of phosphorus-containing intermediates, mM; $[\text{Interme}]_n$, the concentration of nitrogen-containing intermediates, mM; $[\text{Interme}]_c$, the concentration of organic intermediates, mM; k_m , the pseudo-first order decomposition rate constant of monocrotophos, min⁻¹; k_p , the pseudo-first order formation rate constant of phosphate, min⁻¹; k_n , the pseudo-first order formation rate constant of nitrate, min⁻¹; k_c , the pseudo-first order formation rate constant of carbonate, min⁻¹.

Using the reaction rate equations proposed above, the rate constants were determined by regressing the experimental data. The temporal behavior of reacting species during the decomposition of monocrotophos by UV/O₃ process were reasonably consistent with the model and the results are shown in Fig. 6 for pH 9. Similar satisfactory results were also obtained for other solution pH conditions. The pseudo-first order reaction rate constants for monocrotophos decomposition and for the release of constituent anions at

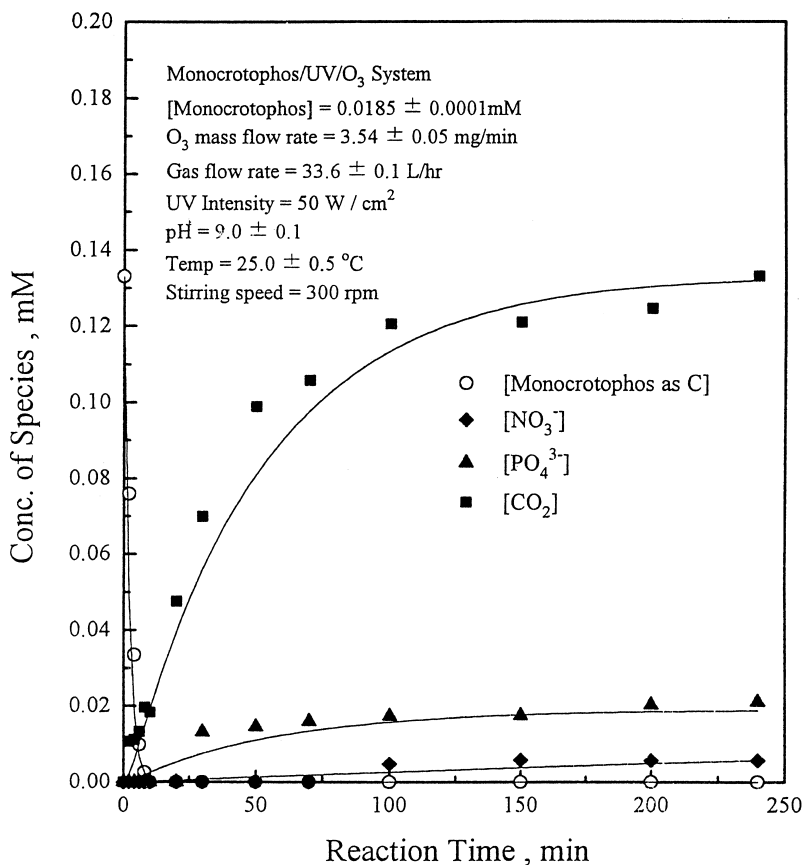


Fig. 6. The temporal behavior of reacting species modeled by the simplified consecutive reaction scheme during the decomposition of monocrotophos at solution pH 9 by UV/O₃ process.

various pH values are summarized in Table 2. The decomposition rate constants of monocrotophos by UV/O₃ process was decreased with increasing solution pH.

This result differs from the experimental findings reported by several researchers on the ozonation of several phenols [3,12,17] which stated that the decomposition rates was increased with solution pH because of the formation of OH· radicals. The decomposition of monocrotophos species, protonated and unprotonated, by UV/O₃ process might vary with solution pH conditions. For pH lower than pK_a, the positively-charged protonated monocrotophos predominates in aqueous solutions and is more favorably decomposed into organic intermediates by the resonance-stated ozone molecule with significant dipole moment [18]. But further mineralization of organic intermediates was proceeded by the OH· free radicals formed by the UV irradiation and OH⁻ catalysis of ozone molecules. Even though the decomposition rate of monocrotophos is lowered with increasing solution pH, the mineralization of organic intermediates could further proceed by OH· free radicals as shown in Table 2. The temporal distribution of reaction species

during the decomposition of monocrotophos shown in Fig. 6 was quite similar to that of the same solution pH by ozonation conducted in the previous work [18]. Using the same mass flow rate of ozone in the processes, the decomposition rate constants for monocrotophos at low and neutral pH values (pH 3, 5, 7) by UV/O₃ process were found to be smaller than those by ozonation [18]. In addition, the decomposition rate constants of monocrotophos by ozonation was found to be decreased with increasing solution pH. This experimental result of the pH effect differs from the experimental findings reported by several researchers on AOPs of other organic pollutants in aqueous solution [4,16,19]. However, the experiments reported by Yocum et al. [26] and Baillod et al. [1] also show some controversial results. They found that the ozonation rate of toluene-2,4-diisocyanate and 2-chlorophenol, respectively, in aqueous solutions decreased with increasing solution pH. Thus, it was postulated that the pH effect on the ozonation of organics might also depend on the molecular structure of target organic compounds and needs more detailed research. Conclusions based solely on the formation of OH · radicals may not be concrete.

This unique phenomena can be explained such that protonated monocrotophos (the predominant in aqueous solution at low and neutral solution pH values) is more refractory to be attacked by the OH · free radicals rather than oxidation by ozone molecules. Ozone, in UV/O₃ process, can be excited by UV light to generate OH · radicals and inhibit the decomposition of monocrotophos by ozonation. Thus, the decomposition rate for monocrotophos by UV/O₃ process would be less than at low and neutral solution pH by ozonation. Moreover, the reaction $2\text{OH} \cdot \rightarrow \text{H}_2\text{O} + 1/2 \text{O}_2$ may occur at elevated pH levels [25]. The self-combination of OH · radicals also seems to be a possible ratiocination for the low decomposition rate of monocrotophos in alkaline solutions.

The mineralization rate constant of organic intermediates by UV/O₃ process could be raised with increasing solution pH because of the increasing of the concentration of the hydroxide ions to generate more OH · radicals in alkaline solutions. Thus, the solution pH not only altered the distribution of monocrotophos species, but also the distribution of less-oxidative ozone molecules and more-oxidative OH · free radicals.

4. Conclusion

UV/O₃ process has been shown to be feasible for achieving high degree of monocrotophos decomposition in aqueous solutions. The decomposition rates of monocrotophos by ozonation were increased with decreasing solution pH possibly due to the species distribution of monocrotophos and ozone in aqueous solution, but the mineralization of organic intermediates was significantly promoted in alkaline solutions possibly due to the formation of OH · free radicals generated by the reaction of ozone and hydroxide ions. The presence of UV light can alter the decomposition mechanism of monocrotophos by ozonation and inhibit the decomposition rate of monocrotophos, but apparently promoted the mineralization of the organic intermediates. The decomposition pathway of monocrotophos by UV/O₃ was proposed and the breakage of carbon–carbon double bond was found to occur at the early stage of the decomposition of monocro-

tophos to form various nitrogen- and phosphorus-containing intermediates. The temporal behavior of various species for the decomposition of monocrotophos could be globally described by a simplified consecutive-parallel reaction kinetics.

5. Nomenclature

$[\text{Interme}]_p$	the concentration of phosphorus-containing intermediates, mM
$[\text{Interme}]_n$	the concentration of nitrogen-containing intermediates, mM
$[\text{Interme}]_c$	the concentration of organic intermediates, mM
k_m	the pseudo-first order decomposition rate constant of monocrotophos, min^{-1}
k_p	the pseudo-first order formation rate constant of phosphate, min^{-1}
k_n	the pseudo-first order formation rate constant of nitrate, min^{-1}
k_c	the pseudo-first order formation rate constant of carbonate, min^{-1}
M	the concentration of monocrotophos, mM
M_o	the initial concentration of monocrotophos, mM
λ	wavelength

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