JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Hydrolytic Products and Kinetics of Triazophos in Buffered and Alkaline Solutions with Different Values of pH

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The hydrolysis of triazophos was studied in buffered solutions in the range of pH 4−10 and in sodium hydroxide solutions with pH values up to 12. The results showed that the degradation of triazophos in the above solutions followed simple pseudo-first-order kinetics. At 35 °C, the rate constants in buffered solutions ranged from 0.0222 d^{-1} at pH 4 to 0.5357 d^{-1} at pH 10, and increased to 0.6251 h^{-1} in 0.01 mol/L sodium hydroxide solution. The results also indicated that the base-catalysis was more important than acid-catalysis in the hydrolysis of triazophos. On the basis of the Arrhenius plot, the calculated activation energy (E_a) and the frequency factor (A) for the hydrolysis of triazophos in buffered solution of pH 10 were 78.6 kJ/mol and 1.13×10^{13} d^{-1}, respectively. Hydrolytic products of triazophos in buffered solutions of pH 4 and 10, as well as in sodium hydroxide solution of pH 11, were identified as their corresponding trimethylsilyl derivatives with a gas chromatography−mass spectrometer (GC−MS). The possible hydrolytic pathways of triazophos were also proposed.

KEYWORDS: Triazophos; Hostathion; hydrolysis; degradation; kinetics

INTRODUCTION

Triazophos (CAS Registry No. 24017-47-8) is the common name for *O*,*O*-diethyl *O*-1-phenyl-1*H*-1,2,4-triazol-3-yl phosphorothioate (**Figure 1**). It is one of the mid-toxic and broad-spectrum nonsystemic contact organophosphorus pesticides (OPs). It has been put into agriculture use since the late 1970s, on various crops such as cotton, maize, paddy, and vegetable. In recent years, most high-toxic and high-residual OPs, for example, methamidophos, parathion, and methyl parathion, were banned to use on crops by the Agriculture Department of China. As a good alternative, less toxic and residual triazophos has more widespread applications. The evaluation of the degradation and fate of triazophos in the environment is thus of great concern.

The degradation of OPs in water occurs via various pathways, such as oxidation, photodegradation, and hydrolysis (*1*), among which hydrolysis is the dominant way. Study on the hydrolysis of triazophos in an aquatic environment is vital to assess its environmental safety; however, not much research has been done (*2*−*4*). The hydrolysis of triazophos in water, especially the hydrolytic kinetics and degradation products, has not been further investigated. In this study, the hydrolytic kinetics of triazophos under different pH and temperature conditions were investigated, the hydrolytic products were analyzed, and the possible mechanism was proposed.

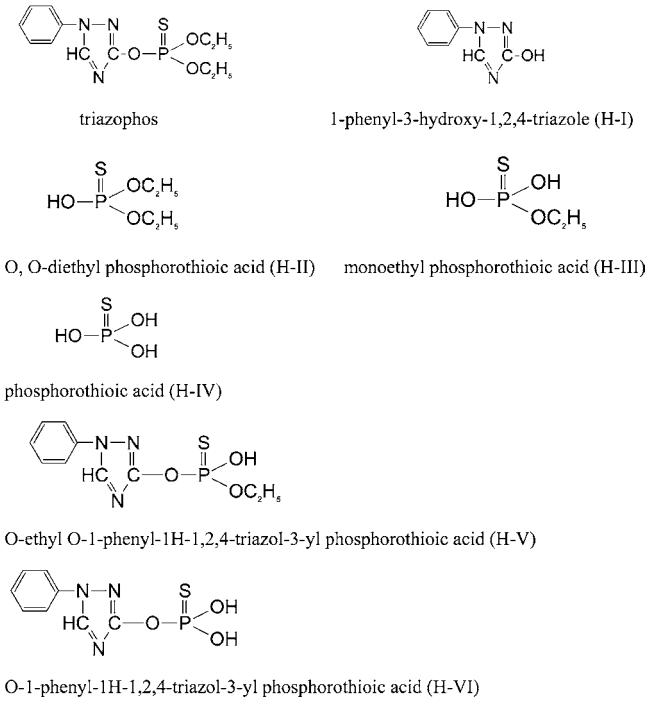

Figure 1. Chemical structures of triazophos and its possible hydrolytic products.

MATERIALS AND METHODS

Instrumentation. The analysis of triazophos residue extracted from aqueous solutions was performed using an Agilent model 6890 plus gas chromatography (GC) equipped with a flame photometric detector (FPD) and phosphorus filter (Agilent Technologies, Inc.). Injection port, 250 °C, splitless injection, 1 μL injection volume; capillary column, SPB1701 (Supelco, Inc.), 30 m × 0.32 mm i.d. and 0.25 μm film thickness; column temperature program, 160 °C − 20 °C/min −

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10.1021/jf049441i CCC: $27.50
Published on Web 07/27/2004

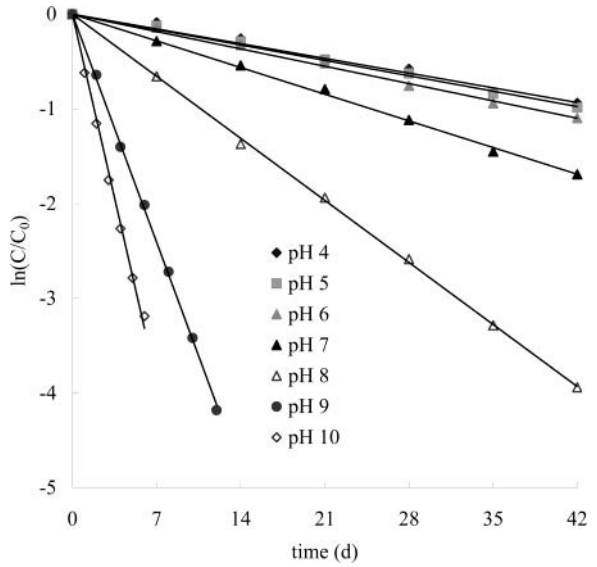

Figure 2. Relationship of $\ln(C/C_0)$ and hydrolysis time for triazophos at 35 °C in buffered solutions.

Table 1. Kinetic Data of the Hydrolysis of Triazophos at 35 °C in Buffered Solutions

pH	k_{obsd} (d^{-1})	$t_{1/2}$[a] (d)	corrln coeff
4	0.0222	31.2	0.9917
5	0.0230	30.1	0.9972
6	0.0262	26.5	0.9974
7	0.0402	17.2	0.9988
8	0.0930	7.5	0.9998
9	0.3467	2.0	0.9997
10	0.5357	1.3	0.9978

[a] Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.

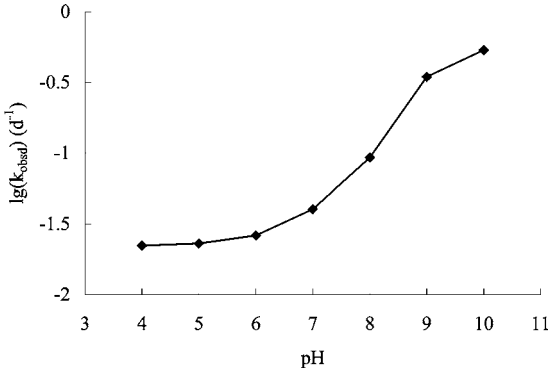

Figure 3. Relationship between $\lg(k_{obsd})$ and pH for triazophos hydrolysis in buffered solutions.

Table 2. Kinetic Data of the Hydrolysis of Triazophos at Different Temperatures with pH 10

T (°C)	k_{obsd} (d^{-1})	$t_{1/2}$[a] (d)	corrln coeff
25	0.1802	3.8	0.9962
30	0.3475	2.0	0.9978
35	0.5357	1.3	0.9974
40	0.8132	0.9	0.9959
45	1.424	0.5	0.9994

[a] Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.

260 °C (6 min); flow rates, carrier gas nitrogen 1.5 mL/min, make up gas nitrogen 25 mL/min, air 100 mL/min, hydrogen 75 mL/min; detector, 250 °C. Instrument control and chromatography data were managed by a personal computer running the GC ChemStation software

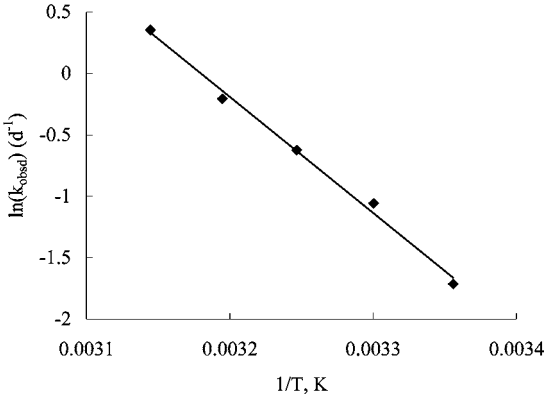

Figure 4. Relationship between $\ln(k_{obsd})$ and $1/T$ for triazophos hydrolysis in buffered solution of pH 10.

Table 3. Kinetic Data of Triazophos Hydrolysis in Sodium Hydroxide Solutions of Different Concentrations at 35 °C

concentration (mmol/L)	k_{obsd} (h^{-1})	$t_{1/2}$[a] (h)	corrln coeff
0.625	0.0405	17.1	0.9942
1.25	0.082	8.5	0.9983
2.50	0.1574	4.4	0.9928
5.00	0.2964	2.3	0.9965
10.00	0.6251	1.1	0.9995

[a] Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.

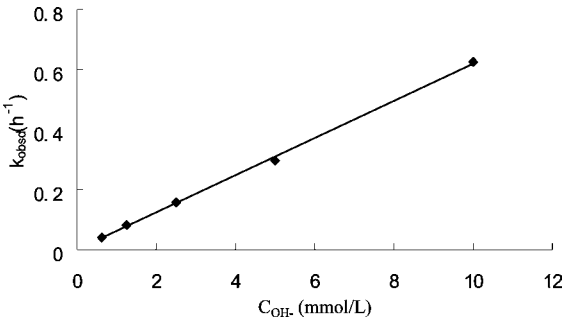

Figure 5. Relationship between k_{obsd} and sodium hydroxide concentration for triazophos hydrolysis at 35 °C.

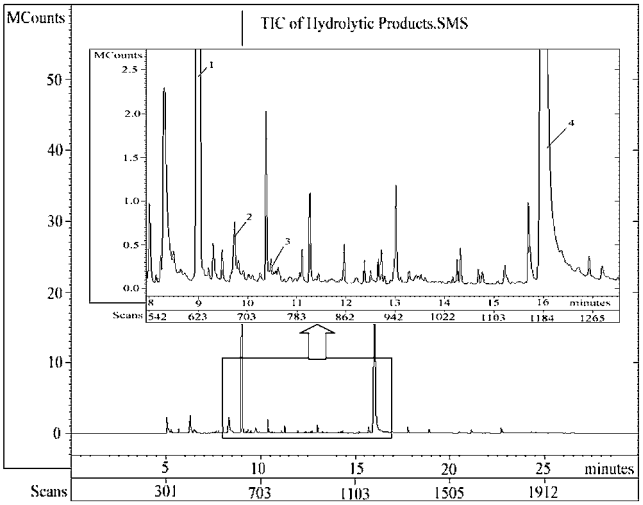

Figure 6. TIC chromatogram in the full-scan mode for trimethylsilyl derivatives of hydrolytic products of triazophos.

(Rev. A.08.03[84], Agilent Technologies, Inc.). The retention times of triazophos and triphenyl phosphate were 8.905 and 9.125 min, respectively.

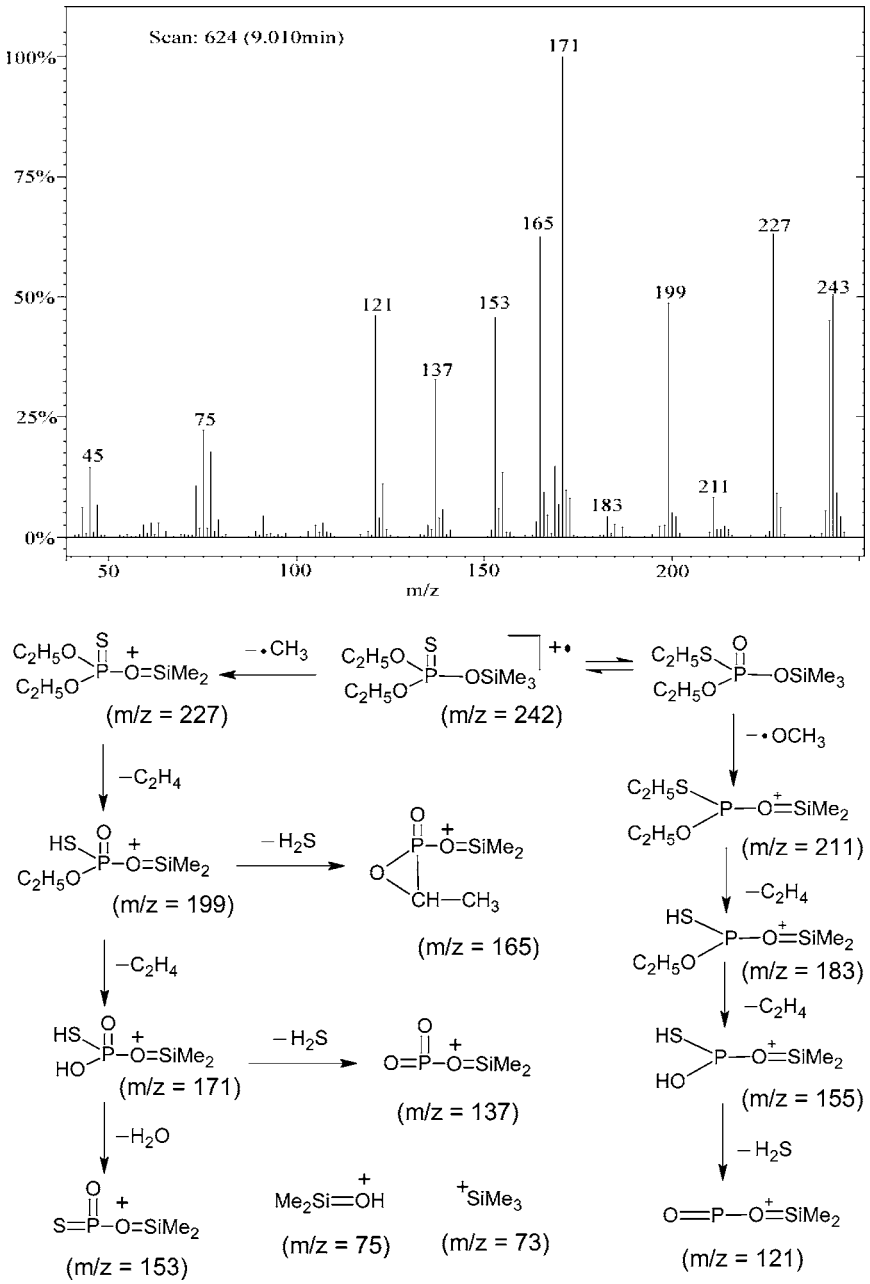

Figure 7. Mass spectrum of peak 1 and its interpretation.

The analysis of derivatives of hydrolytic products of triazophos was performed on a Varian 3900 GC directly connected to a Saturn 2000 ion-trap mass spectrometer (Varian, CA). The mass spectrometer operated in the EI Auto mode with 70-eV ionization energy was used for full scan at a *m/z* range from 40 to 500 Da. Standard injection port, 250 °C, splitless injection, 1 μL injection volume; capillary column, CP-Sil 8 MS (Varian, CA), 30 m × 0.25 mm i.d. and 0.25 μm film thickness; column temperature program, 80 °C (3 min) − 10 °C/min − 280 °C (7 min); carrier gas flow rate, helium 1.0 mL/min; manifold, trap, and transfer line temperatures were set at 40, 170, and 260 °C, respectively. Instrument control and mass spectrometry data were managed by a Saturn GC/MS Workstation (Version 5.52, Varian, Inc.).

Chemicals and Reagents. Triazophos with purity higher than 97.5% was purchased from Kefa New Technology Development Ltd. Co. (Shenyang, China). HPLC-grade acetone, ethyl acetate, and dichloromethane were purchased from Tedia Company (OH). Triphenyl phosphate with purity higher than 99% was purchased from Acros Organics (NJ). Derivatization reagent *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 vol % trimethylchlorosilane (TMCS) was purchased from Supelco Inc. (PA). Analytic reagents anhydrous sodium sulfate, hydrochloric acid, sodium hydroxide, potassium chloride, potassium biphthalate, potassium dihydrogen phosphate, and boric acid were purchased from Shanghai Chemical Reagents Co. (Shanghai, China).

Preparation of Solutions. A triazophos stock solution with a concentration of 5000 μg/mL and a triphenyl phosphate solution of 10 μg/mL were prepared by dissolving a certain amount of the analyte with acetone, respectively. Working standards were prepared by diluting the stock solution with acetone. All of the solutions were stored in a freezer at −10 °C while not in use.

Buffer solutions of pH 4.0−6.0 were prepared by mixing certain volumes of 0.1 mol/L sodium hydroxide solution with 0.1 mol/L potassium biphthalate solution; solutions of pH 7.0 and 8.0 were prepared from 0.1 mol/L sodium hydroxide solution and 0.1 mol/L potassium dihydrogen phosphate solution; solutions of pH 9.0 and 10.0 were prepared with 0.1 mol/L sodium hydroxide solution and 0.1 mol/L boric acid solution. The deionized water was sterilized before use to avoid biotic degradation.

Incubation and Hydrolysis of Triazophos in Buffered and Alkaline Solutions. Aliquots of 500 μL of triazophos stock solution were added into 100 mL buffer and alkaline solutions to prepare test sample solutions with a triazophos concentration of 25.0 μg/mL. The

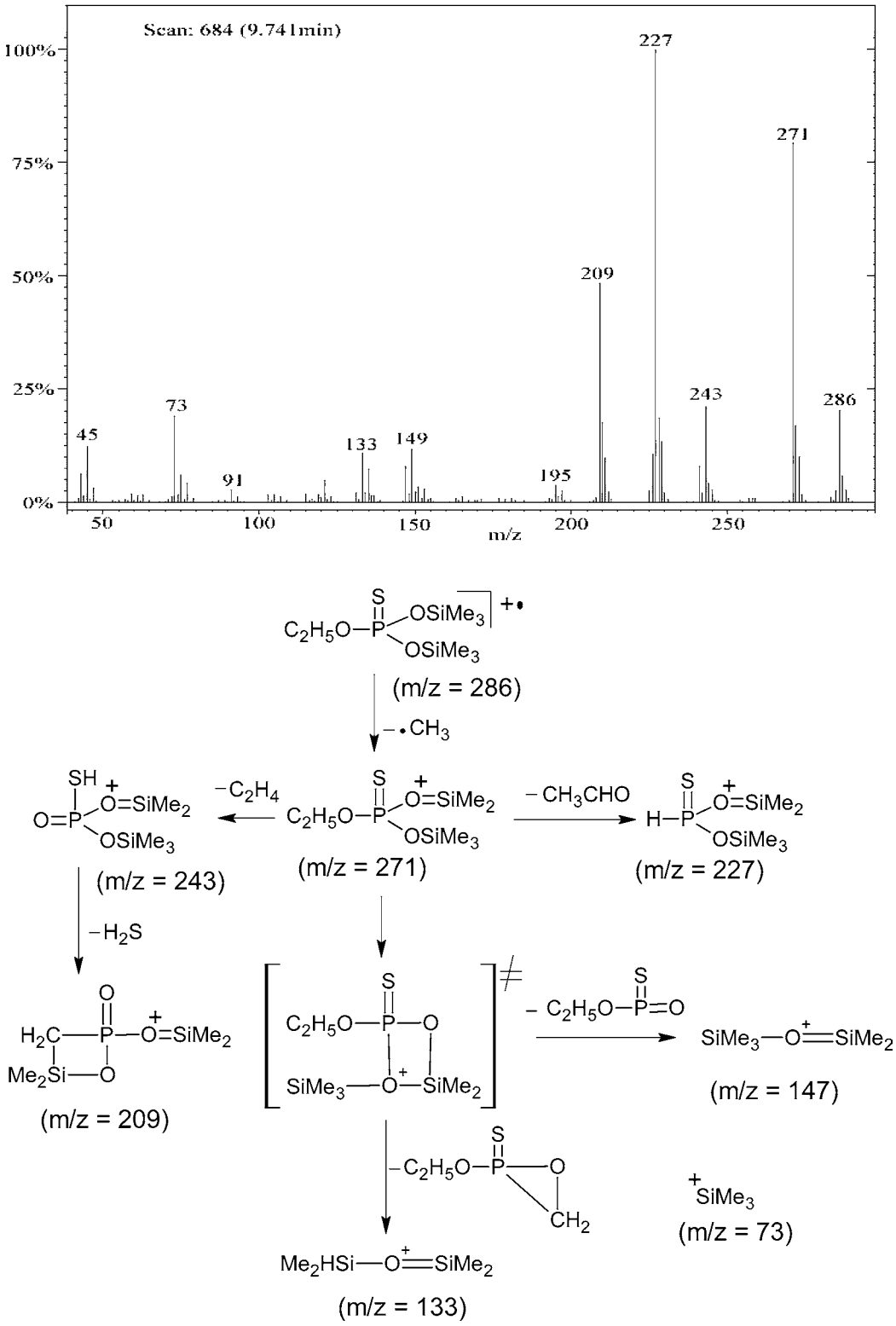

Figure 8. Mass spectrum of peak 2 and its interpretation.

solubility of triazophos in water at 23 °C is 39 mg/L. All of the test samples were sealed and incubated in an incubator to process the hydrolysis. Portions of 1.0 mL of each sample were collected at designated time intervals to analyze triazophos residue for the kinetics study.

Determination of Triazophos Residue in Test Solutions. A method for the determination of triazophos residue in solutions was carried out on the basis of EPA Method 1657 (*5*). The 1.0 mL collected sample was transferred into a 250 mL separatory funnel and diluted with 50 mL of deionized water. One hundred microliters of triphenyl phosphate of 10 μg/mL was added as a surrogate for data quality control. The sample was then extracted three times, each with 10 mL of dichloromethane and vigorous shaking for 2 min. The organic phases were collected and combined together. The extract was filtered with a glass funnel filled with anhydrous sodium sulfate, then evaporated to nearly dryness with a gentle nitrogen stream in a 40 °C water bath. The final volume of 1.0 mL was made with ethyl acetate for GC analysis.

The recoveries of triazophos at the concentration of 1.0 μg/mL were within the range of 86.6−96.2%, and the relative standard deviation (RSD) was 5.3% ($n = 3$). The linearity was between 0.1 and 10.0 μg/mL with the correlation coefficient of 0.9996 ($n = 6$). The method detection limit (MDL) of triazophos was 30 μg/L. The recovery of

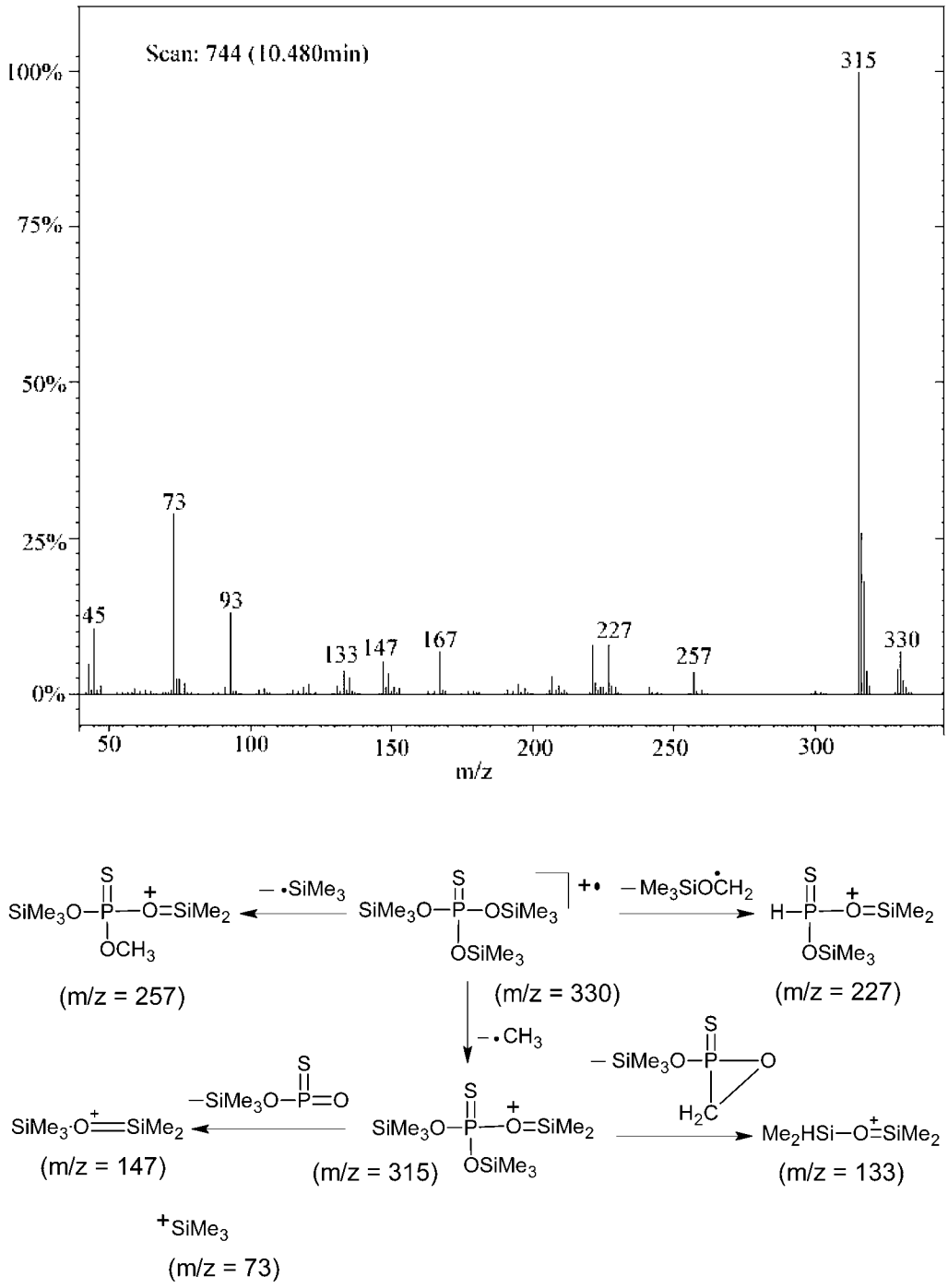

Figure 9. Mass spectrum of peak 3 and its interpretation.

triphenyl phosphate in each test sample was within the rage of 92.1−95.6% with an RSD of 2.3% ($n = 3$).

Identification of Hydrolytic Products. Hydrolytic product identification was carried out at the end of one half-life. Thin-layer chromatography (TLC) was usually used for qualitative analysis of OPs degradation products (*6*−*8*). Recently, GC−MS has been widely applied to the identification of the degradation products of OPs (*9*, *10*). However, the degradation compounds usually are not suitable for direct analysis with GC−MS because of their low evaporating ability. Therefore, the derivatization is necessary. Silylation, one of the most popular derivatization techniques, is applicable to a wide variety of compounds. Matthews et al. (*11*) used the method of extraction-silylation followed by GC−FPD to determine trace phosphate in aqueous media.

In this study, hydrolytic products were identified via the extraction-derivatization-GC−MS method. One hundred milliliters of sample was acidified to pH 2 with 10% hydrochloric acid and was extracted three times with 50 mL of ethyl acetate each. The organic phases were combined, dried with anhydrous sodium sulfate, and concentrated to 0.5 mL with a gentle nitrogen stream and in a 40 °C water bath. To silylate the extracted compounds, equal volumes (100 μL) of the extract and silylating reagent BSTFA−1%TMCS were put together in a septum-capped glass vial and reacted for 2 h in a 60 °C water bath. The large excess of BSTFA−1%TMCS ensured the derivatization was complete. An aliquot of 1 μL of silylated sample was taken for GC−MS analysis.

RESULTS AND DISCUSSION

Effect of pH on Hydrolysis with Buffered Solutions of pH 4−10. Hydrolysis of triazophos in buffered solutions of pH 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 was investigated. The concentra-

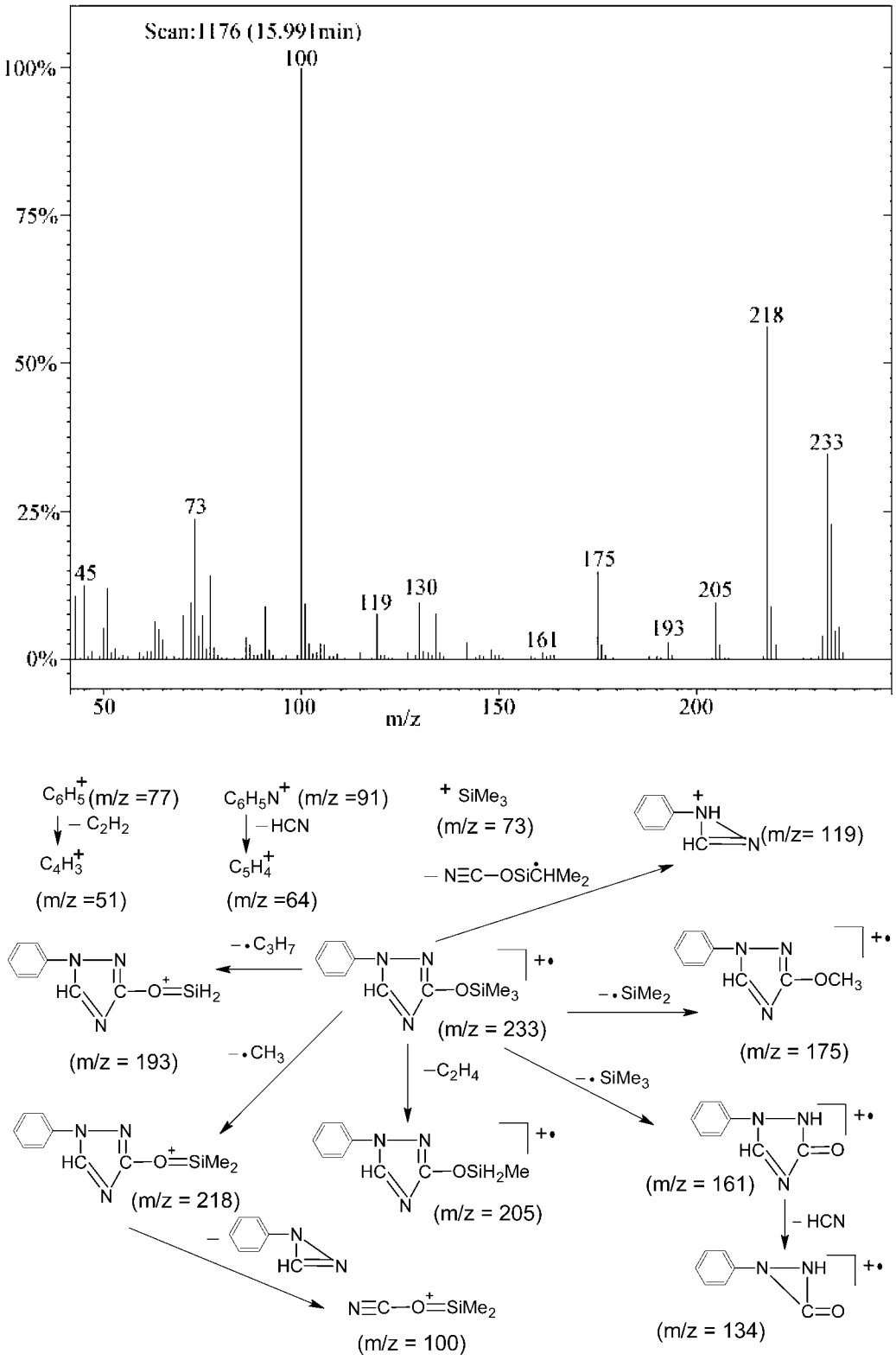

Figure 10. Mass spectrum of peak 4 and its interpretation.

tion of triazophos in each test sample at the designed time was determined, and the data were analyzed. It was found that the hydrolysis of triazophos in buffered solutions could be treated as a pseudo-first-order reaction; thus the following equation might be applied, $dC/dt = -k_{obsd}C$, or $\ln(C/C_0) = -k_{obsd}t$, where C_0 and C are the triazophos concentrations in initial solutions and test samples, respectively. The observed rate constant for the hydrolysis reaction, k_{obsd}, is assumed to be the sum of three terms, $k_{obsd} = k_a[H^+] + k_N + k_b[OH^-]$, where k_a, k_b, and k_N represent the rate constants for acid-catalyzed, base-catalyzed, and neutral hydrolysis pathways, respectively (*12*). When the plot of $\ln(C/C_0)$ versus reaction time is derived, k_{obsd} is equal to the slope. **Figure 2** shows such plots for triazophos hydrolysis in the buffered solutions of pH 4−10, and the corresponding kinetic data are listed in **Table 1**.

The results indicated that the hydrolysis of triazophos in buffered solutions fit very well with the pseudo-first-order reaction model. From the half-lives of triazophos in buffered

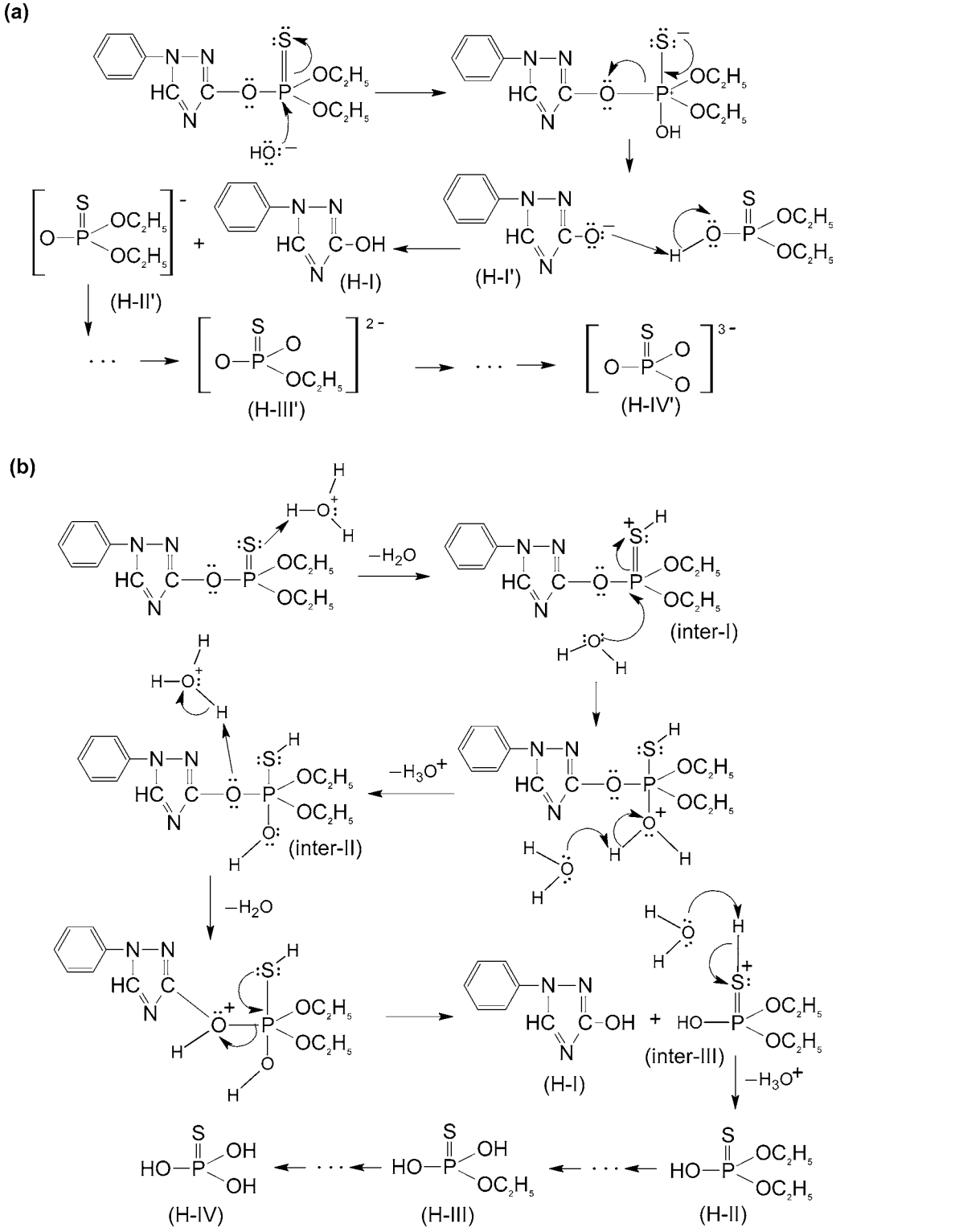

Figure 11. Possible hydrolytic pathways for triazophos in (**a**) pH 10 and (**b**) pH 4 solutions, respectively.

solutions with different pH values shown in **Table 1**, it could be concluded that triazophos was relatively stable and not easy to hydrolyze under acidic and neutral aquatic conditions, while it readily decomposed under basic aquatic conditions. The relationship between lg(k_{obsd}) and pH values for the hydrolysis of triazophos in buffered solutions is shown in **Figure 3**. Within the pH range of 4−6, pH had a very small effect on k_{obsd}, which indicated that the term $k_a[H^+]$, especially k_a, was quite small and acid-catalyzed hydrolysis was to a small extent. In the pH range of 7−10, the k_{obsd} values changed greatly as pH increased, indicating that base-catalysis played a dominating role in the hydrolysis of triazophos.

Effect of Temperature on Hydrolysis. To study the influence of temperature on the hydrolytic rate, the k_{obsd} values for the hydrolysis in buffered solution of pH 10 at 25, 30, 35, 40, and 45 °C were determined. The results are listed in **Table 2**. It can be found that the increasing reaction temperature led to a higher hydrolytic rate. When the temperature was increased by 10 °C, the k_{obsd} increased about 2.3−3.0 times.

According to the Arrhenius equation, $k_{obsd} = Ae^{-E_a/RT}$, where A is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the reaction temperature, the Arrhenius plot is established in **Figure 4** based on the kinetic data shown in **Table 2**. The linear relationship of $\ln(k_{obsd})$ and $1/T$ was found to be $\ln(k_{obsd}) = -9451.7(1/T) + 30.054$, with $n = 5$ and $r = 0.9972$. The E_a and A for the triazophos hydrolysis with pH 10 were calculated as 78.6 kJ/ mol and 1.13×10^{13} d^{-1}, respectively. The calculated E_a value was consistent with the activation energies for hydrolysis of various other OPs, ranging from 58.8 to 92.4 kJ/mol (*13*).

Hydrolysis in Alkaline Solution. The hydrolysis of triazophos at pH higher than 10 in alkaline solutions was investigated in a series of sodium hydroxide solutions with concentrations of 10.00, 5.00, 2.50, 1.25, and 0.625 mmol/L at the temperature of 35 °C, respectively. The results shown in **Table 3** and the k_{obsd} versus $[OH^-]$ as plotted in **Figure 5** revealed that the hydrolysis of triazophos in sodium hydroxide solutions also followed simple pseudo-first-order kinetics. The linear equation was derived as $k_{obsd} = 0.0619[OH^-] + 0.0004$, where $n = 5$ and $r = 0.9994$. The rate constant for base-catalyzed hydrolysis, k_b, was calculated to be 62.0 L/mol·d.

Identification of Hydrolytic Products and Hydrolysis Mechanism. Until now, no data about the hydrolytic products of triazophos were available. On the basis of the chemical structure of triazophos and in comparison with the hydrolysis of other similar OPs in aquatic media (*14*, *15*), some of the possible hydrolytic product's structures were put forward in **Figure 1** (H-I to H-VI). To verify the possible hydrolytic compounds, analyses were carried out when the hydrolysis reactions were at the end of one half-life. At 35 °C, the hydrolytic products of triazophos in buffered solution of pH 10 were examined, and the total ion current (TIC) chromatogram of GC−MS is illustrated in **Figure 6**. The mass spectra of peaks 1−4 in **Figure 6** and their interpretation are shown in **Figures 7**−**10**, respectively. Four compounds corresponding to peaks 1−4 in **Figure 6** could be tentatively identified as H-I to H-IV, respectively. In addition to a buffered solution of pH 10, the identified products were also found at 35 °C in a buffered solution of pH 4 and in a sodium hydroxide solution of pH 11. However, H-V and H-VI were not detected.

The proposed mechanism for base-catalyzed hydrolysis is shown in **Figure 11a**. In a basic solution of pH 10, the polarization of the O−P bond in triazophos results from the differing electronegativities of the oxygen atom and phosphorus atom. Therefore, there is an electron deficiency at the phosphorus atom. The nucleophile, hydroxide ion, approaches the phosphorus atom in triazophos and displaces H-I′, which acts as the leaving group to form H-I. The other product H-II′, is further attacked by the hydroxide ion and again undergoes similar nucleophilic reactions, to form the products of H-III′, H-IV′, and ethyl alcohol.

Figure 11b illustrates the mechanism of acid-catalyzed hydrolysis. In the solution of pH 4, the protonation of the P═S bond is the first step in the hydrolysis of triazophos. The protonated inter-I is attacked by water. Loss of a proton gives a pentahedral inter-II, which can be further converted to form inter-III. By attacking water, inter-III is finally deprotonated to produce H-II. H-II undergoes similar reactions to give H-III and H-IV.

Conclusions. The investigation results showed that triazophos is relative stable in acidic and neutral solutions and easily hydrolyzes in basic solutions. The base-catalyzed and acid-catalyzed hydrolyses occur possibly through two different pathways, respectively; however, they produce the same products.

ACKNOWLEDGMENT

This work was supported by the Fund of Science and Technology of Fujian, China (No. 02003Y010). We highly appreciate the expert interpretation of the mass spectra by Prof. Li Yugui.

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Received for review April 5, 2004. Revised manuscript received June 13, 2004. Accepted June 16, 2004.

JF049441I