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Reaction of Thiometon and Disulfoton with Reduced Sulfur Species in Simulated Natural Environment

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The reactions of thiometon and its ethyl analogue, disulfoton, with reduced sulfur species [e.g., bisulfide (HS^-), polysulfide (S_n^{2-}), thiophenolate (PhS^-), and thiosulfate ($S_2O_3^{2-}$)] were examined in well-defined aqueous solutions under anoxic conditions. The role of reduced sulfur species was investigated in the abiotic degradation of thiometon and disulfoton. Experiments at 25 °C demonstrated that HS^-, S_n^{2-}, PhS^-, and $S_2O_3^{2-}$ promoted the degradation of thiometon to a great extent while only S_n^{2-} and PhS^- showed a small accelerating effect in the degradation of disulfoton. Reactions were monitored at varying concentrations of reduced sulfur species to obtain the second-order rate constants. The reactivity of the reduced sulfur species decreased in the following order: $S_n^{2-} > PhS^- > HS^- \approx S_2O_3^{2-}$. Transformation products were confirmed by standards or characterized by gas chromatography mass spectrometry. The results illustrate that multiple pathways occur in the reactions with reduced sulfur species, among which the nucleophilic attack at the α-carbon of the alkoxy group was the predominant pathway. Activation parameters of the reaction of thiometon and disulfoton with HS^- were also determined from the measured second-order rate constants over a temperature range. $\Delta H^{\neq}$ values indicated that the reactivity of thiometon toward HS^- was much greater than for disulfoton. Nucleophilic attack at the alkoxy group was more important for thiometon than disulfoton. When the measured second-order rate constants at 25 °C are multiplied by $[HS^-]$ and $\sum[S_n^{2-}]$ reported in saltmarsh porewaters, predicted half-lives show that reduced sulfur species present at environmentally relevant concentrations may present an important sink for thiometon in coastal marine environments.

KEYWORDS: Thiometon; disulfoton; nucleophilic substitution; organophosphates; S_N2; reduced sulfur species

INTRODUCTION

Esters and thioesters of phosphoric acid and thiophosphoric acid are widely applied as pesticides in agricultural and urban environments, taking advantage of their inhibitory action on cholinesterase (*1*). Organophosphorus pesticides are in the first priority group of pesticides to be reviewed under the Food Quality Protection Act due to their potential of influencing the function of the central nervous system since they have been reported to be neurodevelopmentally toxic at very low doses (*2*, *3*). The organophosphorus pesticides are discharged as nonpoint source pollutants (*4*) and released into sensitive coastal environments such as estuaries and saltmarshes, in which relatively high concentrations of reduced sulfur species have been reported (*5*). Some organophosphorus pesticides present in the surface water may associate with particles and can eventually become part of the sediment phase, in which anoxic conditions are prevalent. In order to predict the environmental fate of a pesticide, it is necessary to know its mobility, the rate of degradation under the given environmental conditions, and its degradation products. Both microbial and abiotic transformation can play a role in the degradation of the pesticides. The abiotic processes, including oxidation, reduction, photolysis, hydrolysis, and other chemical degradation, may represent important pathways, which have to be investigated to understand the fate of organic pollutants (*6*).

Thiometon (**1a**, **Scheme 1**) and its ethyl analogue, disulfoton (**1b**, **Scheme 1**), are systemic insecticides and acaricides belonging to the phosphorodithiolate subgroup. Thiometon is effective against sucking insects, mainly aphids and mites, on most crops. About 1.2 million pounds of disulfoton is used annually in the United States, most of which is applied to cotton, wheat, potatoes, and tobacco (*7*). Asparagus and Christmas trees are also important use sites, with 40 and 65% of acres treated with disulfoton, respectively (*7*). Thiometon and disulfoton enter the environment primarily during their uses as insecticides/acaricides in crops and vegetables and in homes and gardens. The processes that may introduce the pesticides to aquatic environmental media include leaching to groundwater and runoff to surface water (*8*−*11*). Biotransformation, abiotic hydrolysis,

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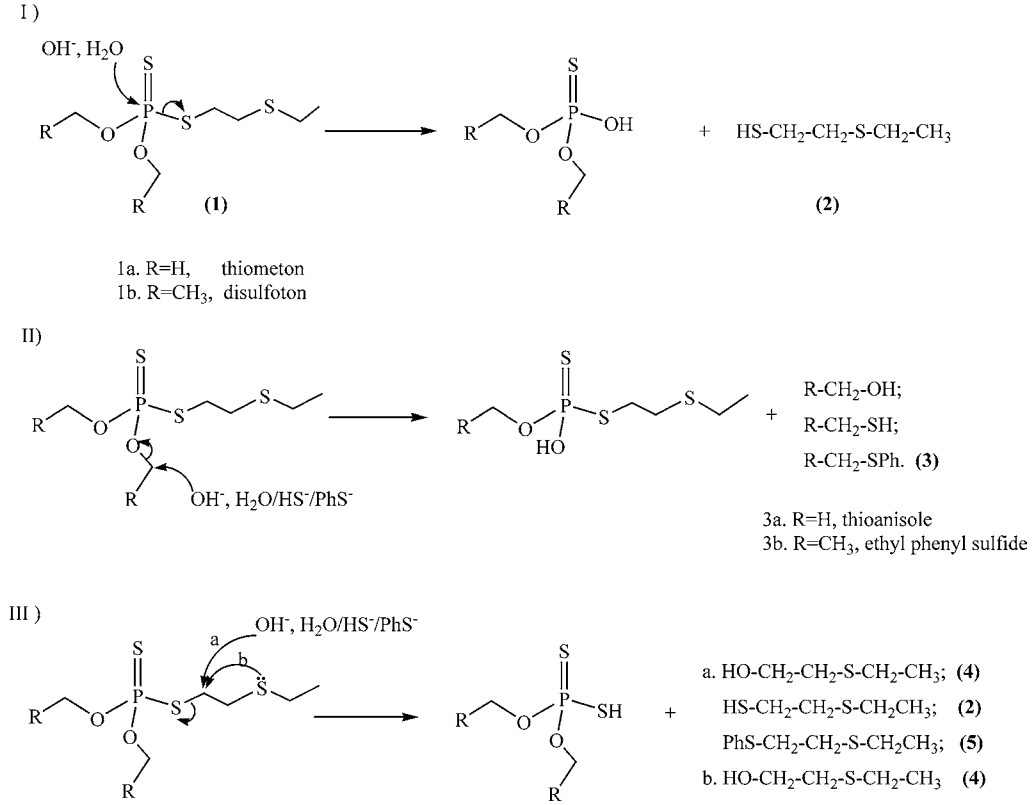
Scheme 1. Possible Mechanisms of the Reaction of Thiometon and Disulfoton in pH Buffer Containing Reduced Sulfur Species[a]



[a] (I) Nucleophilic attack on phosphorus atom leading to the breakage of the P–S Bond. (II) O-Dealkylation of the side chain. (III) Nucleophilic displacement at the 2-(ethylthio)ethyl group, including an intermolecular (a) and an intramolecular (b) attack.

to a lesser extent, and sensitized oxidation are principally responsibile for the loss of the pesticides from water (*12*−*14*). Wanner and co-workers reported a model prediction of the concentration−time courses of thiometon and disulfoton in the Rhine River (*14*), concluding that biotransformation and abiotic reactions are important processes in the reduction of the total load from the river. The fate of thiometon and disulfoton, once in the surface water and sediments, and the likely concentration therein, is very difficult to be modeled with a high degree of certainty since only few data are available for the aerobic and anaerobic aquatic degradation rates. There are only a few studies available on the reactivity of organophosphorus compounds in aquatic systems despite their occurrence in the environment. Direct photolysis of thiometon and disulfoton is negligible, since the two compounds do not significantly absorb sunlight, while indirect photolysis can play a role in the degradation (*14*, *15*).

Reduced sulfur species are versatile environmental reagents capable of reacting with a wide range of pollutants, including many organic contaminants that undergo nucleophilic substitution and reductive dehalogenation. In recent years, the degradation of organic contaminants in the presence of reduced sulfur species has received increasing attention because of the reactivity of the reduced sulfur species and their occurrence in aquatic environments (*16*−*21*). In addition to the reaction with reduced sulfur species, hydrolysis (reaction with H_2O and OH^-) is a competing reaction. The most likely hydrolysis mechanisms for thiometon and disulfoton were summarized by Wanner and co-workers (*14*). On the basis of the principle of hard and soft acids and bases (*22*), the mechanism of the reactions of thiometon and disulfoton in the aqueous solutions containing reduced sulfur species is postulated (**Scheme 1**). The important pathways of the degradation of thiometon and disulfoton can be the nucleophilic attack by OH^-/H_2O on the phosphorus atom leading to the breakage of the P−S bond (pathway I) and O-dealkylation of the side chain (pathway II). At the same time, there is also the possibility of nucleophilic displacement at the 2-(ethylthio)ethyl group, which can be intramolecular and/or intermolecular (pathway III).

This study is focused on the chemical transformation of thiometon and disulfoton in simulated natural sulfidic environments. The primary purpose of the research was to determine the role of reduced sulfur species in enhancing the transformation of thiometon and disulfoton and to identify the degradation products. Kinetic and thermodynamic studies are the two most important tools for the elucidation of reaction mechanisms besides product identification. Reactions were monitored at varying concentrations of reduced sulfur species including bisulfide (HS^-), thiophenolate (PhS^-), polysulfide (S_n^{2-}), and thiosulfate ($S_2O_3^{2-}$) so as to obtain the second-order reaction rate constant and compare the reactivity of different sulfur species. The activation parameters were investigated via the temperature dependence of the reaction rate constants of thiometon and disulfoton with bisulfide. This study also represents an experimental investigation of substituent effects on reactivity and reaction mechanisms. The subtle structural difference may result in drastic differences in reactivity and mechanism. Studies of the structural analogues can provide invaluable, although indirect and unclear, information regarding the mechanisms through which the pesticides react with the reduced sulfur species.

MATERIALS AND METHODS

Chemicals. All chemicals were used as received. Thiometon (*S*-2-ethylthioethyl *O*,*O*-dimethyl phosphorodithioate; 95.0%) and disulfoton (*S*-2-ethylthioethyl *O*,*O*-diethyl phosphorodithioate; 99.1%) were ob-

tained from Chem Service (West Chester, PA). 2-(Ethylthio)ethanol and thioanisole were obtained from TCI (Portland, OR). 2-Chloroethyl ethyl sulfide was obtained from TCI (Tokyo, Japan). Ethyl phenyl sulfide was obtained from Avocado Research Chemicals (Heysham, Lancashire, England). 2-(Ethylthio)ethanethiol was prepared from 2-chloroethyl ethyl sulfide in our lab according to the method reported by Furukawa (*23*). (Details of the synthesis are described in the Supporting Information.) In the standard solutions prepared in methanol, 2-(ethylthio)ethanethiol was entirely present as dimer, 2-(ethylthio)-ethyl disulfide. All solvents and reagents that were used were analytical grade or equivalent. Ethyl acetate and methanol were high-performance liquid chromatography grade and were obtained from Fisher Scientific (Pittsburgh, PA). All reaction solutions were prepared in an anaerobic glovebox (5% H_2 and 95% N_2), and aqueous solutions were prepared from argon-purged deionized water (DW) (Milli-Q gradient system, Millipore, Bedford, MA).

Reduced Sulfur Solutions. Sodium sulfide stock solutions were prepared under argon from $Na_2S{\cdot}9H_2O$ crystals (sodium sulfide, hydrated, Merck KGaA, Darmstadt, Germany) using deoxygenated deionized water according to the procedure described by Jans and Miah (*24*). Thiophenol stock solutions were prepared by dissolving thiophenol (99%, Lancaster Synthesis, Inc., Pelham, NH) in deoxygenated methanol. Polysulfide stock solutions were prepared by dissolving the toluene-washed sodium sulfide (Na_2S_4, technical grade, 90+%, H_2O 5% max, Alfa Aesar, Ward Hill, MA) in 100 mM sodium tetraborate buffer. The reaction solutions were prepared by dilution of reduced sulfur stock solution into 50 mM phosphate or borate pH buffer with 5% methanol and 100 mM NaCl. The total hydrogen sulfide concentration ($[H_2S]_T$), the sum of all hydrogen sulfide species ($[H_2S] + [HS^-] + [S^{2-}]$); the total thiophenol concentration ($[PhSH]_T$), the sum of [PhSH] and [PhS^-]; and the total S(II) concentration ($[S(II)]_T$), the sum of $[H_2S]_T$ and $[H_2S_n]_T$ ($[S_n^{2-}] + [HS_n^-] + [H_2S_n]$, $n = 2-5$) in polysulfide solutions and thiosulfate concentrations ($[S_2O_3^{2-}]$) were determined by iodometric titration using a starch end point. An Accumet pH meter (Fisher Scientific) with a Ross combination pH electrode (ThermoOrion, Beverly, MA) was used to measure the pH value in the reduced sulfur reaction solutions. Bisulfide ion concentrations were calculated from $[H_2S]_T$ and measured pH values via ionization constants for H_2S at 25 °C that were corrected for ionic strength using coefficients determined from the Davies approximation. In addition, bisulfide concentrations at the different temperatures were calculated according to the temperature dependence of pK_a values reported by Millero (*25*). Thiophenolate ion concentrations were determined in the same way as for HS^- from the total thiophenol concentration and the measured pH values. To the best of our knowledge, methods appropriate for determining concentrations of individual polysulfide species in complex matrixes have not been developed. The total concentration of polysulfide dianions ($\sum[S_n^{2-}]$) was determined via speciation calculations from the measured $[S(II)]_T$ and pH values based on the reported equilibrium constants (*26*, *27*). The resulting values of $\sum[S_n^{2-}]$ were used to compute the second-order rate constant ($k''_{S_n^{2-}}$) for the reaction of thiometon and disulfoton with polysulfide.

Experimental System. All glassware was soaked in 1 M HNO_3 overnight, rinsed several times by deionized water, and dried at 200 °C. Glassware used with sulfidic solutions was washed with methanol/NaOH to remove the traces of sulfur impurities before acid washing. The reaction solution was transferred into a 20 mL syringe equipped with a polycarbonate stopcock and a tetrafluoropolyethylene needle tubing and preequilibrated at selected temperatures. Four glass rings were placed in the syringe to facilitate mixing of the reaction solution. Reactions were initiated by spiking the stock solution of the pesticides into the syringe and vigorously mixed for 30 s in the golvebox. The starting concentration of thiometon and disulfoton was ~30 μM. The concentrations of $[H_2S]_T$, $[PhSH]_T$, and $[S(II)]_T$ in the reactions with thiometon were 4.3−10.3, 1.2−3.5, and 4.2−7.6 mM, respectively, and they were 5.2−25, 1.2−2.6, and 2.2−16.5 mM in the reactions with disulfoton, respectively. The reaction solution contained 5% methanol in order to increase the solubility of possible degradation products. Preliminary experiments showed that up to 20% methanol had no effect on the measured rate constants. Reaction mixtures were maintained anoxic and incubated in a water bath at the selected temperatures. The kinetics were monitored by extracting aliquots (~1 mL) of the reaction mixture with 1 mL of ethyl acetate throughout the course of experiments. The extraction efficiency of thiometon and disulfoton was determined to be 90−105%. The resulting extracts were subjected to gas chromatography flame ionization detection (GC/FID) and gas chromatography/mass spectrometry (GC/MS) analysis.

Chromatographic Analysis. Ethyl acetate extracts were analyzed on a Fisons GC 8000 equipped with an AS 800 autosampler, a FID-80 flame ionization detector (Carlo Erba Instruments), a split/splitless injector, and a 30 m DB-5, 0.25 mm i.d. × 0.25 μm, fused silica capillary column (J&W, Folsom, CA). The carrier gas was helium (99.999%), and the flow rate was 20 mL/min. Splitless injection was used. The injector temperature and detector temperature were set at 250 and 275 °C, respectively. The column temperature was held at 80 °C for 1 min, then increased at a rate of 20 °C/min to 275 °C, and finally held constant at 275 °C for 4 min. The GC/MS system to identify and analyze the degradation products was equipped with a split/splitless injector and a 30 m AT-5ms, 0.25 mm i.d. × 0.25 μm, fused silica capillary column (Alltech, Deerfield, IL). EI mass spectra were generated using electron energy of 70 eV, monitoring for ions m/z 35−500 in full-scan mode. The source temperature employed for the ionization technique was 200 °C. Splitless injection was used, and the injector temperature was set at 250 °C. The same time program was applied for GC/MS.

Reaction kinetics were determined assuming a pseudo-first-order reaction model, with the initial concentrations of thiometon and disulfoton being more than 50 times smaller than the concentration of the reduced sulfur species. Time courses were allowed to progress over approximately two half-lives. Pseudo-first-order rate constants (k_{obs}) were determined by regressing the natural logarithm of pesticide concentrations vs time. For selected experiments, first-order rate constants of disappearance of parent compounds and formation of the products were determined by fitting observed data for parent compounds and reaction products to numerically integrated solutions of the system of governing differential rate expressions using Scientist for Windows v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT).

RESULTS AND DISCUSSIONS

Hydrolysis of Thiometon and Disulfoton in pH Buffer. Hydrolysis is a major removal process for organophosphorus pesticides in the aqueous system. The hydrolysis of thiometon and disulfoton was investigated in aqueous solution at pH 9.20, 50 mM borate buffer or phosphate buffer, 100 mM NaCl or $NaClO_4$, and 5% methanol at 25 and 50 °C. Because of the relatively low nucleophilicity of perchlorate, comparison experiments were carried out in the pH buffer solution containing $NaClO_4$ rather than NaCl to investigate the influence of chloride ion on the degradation. The influence of chloride ion was explored by comparing the experiments with NaCl and $NaClO_4$. The kinetics data of thiometon hydrolysis display good fit with the pseudo-first-order reaction model. The degradation of thiometon in pH 9.20 in 50 mM sodium tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 and 50 °C is shown in the **Figure 1**. In the experiments, the degradation of thiometon yielded 2-(ethylthio)ethyl disulfide, the dimer of 2-(ethylthio)-ethanethiol (**2**, **Scheme 1**), which forms readily in the presence of oxygen during the extraction. The formation of 2-(ethylthio)-ethyl disulfide accounted for ~70% of the loss of thiometon and resulted from the attack of OH^-/H_2O on the central phosphorus atom (pathway I) and was quantified with the standard prepared in our lab. At the same time, a small amount of 2-(ethylthio)ethanol (**4**, **Scheme 1**) was detected as another degradation product, which was confirmed with a purchased standard. 2-(Ethylthio)ethanol can result from the intramolecular and/or intermolecular nucleophilic attack of OH^-/H_2O at the carbon of 2-(ethylthio)ethyl group (pathway III) and

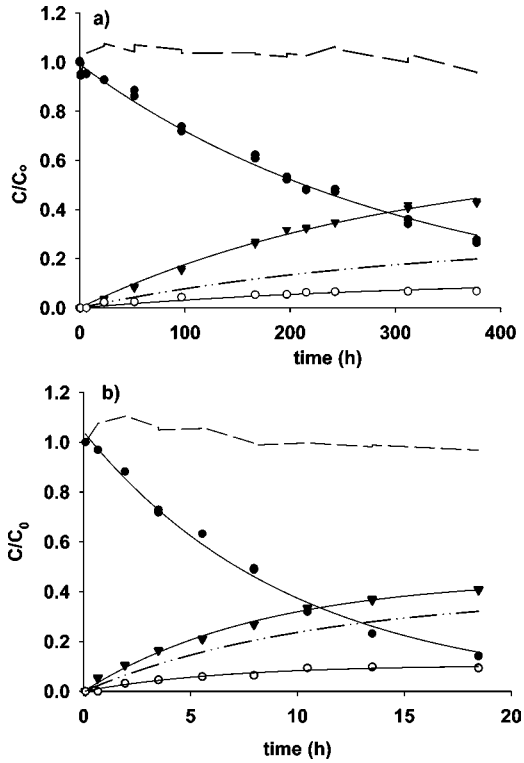


Figure 1. Hydrolysis of thiometon at pH 9.20 (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) (**a**) at 25 °C, indicating the degradation of thiometon (●, $k_h = 0.0032\ h^{-1}$), the formation of 2-(ethylthio)ethanethiol [▼, 2 × 2-(ethylthio)ethyl disulfide, $0.0022\ h^{-1}$], the accelerating effect from Cl^- (– •• – •• –, $0.00092\ h^{-1}$), the formation of 2-(ethylthio)ethanol (○, $0.00037\ h^{-1}$), and the mass balance (- - -) and (**b**) at 50 °C, indicating the degradation of thiometon (●, $k_h = 0.103\ h^{-1}$), the formation of 2-(ethylthio)ethanethiol [▼, 2 × 2-(ethylthio)ethyl disulfide, $0.049\ h^{-1}$], the accelerating effect from Cl^- (– •• – •• –, $0.037\ h^{-1}$), the formation of 2-(ethylthio)ethanol (○, $0.013\ h^{-1}$), and the mass balance (- - -). Solid lines represent model fits to the data assuming exponential decay of thiometon to multiple degradation products simultaneously.

accounted for only ~10% of the loss of thiometon. However, accurate quantification is very difficult for 2-(ethylthio)ethanol due to strong tailing of the peak in the chromatography. The observed rate constant for hydrolysis of thiometon, k_h, was determined to be $0.0032\ h^{-1}$ in pH 9.20, 50 mM sodium tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 °C, while k_h was $0.0022\ h^{-1}$ in the comparing experiment carried out in the buffer solution containing 100 mM $NaClO_4$ instead of NaCl. Although thiometon reacted faster in the presence of Cl^-, no significant increased formation of 2-(ethylthio)ethyl disulfide and 2-(ethylthio)ethanol was observed when compared to the experiment with ClO_4^- (Supporting Information, Figure S-1). The difference of the two rate constants is attributed to Cl^- acting as a nucleophile (accelerating effect), which accounted for ~30% of the loss of thiometon under the chosen conditions. The mass balance in **Figure 1** illustrates that the sum of the three possible contributions accounted for almost 100% of the loss of thiometon, in which the accelerating effect of Cl^- is predicted based on the observed difference of disappearance rate of thiometon in the buffer containing NaCl vs $NaClO_4$. The influence from different buffer salts can be ignored since there is no difference observed between experiments in phosphate buffer vs borate buffer. A relative greater accelerating effect of Cl^- was observed in hydrolysis of thiometon at 50 °C. On the basis of the formation of 2-(ethylthio)ethyl disulfide, the nucleophilic attack at the central phosphorus atom (pathway I) accounted for ~50% of the loss of thiometon at 50 °C. As for thiometon, the relative importance of pathway I is larger at low temperatures than high temperatures. The time course of the degradation of disulfoton in pH 9.20, 50 mM sodium tetraborate buffer, 100 mM NaCl, and 5% methanol at 50 °C is provided in the Supporting Information (Figure S-2). Hydrolysis of disulfoton is much slower than hydrolysis of thiometon. No accelerating effect of Cl^- on the disappearance rate of disulfoton was observed at 25 °C, while a significant accelerating effect was detected at 50 °C. The contributions from each pathway to the observed rate constants in hydrolysis of thiometon and disulfoton are dramatically different. The much smaller formation of 2-(ethylthio)ethyl disulfide in the hydrolysis experiment of disulfoton as compared to the hydrolysis experiment of thiometon suggests that pathway I in disulfoton is not as important as in thiometon. The accelerating effects of Cl^- were greater at higher temperatures than at lower temperatures. The accelerating effect of Cl^- in hydrolysis of disulfoton is more temperature-dependent than in the hydrolysis of thiometon. All of those findings may suggest that the accelerating effect of Cl^- is consistent with a nucleophilic attack of Cl^- at the α-carbon of the alkoxy groups. Such a hypothesis is in agreement with the fact that methyl esters will react faster than corresponding ethyl or other primary alkyl esters in such a reaction (*28*). Our hydrolysis rates of thiometon and disulfoton at 25 °C in phosphate or borate buffer containing $NaClO_4$ are comparable to the calculated rate constants based on the second-order constants at 20 °C and activation parameters reported by Wanner (*14*).

Kinetics of Reaction with HS^-, S_n^{2-}, PhS^-, and $S_2O_3^{2-}$ at 25 °C. The reaction of thiometon with bisulfide was assessed with a pseudo-first-order reaction model. The experiments were conducted in the pH range of 8.90−9.35 and varying concentration of the sulfur nucleophile at 25 °C. The good linearity of the semilogarithmic plot for the decrease of thiometon over two half-lives is indicative of a first-order dependence on the thiometon concentration (**Figure 2a**). No difference in reaction rates and product formation was observed for experiments in phosphate vs borate buffers. Control experiments were conducted in the absence of HS^- to investigate the hydrolysis in the aquatic buffer system. The rate of reaction of thiometon in a bisulfide solution can hence be represented by the following expression:

$$k_{obs} = -\,\mathrm{d[thiometon]}/\mathrm{d}t = k_h + k_{corr} = k_h + k''_{H_2S}[H_2S] + k''_{HS^-}[HS^-] \approx k_h + k''_{HS^-}[HS^-] \quad (1)$$

where k_h is the observed rate constant measured in the control experiment and k_{corr} is the rate constant that is obtained after k_{obs} is corrected for the contribution of k_h. The contribution from H_2S can be neglected due to its much lower reactivity and its small mole fraction in the pH range investigated. Linear regression analysis of log k_{corr} vs log $[HS^-]$ yielded a slope equal to 1.08 (±0.06). The plot of k_{corr} vs $[HS^-]$ (**Figure 2b**) fits a linear model quite well. Linear regression analysis yielded a slope (k''_{HS^-}) equal to 8.4 (±0.5) × $10^{-4}\ M^{-1}\ s^{-1}$ and an intercept not significantly different from zero at the 95% confidence level.

To determine kinetics of the reaction of thiometon with polysulfide, the experiments were conducted at a pH range of 8.85−9.30 and varying concentrations at 25 °C. Experimental solutions contained a substantial concentration of HS^- besides S_n^{2-} species. The influence of HS_n^- can be neglected due to the extremely low concentration in the pH range investigated

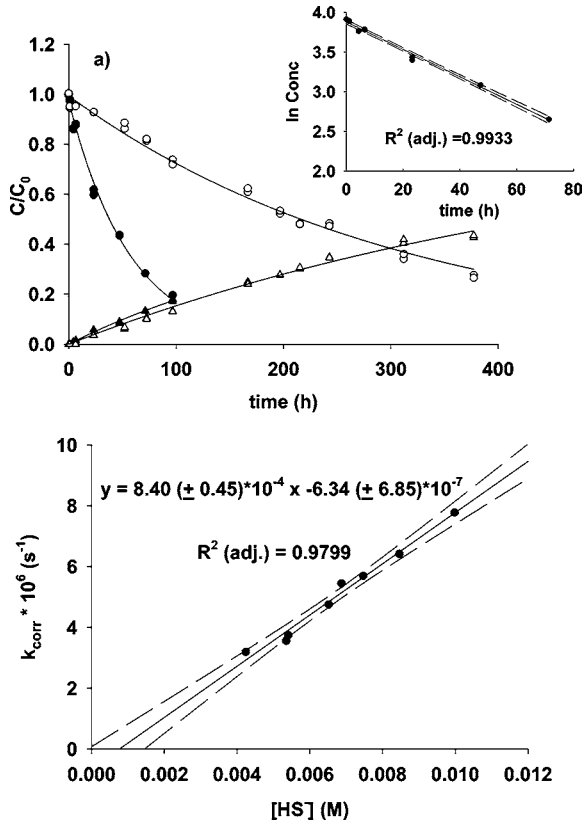


Figure 2. (**a**) Degradation of thiometon at pH 9.20, 5.43 mM $(H_2S)_T$ (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) at 25 °C, indicating the degradation of thiometon (●, $k_{obs} = 0.0175$ h^{-1}) and the formation of 2-(ethylthio)ethanethiol [▼, 2 × 2-(ethylthio)ethyl disulfide, 0.0037 h^{-1}] and hydrolysis of thiometon pH 9.20 (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) at 25 °C, indicating the degradation of thiometon (○, $k_{obs} = 0.0032$ h^{-1}) and the formation of 2-(ethylthio)-ethanethiol [△, 2 × 2-(ethylthio)ethyl disulfide, 0.0022 h^{-1}]. The inset depicts the data plotted in semilogarithmic form to obtain the observed pseudo-first-order reaction rate constants. (**b**) Plot of k_{corr} vs $[HS^-]$ for the reaction of thiometon with biuslfide in 50 mM phosphate or tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 °C. The solid line represents linear regression of the data; the dashed lines represent the 95% confidence interval.

in the study. Hence, the rate of reaction of thiometon in a polysulfide solution can be given by the following expression:

$$k_{obs} = -\,d[\text{thiometon}]/dt \approx k_h + k''_{HS^-}[HS^-] + k_{corr} \approx k_h + k''_{HS^-}[HS^-] + k''_{S_n^{2-}} \sum[S_n^{2-}] \quad (2)$$

Corrections had to be made for the contribution from HS^- in addition to the contribution from hydrolysis in computing the second-order rate constant, $k''_{S_n^{2-}}$. The value of $k''_{S_n^{2-}}$ was determined by conducting linear regression of k_{corr} vs computed $\sum[S_n^{2-}]$, as shown in the Supporting Information (Figure S-3a).

The dependence of the pseudo-first-order rate constants on $[PhS^-]$ and $[S_2O_3^{2-}]$ was determined by conducting experiments at a constant pH of 9.2 and varying the concentration at 25 °C. The contribution from PhSH to k_{obs} can be neglected following the same assumption as for H_2S in the reaction with bisulfide. After correction for hydrolysis, the second-order rate constants can be obtained via the linear regression of k_{corr} vs $[PhS^-]$ (Supporting Information, Figure S-3b). $S_2O_3^{2-}$ is known to be the only dominant species in pH buffer solutions of sodium thiosulfate at the investigated pH 9.2. The linear regression of the observed rate constants corrected for hydrolysis, k_{corr}, vs $[S_2O_3^{2-}]$ would yield $k''_{S_2O_3^{2-}}$ (Supporting Information, Figure S-3c).

The reactions of disulfoton with HS^-, S_n^{2-}, PhS^-, and $S_2O_3^{2-}$ were assessed via the same method. There was no significant acceleration observed in the bisulfide reaction solution containing up to 15 mM HS^- at pH 9.30, which demonstrated that k''_{HS^-} (disulfoton) was too small to be determined exactly at 25 °C. Similarly, $S_2O_3^{2-}$ did not show a significant promotion of the degradation of disulfoton in our experiments, either. The second-order rate constants for disulfoton were obtained via linear regression of k_{corr} vs $[S_n^{2-}]$ and $[PhS^-]$ (Supporting Information, Figure S-4). All of the measured second-order rate constants are summarized in **Table 1**. While HS^- and $S_2O_3^{2-}$ promoted the degradation of thiometon significantly, there is no significant effect of HS^- and $S_2O_3^{2-}$ on the degradation of disulfoton at the concentrations investigated. At the same time, the determined second-order rate constants of S_n^{2-} and PhS^- with disulfoton were much smaller than with thiometon. The measured second-order rate constants for disulfoton were more than 20 times smaller than for thiometon, which is comparable to the larger accelerating effect of Cl^- for thiometon than for disulfoton in the previous discussion. This might suggest that the most important pathway in the reaction of thiometon and disulfoton with reduced sulfur species is the nucleophilic attack at the alkoxy group (pathway II). The large difference in the reactivity of thimeton and disulfoton results from the substituent effect, which is reasonable since the methoxy group is more prone to nucleophilic attack by reduced sulfur species than the ethoxy group. For both thiometon and disulfoton, the reactivity of sulfur species decreased in the following order: $S_n^{2-} > PhS^- > HS^- \approx S_2O_3^{2-}$. The relative order for the reactions of thiometon with three sulfur nucleophiles (S_n^{2-}, PhS^-, and HS^-) tends to parallel that previously reported for S_N2 reactions of methyl bromide (*28*). $S_2O_3^{2-}$ reacts 10 times faster than HS^- with CH_3Br, whereas thiometon reacts faster with HS^- than with $S_2O_3^{2-}$. It is quite likely that steric hindrance is responsible for the lower reactivity of the larger $S_2O_3^{2-}$ nucleophile toward thiometon. The relative reactivity order is comparable to the results for chloroacetanilide herbicides reported by Lippa (*20*) and for chlorpyrifos-methyl reported by Wu (*21*).

Product Analysis. Product identification is a very important tool for the elucidation of reaction mechanisms. In the reaction of thiometon with 5.43 mM $(H_2S)_T$ at pH 9.20 in 50 mM tetraborate buffer containing 5% methanol and 100 mM NaCl at 25 °C, a faster formation of 2-(ethylthio)ethyl disulfide was observed than in the control experiment. The slight increase in the formation of 2-(ethylthio)ethyl disulfide accounts for ~10% of the increase in k_{obs} (**Figure 2a**). This would imply that HS^- attacked partly at the 2-(ethylthio)ethyl group (pathway IIIa). The nucleophilic attack of HS^- at the central P atom would also lead to the formation of 2-(ethylthio)ethyl disulfide. However, it has been reported that such a nucleophilic attack does not occur for structurally related organophosphorus pesticides (*21*). The main reason for the increase in k_{obs} might be the nucleophilic attack of HS^- at the methoxy group (pathway II). This hypothesis is supported by the reactions of thiometon with PhS^-, where thioanisole (**3a**, **Scheme 1**) was detected as a major product. The formation of thioanisole would result from a nucleophilic attack of PhS^- at a methoxy group (pathway II). At the same time, another degradation product, 2-(ethylthio)-ethylthio phenyl sulfide (**5**, **Scheme 1**), was detected in the reactions of thiometon with PhS^-; the EI mass spectrum is shown in **Figure 3**. The formation of 2-(ethylthio)ethyl phenyl

Table 1. Second-Order Rate Constants for Reaction of Thiometon and Disulfoton with Reduced Sulfur Species at 25 °C[a]

	$M^{-1}s^{-1}$			
pesticide	k''_{HS^-}	k''_{PhS^-}	$k''_{S_n^{2-}}$	$k''_{S_2O_3^{2-}}$
thiometon	$8.4\ (\pm0.5)\times10^{-4}$	$2.1\ (\pm0.1)\times10^{-3}$	$6.4\ (\pm0.2)\times10^{-3}$	$7.1\ (\pm0.3)\times10^{-4}$
disulfoton	NA[b]	$8.4\ (\pm0.4)\times10^{-5}$	$1.1\ (\pm0.1)\times10^{-4}$	NA[b]

[a] Stated uncertainties represent the 95% confidence interval. [b] No significant acceleration of the disappearance of disulfoton was observed in the presence of up to 15 mM HS^- or $S_2O_3^{2-}$ at 25 °C.

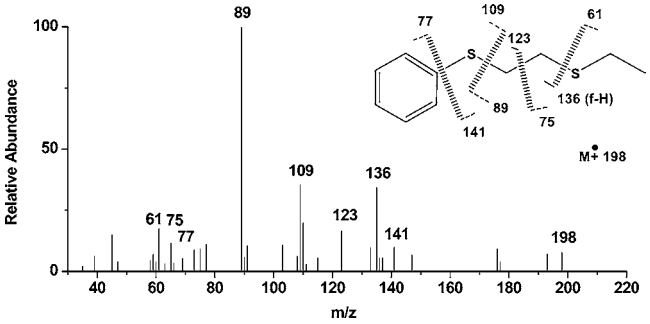


Figure 3. EI mass spectra for product (with retention time of 7.53 min) obtained in reaction of thiometon and disulfoton with thiophenolate. The retention times for thiometon and disulfoton under these conditions were 7.89 and 8.49 min, respectively.

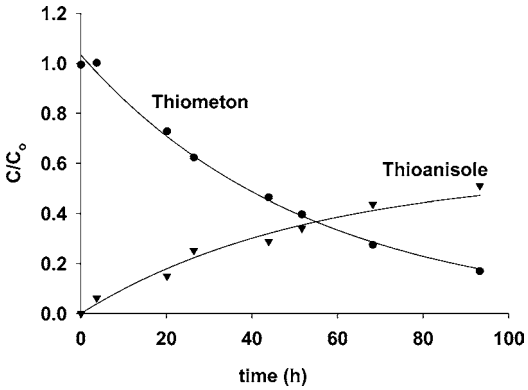


Figure 4. Degradation of thiometon at pH 9.20, 1.82 mM $(PhSH)_T$ (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) at 25 °C, indicating the degradation of thiometon (●, $k_{obs} = 0.0188\ h^{-1}$) and the formation of thioanisole (▼, $0.0109\ h^{-1}$). Solid lines represent model fits to the data assuming exponential decay of thiometon to degradation product thioanisole simultaneously.

sulfide may be attributed to the nucleophilic attack by PhS^- at the 2-(ethylthio)ethyl group (pathway IIIa), which is consistent with the nucleophilic attack by HS^- at the 2-(ethylthio)ethyl group in the reaction with bisulfide. Unfortunately, 2-(ethylthio)-ethyl phenyl sulfide was not quantified due to the lack of a commercial standard. The time course of the reaction of thiometon with 1.82 mM $[PhSH]_T$ in pH 9.20, 50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 °C is shown in **Figure 4**. The rate constants for the loss of thiometon (k_{obs}) and the formation of thioanisole (k_{PhSMe}) were determined by simultaneously fitting the data for thiometon and thioanisole to numerically integrated solutions of the system of governing differential rate expression using Scientist. k_{obs} and k_{PhSMe}were determined to be 0.188 and 0.104 h^{-1}, respectively. The formation of thioanisole therefore accounted for ~60% of the loss of thiometon. Similarly, ethyl phenyl sulfide (**3b**, **Scheme 1**) was detected as a major product in the reaction of disulfoton with PhS^-, which accounted for ~35% of the loss of disulfoton in the reaction of disulfoton with 2.55 mM $(PhSH)_T$ in pH 9.20,

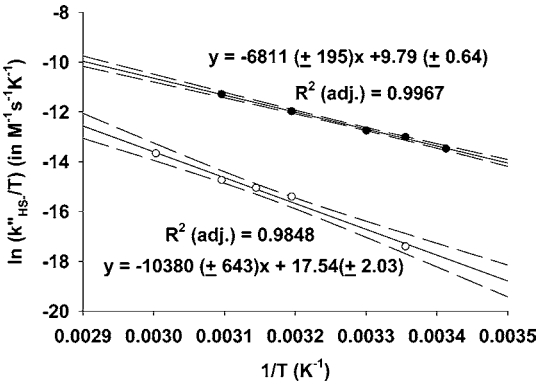


Figure 5. Temperature dependence of reaction of thiometon (●) and disulfoton (○) with bisulfide. The experiments of thiometon were conducted in pH 9.20, 9.63 mM $(H_2S)_T$, 50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol over 20–50 °C. The experiments of disulfoton were conducted in pH 9.20, 10.07 mM $(H_2S)_T$, 50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol over 25–60 °C, except that the reaction at 25.0 °C was carried out in pH 9.20 buffer containing 20.05 mM $(H_2S)_T$. The solid line represents linear regression of the data; the dashed lines represent the 95% confidence interval.

50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 °C (Supporting Information, Figure S-5). It can be concluded that the nucleophilic attack at the alkoxy group (pathway II) is a very important pathway in the reaction of thiometon and disulfoton with reduced sulfur species. This pathway seems to be relatively more important for thiometon than for disulfoton, which agrees well with the much slower reaction of disulfoton with reduced sulfur species than thiometon.

Activation Parameters for Reaction with Bisulfide. Activation energy analysis is very useful in estimating the relative contribution of each pathway when multiple reaction pathways are present. To explore the multiple reaction pathways for enthalpic and entropic effects, the temperature dependence of k_{HS^-} of thiometon was determined in bisulfide solutions (pH 9.20, $[H_2S]_T = 9.63$ mM) over the temperature range of 20.0−50.0 °C. The reaction of disulfoton was investigated in bisulfide solutions (pH 9.20, $[H_2S]_T = 10.07$ mM) from 25.0 to 60.0 °C, except that the reaction at 25.0 °C was carried out in pH 9.20 buffer containing 20.05 mM $(H_2S)_T$. The control experiments in the presence of bisulfide were conducted at these same temperatures. Data for thiometon and disulfoton were plotted as shown in **Figure 5** according to a linearized version of the Eyring equation (*29*):

$$\ln(k''_{HS^-}/T) = \ln(k/h) - \Delta H^{\neq}/RT + \Delta S^{\neq}/R \qquad (3)$$

where k is the Boltzmann's constant, h is the Planck's constant, R is the gas constant, T is the temperature in Kelvin, and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the enthalpic and entropic contributions to the overall activation barrier $\Delta G^{\neq}$, respectively. Linear regression analyses of the data yielded $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Activation parameters are provided in **Table 2**. The much lower $\Delta H^{\neq}$ of

Table 2. Calculated Activation Barriers for Reaction of Thiometon and Disulfoton with Bisulfide[a]

pesticide	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol K)	$\Delta G^{\neq}$ (kJ/mol)[b]	E_a (kJ/mol)
thiometon	56.6 (±1.6)	−116.2 (±5.3)	91.3 (±2.3)	59.1 (±1.6)
disulfoton	86.3 (±5.3)	−51.7 (±16.8)	101.7 (±9.4)	88.8 (±5.3)

[a] Stated uncertainties represent the 95% confidence interval. [b] Calculated at 298.15 K.

thiometon is consistent with the greater reactivity. Although precise experimental measurements of $\Delta S^{\neq}$ are difficult to determine (*30*), such negative $\Delta S^{\neq}$ values suggest a highly ordered transition state. The S_N2 reaction could play a predominant role in the reaction of thiometon and disulfoton with reduced sulfur species. The presence of the two larger ethoxy groups, rather than methoxy groups, would result in a relatively lower ordered transition state in the reaction of disulfoton as compared to thiometon. The smaller steric hindrance for thiometon would make thiometon more suited for nucleophilic attack. The much more negative $\Delta S^{\neq}$ of thiometon partly explains why thiometon is more reactive toward reduced sulfur species relative to disulfoton. An additional attempt to interpret $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be undertaken by looking at the individual contributions of the different pathways. In the reaction with HS^-, the formation rate of 2-(ethylthio)ethanethiol (**2**, **Scheme 1**), k_2, can be assumed to be the sum of the contribution from the nucleophilic attack on the P atom during hydrolysis (pathway I), k_I, and nucleophilic attack of HS^- at the 2-(ethylthio)ethyl group (pathway IIIa), k_{IIIa}. Hence, the contribution from pathway IIIa in the reaction of thiometon with HS^- can be obtained by comparing k_2 in hydrolysis and k_2 in the reaction with HS^-. The results at pH 9.20 over the temperature range of 25−50 °C are listed in the Supporting Information (Table S-1). The percentage of the contribution of pathway IIIa to the nucleophilic attack of HS^- at thiometon (k_{HS^-}) is also included in the Supporting Information (Table S-1). The activation parameters for pathway IIIa in the reaction of thiometon with HS^- can therefore be obtained from the resulting k_{IIIa}. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated to be 82.1 kJ/mol and −49.4 J/mol K (Supporting Information, Figure S-6), which is higher and less negative than $H^{\neq}$ and $\Delta S^{\neq}$ for the overall reaction of thiometon with HS^- reported in **Table 2** (56.6 kJ/mol and −116.2 J/mol K, respectively). Considering the greater importance of the nucleophilic attack at the alkoxy group (pathway II) for thiometon than for disulfoton, the effect of pathway IIIa on the activation parameters of the overall reaction with HS^- would be greater for disulfoton than for thiometon, which would explain why higher $\Delta H^{\neq}$ and less negative $\Delta S^{\neq}$ values were obtained for the reaction of disulfoton with HS^- (86.3 kJ/mol and −51.7 J/mol K). Therefore, the differences of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for thiometon and disulfoton are likely caused by multiple pathways and the different relative importance of each pathway for thiometon and disulfoton.

Conclusions. Our results demonstrate that bisulfide and polysulfides are reactive nucleophiles that could potentially control the environmental fate of thiometon within hypoxic coastal marine environments. Bisulfide is not reactive enough to influence the chemical fate of disulfoton in sulfidic environments while S_n^{2-} showed a little promotion of the transformation of disulfoton. The results demonstrate that polysulfide is the most reactive nucleophile with thiometon and disulfoton among the reduced sulfur species investigated in this study. PhS^- was chosen in this study as a model to investigate the role of aromatic sulfur nucleophiles in degradation of thiometon and disulfoton. Aromatic sulfur nucleophiles can form when natural organic matter reacts with reduced sulfur species (e.g., H_2S and HS^-) (*31*, *32*). Moreover, the investigation of the reaction with PhS^- is very helpful to elucidate the reaction mechanism.

Wanner and co-workers also reported that the half-lives of diffusion of thiometon and disulfoton into the sediment are calculated to be 240 days at 25 °C (*14*). The hydrolysis half-lives of thiometon and disulfoton at pH 7.0 in the absence of sulfur species at 25 °C can be calculated to be 39 and 37 days according to the data reported by Wanner (*14*). On the basis of the measured second-order rate constants listed in **Table 1**, we can predict the persistence of thiometon and disulfoton under environmentally relevant sulfidic conditions. Half-lives for thiometon and disulfoton in marine porewaters containing reduced sulfur species were calculated by multiplying second-order rate constants by the concentrations of HS^- and S_n^{2-} reported for saltmarsh sediment (*5*). The results indicate that the calculated half-life of thiometon at pH 7.0 containing 5.6 mM HS^- and 0.33 mM S_n^{2-} at 25 °C is 28.2 h, which is ∼30 times shorter than only hydrolysis. Under the same conditions, the calculated half-life of disulfoton is 31 days, which was 6 days shorter. In particular, although polysulfide concentration is much lower than bisulfide, the contribution from polysulfide is still important due to its high reactivity. Marine porewaters in sulfate reducing zones may have lower pH values (<7.0) due to the "titration" of carbon dioxide from microbial metabolic processes, in which 3.36 mM $(H_2S)_T$ and pH 6.8 was reported (*33*). Under such circumstances, the half-life of thiometon is predicted to be 90.1 h, while the hydrolysis half-life at pH 6.8 can be calculated to be 40 days at 25 °C. Hence, the reduced sulfur species at environmentally relevant concentration may represent an important sink for thiometon in anoxic coastal marine environments.

Polysulfides are actually applied as a 30% aqueous solution in commercial preparation used for agricultural soil conditioning and for fungal, mite, and insect control (*34*). Elemental sulfur is also added to soil due to its fungicidal qualities as well as its role of an essential nutrient. Under anoxic conditions, this elemental sulfur could undergo dissimilatory reduction by microorganisms to produce polysulfides and bisulfide (*35*). Therefore, abiotic reactions with reduced sulfur species may also represent important reactions in agricultural soils.

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Supporting Information Available: Scheme and procedure for the synthesis of 2-(ethylthio)ethanethiol, time courses of hydrolysis of thiometon at pH 9.20 (50 mM tetraborate buffer, 100 mM $NaClO_4$, and 5% methanol) at 25 and 50 °C, time courses of hydrolysis of disulfoton at pH 9.20 (50 mM tetraborate buffer, 100 mM NaCl or $NaClO_4$, and 5% methanol) at 50 °C, plots of k_{corr} vs $\sum[S_n^{2-}]$, $[PhS^-]$, or $[S_2O_3^{2-}]$ for thiometon and plots of k_{corr} vs $[S_n^{2-}]$ or $[PhS^-]$ for disulfoton to determine the second-order rate constants at 25 °C, time course of degradation of disulfoton at pH 9.20 for 2.55 mM $(PhSH)_T$ (50 mM tetraborate buffer containing 100 mM NaCl and 5% methanol) at 25 °C, table of contribution of pathway IIIa to the nucleophlic attack of HS^- at thiometon at pH 9.20 (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) over 25−50 °C, and temperature dependence of nucleophilic attack of HS^- at 2-(ethylthio)ethyl group (pathway IIIa) in the

reaction of thiometon with HS^- over a temperature range of 25−50 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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