

Nucleophilic Reactions of Phorate and Terbufos with Reduced Sulfur Species under Anoxic Conditions

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The reactions of phorate and terbufos with bisulfide (HS^-), polysulfide (S_n^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and thiophenolate (PhS^-) were examined in well-defined aqueous solution under anoxic conditions to investigate their role in the degradations of phorate and terbufos. Reactions were monitored at various concentrations of reduced sulfur species to obtain the second-order rate constants. The reactivity of the reduced sulfur species decreased in the order $\text{S}_n^{2-} > \text{PhS}^- > \text{HS}^- > \text{S}_2\text{O}_3^{2-}$. Hydrolysis products, formaldehyde and diethyl disulfide/di-*tert*-butyl disulfide, indicated that $\text{OH}^-/\text{H}_2\text{O}$ attacked the carbon atom between the two sulfur atoms, the so-called thioacetal carbon, which is very reactive due to the presence of the two neighboring sulfur atoms. The reaction of phorate and terbufos with PhS^- was investigated to study the transformation products in the reactions with reduced sulfur species. The transformation products demonstrated that the observed increase in rate constants in the reaction with reduced sulfur species compared to hydrolysis could result from the nucleophilic attack of reduced sulfur species at the α -carbon of the ethoxy group and at the thioacetal carbon atom. The temperature dependence of measured second-order rate constants of the reaction of phorate and terbufos with HS^- over 25–50 °C was investigated to explore activation parameters, which are not significantly different for phorate and terbufos. All of the observations may imply similar pathways in the degradation of phorate and terbufos in the presence of reduced sulfur species. Slightly higher hydrolysis rates of terbufos and second-order reaction rate constants for the reactions with sulfur species of terbufos compared with those for phorate are observed, which could be attributed to the slightly different substituents.

KEYWORDS: Phorate; terbufos; nucleophilic substitution; bisulfide; polysulfide; thiophenolate; thiosulfate

INTRODUCTION

Most esters and thioesters of phosphoric and thiophosphoric acids are widely used as pesticides throughout the world for their inhibitory activity toward cholinesterase, a key enzyme that is essential for the proper working of the nervous systems of both humans and insects (1, 2). The organophosphorus pesticides (OPs) have in many cases replaced the organochlorine pesticides (OCPs) that have been, to a large extent, prohibited in the United States since the 1970s due to their persistence in the environment and bioaccumulation along the food chain. OPs often lack selectivity between nontarget organisms and insect pests. OPs become pollutants when they are transported beyond their intended area of influence. A good knowledge of the fate of a pesticide is necessary to properly assess human exposure and environmental impact. OPs are among the most prevalent

pesticides encountered in groundwater and surface waters (3–6), resulting in the occurrence of OPs in sensitive environments such as saltmarshes, estuaries, and associated sediment phases, in which anaerobic conditions are common (7). Abiotic processes need to be considered to understand the fate of organic contaminants under anoxic conditions (8, 9). When oxygen is consumed more rapidly than it can be replenished by mixing processes, microbial sulfate reduction can give rise to locally high concentrations of hydrogen sulfide species (H_2S and HS^-) and polysulfide ions (S_n^{2-}). For example, high concentrations of reduced sulfur species such as 5.6 mM hydrogen sulfide (7), 0.6 mM thiosulfate (10), and 0.33 mM polysulfides (11) in porewater of marine sediments have been reported. Boulegue et al. also reported 3.4 mM HS^- and 0.33 mM S_n^{2-} for the porewater of the Great Salt Marsh in Delaware (12). Reduced sulfur species, potent environmental “reagents”, are capable of reacting with a wide array of pollutants, including many organic contaminants that undergo nucleophilic substitution and reductive dehalogenation processes (13–18).

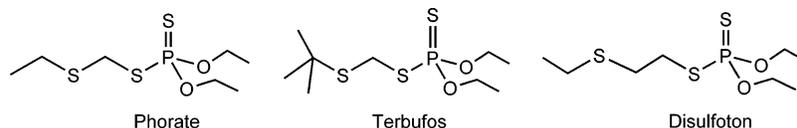
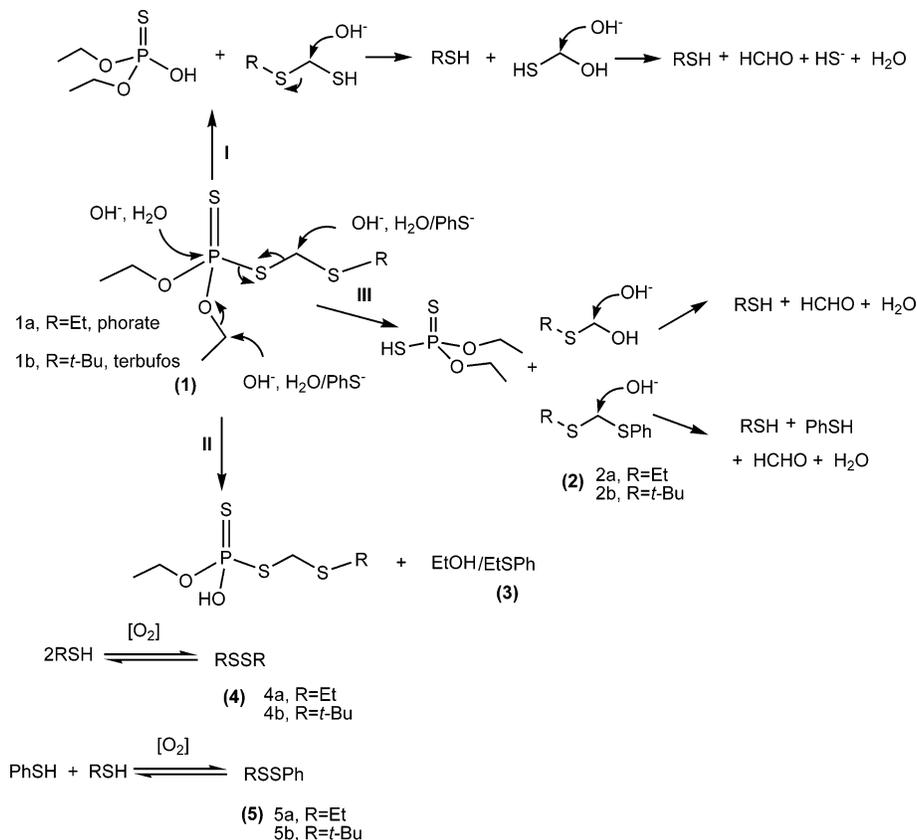
Phorate [*O,O*-diethyl-*S*-[(ethylthio)methyl] phosphorodithioate] and its structural analogue, terbufos [*S*-[(1,1-dimethyleth-

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Chart 1. Structures of Phorate, Terbufos, and Disulfoton

Scheme 1. Proposed Mechanism of Reactions of Phorate and Terbufos (with PhS⁻ as a Surrogate for All Investigated Reduced Sulfur Species)^a

^a I, nucleophilic attack by H₂O/OH⁻ at central P atom; II, nucleophilic attack by reduced sulfur species at α -carbon of ethoxy group; III, nucleophilic attack by H₂O/OH⁻/reduced sulfur species at the thioacetal carbon.

ylthio)methyl]-*O,O*-diethyl phosphorodithioate] (**Chart 1**), are systemic insecticides used against soil pests, sucking pests, and chewing pests. Phorate is used in pine forests and on root crops and field crops, including corn, cotton, coffee, and some ornamental plants and bulbs (19). Terbufos controls wireworms, seedcorn maggots, white grubs, corn rootworm larvae, and other pests (20). In 2001, U.S. annual uses of phorate and terbufos were estimated at 3.2 and 7.5 million pounds, respectively (21, 22). They can be oxidized to the corresponding oxon, sulfoxide, sulfone, etc., via either abiotic or biotic pathways (23–26). Hydrolysis and biodegradation are two primary dissipation processes for phorate and terbufos. Formaldehyde has been observed as a phorate and terbufos degradate in studies in which hydrolysis is a major route of dissipation (27–29). The mechanisms of hydrolysis of the organophosphorus pesticides have been proposed in recent years. It is important to realize that phosphate and thiophosphate esters may react like alkyl halides by nucleophilic displacement (S_N2) both at the central phosphorus atom (with an alcohol moiety being the leaving group) (pathway I, **Scheme 1**) and at the carbon bound to the oxygen of an alcohol moiety (with the diester being the leaving group) (pathway II, **Scheme 1**). The S_N2 mechanism usually dominates with a water molecule and/or hydroxide ion as the nucleophile (30). The instability of any carbon atom possessing two functional groups is well-known. Therefore, it is particularly

noteworthy that a single carbon atom situated between two heteroatoms (e.g., sulfur in the case of phorate and terbufos) in the ester side chain might be a reactive center that is susceptible to nucleophilic attack. The very active carbon between the two sulfur atoms in phorate and terbufos is referred to as the thioacetal carbon throughout this paper. The possible degradation pathways of phorate and terbufos in the aqueous solution containing reduced sulfur species are summarized in **Scheme 1**. Besides the normal hydrolysis pathways for most OPs, the nucleophilic attack of a water molecule and/or hydroxide ion at the thioacetal carbon might be another important mode in the hydrolysis of phorate and terbufos. This attack at that thioacetal carbon might result in much different kinetics compared to the kinetics of the structural cousin, disulfoton (**Chart 1**). The hydrolysis of phorate and terbufos was reported by Pehkonen and co-workers (27–29). The hydrolysis rates, mechanisms, and product analysis were discussed in detail. Their reported hydrolysis rate constants of phorate and terbufos are much faster than the hydrolysis rates of disulfoton reported in our previous study (31). The dominant hydrolysis reaction is the nucleophilic attack of OH⁻/H₂O at the thioacetal carbon. The identified degradation products confirm that the pathways for the hydrolysis of phorate are different from those for the hydrolysis of disulfoton. Formaldehyde and diethyl disulfide or di-*tert*-butyl disulfide were reported as degradation products

in the hydrolysis of phorate and terbufos (**Scheme 1**). In our study, emphasis is given to the influence of reduced sulfur species on the degradation of phorate and terbufos in aqueous solution under anoxic conditions. A comparison with the kinetics and pathways of degradation of disulfoton is also undertaken. The effects of small structural difference (ethyl versus *tert*-butyl) on the kinetics of degradation of phorate and terbufos are also investigated in this study. The higher relative nucleophilicities of reduced sulfur species compared to OH⁻ may result in two possible pathways in the reaction with phorate and terbufos: (i) nucleophilic attack of reduced sulfur species at the thioacetal carbon and (ii) nucleophilic attack at the α -carbon of the ethoxy group (**Scheme 1**).

This study investigates the chemical transformations of phorate and terbufos in simulated natural sulfidic environments. The primary purpose of this study was to more closely examine rates and products of the degradation of phorate and terbufos in sulfidic environments. Kinetic studies, thermodynamic studies, and product identification are three important tools for the elucidation of reaction mechanisms. Reactions were monitored at various concentrations of reduced sulfur species including bisulfide (HS⁻), thiophenolate (PhS⁻), polysulfide (S_n²⁻), and thiosulfate (S₂O₃²⁻) to obtain the second-order reaction rate constants and compare the reactivities of different sulfur species. PhS⁻ was chosen in this study as a model for the role of aromatic sulfur nucleophiles in the degradation of phorate and terbufos. Aromatic sulfur nucleophiles can form when natural organic matter (NOM) reacts with reduced sulfur species (32, 33). Activation parameters were investigated via the temperature dependence of the reaction of phorate and terbufos with bisulfide. This study also represents an experimental investigation of the influence of two different substituents on reactivity and kinetics. Studies of structural analogues can provide invaluable, although indirect and unclear, information regarding the mechanisms through which the pesticides react with reduced sulfur species. The results of this study can be incorporated in fate and assessment models to predict the environmental risk associated with the discharge of phorate and terbufos.

MATERIALS AND METHODS

Chemicals. All chemicals were used as received. Phorate [*O,O*-diethyl-*S*-[(ethylthio)methyl] phosphorodithioate; 96%] and terbufos [*S*-[(1,1-dimethylethylthio)methyl]-*O,O*-diethyl phosphorodithioate; 99.5%] were obtained from Chem Service (West Chester, PA). Ethyl phenyl sulfide was obtained from Avocado Research Chemicals (Heysham, Lancashire, U.K.). *O*-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA·HCl) was obtained from TCI-SU (Tokyo, Japan). All solvents and reagents were of analytical grade or equivalent. Ethyl acetate and methanol were of HPLC grade from Fisher Scientific (Pittsburgh, PA). Hexane (95% *n*-hexane) for pesticide residue analysis was obtained from Mallinckrodt Baker, Inc. (Phillipsburg, NJ). All of the reaction solutions were prepared in an anaerobic glovebox (5% H₂, 95% N₂), 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 Na₂S·9H₂O crystals (sodium sulfide, hydrated, Merck KGaA, Darmstadt, Germany) using deoxygenated deionized water according to the procedure described by Jans and Miah (16). 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 tetrasulfide (Na₂S₄, technical grade, 90+%, H₂O 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 tetraborate buffer with

5% methanol and 100 mM NaCl. The total hydrogen sulfide concentration ([H₂S]_T = [H₂S] + [HS⁻] + [S²⁻]), total thiophenol concentration ([PhSH]_T = [PhSH] + [PhS⁻]), and total S(II) concentration ([S(II)]_T) = [H₂S]_T + [H₂S]_n = [H₂S]_T + [S_n²⁻] + [HS_n⁻] + [H₂S_n], *n* = 2–5), in polysulfide solutions and thiosulfate concentration ([S₂O₃²⁻]) were determined by iodometric titration using a starch endpoint. An Accumet pH-meter (Fisher Scientific, Pittsburgh, PA) with a Ross combination pH electrode (ThermoOrion, Beverly, MA) was used to measure pH in the reduced sulfur reaction solutions. Bisulfide ion concentrations were calculated from [H₂S]_T and measured pH values via ionization constants for H₂S 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 (34). 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 matrices have not been developed. The total concentration of polysulfide dianions ($\Sigma[S_n^{2-}]$) was determined via speciation calculations from the measured [S(II)]_T and pH values on the basis of the reported equilibrium constants (35, 36). The resulting values of $\Sigma[S_n^{2-}]$ were used to compute the second-order rate constants (*k*_{s²⁻}) for the reaction of phorate and terbufos with polysulfide.

Experimental System. All glassware was soaked in 1 M HNO₃ overnight, rinsed several times with 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 solutions were transferred into 20 mL syringes 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 glovebox. The starting concentrations of phorate and terbufos were ~50 and ~25 μM, respectively. The concentrations of (H₂S)_T, (PhSH)_T, [S(II)]_T and S₂O₃²⁻ in the reaction with phorate were 1.6–11.7, 0.4–3.2, 3.5–17.3, and 4.2–6.8 mM, respectively. These concentrations in the reaction with terbufos were 3.6–12.0, 1.5–3.2, 2.9–13.1, and 3.8–7.2 mM, respectively. The reaction solution contained 5% methanol 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 efficiencies of phorate and terbufos were determined to be 90–105%. The resulting extracts were subjected to GC-FID and 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%). A GC-MS system to identify and analyze the degradation products was equipped with a split/splitless injection and 30 m AT-5ms, 0.25 mm i.d. × 0.25 μm fused-silica capillary column (Alltech, Deerfield, IL). Electron ionization (EI) mass spectra were generated using electron energy of 70 eV, monitoring for ions *m/z* 35–500 in full-scan modes. The source temperature employed for the ionization technique was 200 °C. Injector temperature and detector temperature were set at 250 and 275 °C, respectively. The column temperature was held at 100 °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.

Product Derivatization. The possible hydrolysis products in the buffer solutions were qualitatively analyzed by GC-MS. Formaldehyde can be determined via the analysis method for aldehyde and carbonyl compounds with pentafluorobenzylhydroxylamine hydrochloride (PFBHA·HCl) as a derivatizing agent. The method was first described by Yamada and Somiya (37) and later improved by Glaze and co-workers (38). The technique utilizes a direct aqueous derivatization with the reagent PFBHA, which reacts with the carbonyl groups to

form the corresponding oximes. Two geometric isomers are formed [pentafluorobenzoyloxime (*syn*) and pentafluorobenzoyloxime (*anti*)] with most aldehydes except symmetrical carbonyls, for which only one isomer is formed (Scheme S-1). The detailed derivatization procedure is provided in the Supporting Information. The standards of formaldoxime were prepared from formaldehyde standard solutions treated according to the same procedure. More than 90% recovery of formaldehyde in the derivatization method was reported for the detection of concentration of formaldehyde in drinking water (39) and was also observed in our experiments.

Reaction kinetics were determined assuming a pseudo-first-order reaction model, with the initial concentrations of phorate and terbufos being more than 10 times smaller than the concentration of the reduced sulfur species. Degradations were allowed to progress over approximately 2–3 half-lives. Pseudo-first-order rate constants (k_{obs}) were determined by regressing the natural logarithm of pesticide concentrations versus time. For selected experiments, first-order rate constants of the 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 DISCUSSION

Hydrolysis at 25 °C. Hydrolysis of phorate was investigated over a pH range of 7.40–9.30 in 50 mM phosphate or tetraborate buffer containing 100 mM NaCl and 5% methanol at 25 °C. The control experiments of hydrolysis of phorate in pH buffer containing 100 mM NaClO₄ rather than NaCl were carried out to investigate the influence of chloride ion on degradation. The measured hydrolysis rate constants (k_{h}) are listed in Table S-1. No influence of Cl⁻ was observed for phorate and terbufos. After the reaction, the reaction mixture was derivatized with PFBHA·HCl and formaldoxime was detected. The electron ionization spectrum of formaldoxime is available in Figure S-1. On the basis of the >90% recovery of formaldehyde in the derivatization method, the formaldehyde concentration after 3 half-lives was measured to be 42.2 μM in the hydrolysis of phorate at pH 9.0 at 25 °C with [phorate]_{initial} = 50.3 μM. In the pH range of 7.40–9.30, hydrolysis rate constants for phorate lay in the narrow range of (2.66–2.86) × 10⁻⁶ s⁻¹, which indicates no significant pH dependence and that neutral-catalyzed hydrolysis can be assumed to be the dominant pathway in this pH range. In contrast, the hydrolysis rate constant of disulfoton was determined to be 2.0 (±0.05) × 10⁻⁷ s⁻¹ at pH 9.20 and 25 °C in our recent work (31), which is more than 10 times slower than phorate under the same conditions. Diethyl disulfide (4a, Scheme 1), the dimer of ethanethiol, which might be formed during the extraction, was identified in the experiment. Unfortunately, it is problematic to quantify the formation of ethanethiol or diethyl disulfide exactly because diethyl disulfide was not constantly detected in the continuous samples. This might be due to its instability caused by further oxidation of diethyl disulfide. Our measured hydrolysis rate constants at 25 °C were comparable to those reported by Hong and Pehkonen at room temperature (25–28 °C) (27). Their results show that homogeneous hydrolysis rate constants for phorate at pH 5.7 (0.01 M sodium acetate buffer), 8.5, and 9.4 (0.01 M boric acid buffer) are 3.71 (±0.40) × 10⁻⁶, 3.15 (±0.50) × 10⁻⁶, and 3.11 (±0.06) × 10⁻⁶ s⁻¹, respectively, which are only slightly faster than our rate constants. Considering the structural similarity between phorate and disulfoton, it is plausible that, like disulfoton, hydrolysis does not easily happen at an ethoxy group of phorate (pathway II). Moreover, no significant difference in the hydrolysis rate constants for phorate in the buffer containing NaCl

or NaClO₄ was observed at 25–50 °C. The possible accelerating effect of chloride ion observed in studies with related compounds was explained as a nucleophilic attack of chloride ion at the ethoxy group (31). Whereas the chloride ion showed no acceleration of the hydrolysis of disulfoton at 25 °C, there was a small promotion effect observed at 50 °C. The fact that no effect from chloride ion was observed for the hydrolysis of phorate at 25–50 °C could be explained by the much faster hydrolysis of phorate than of disulfoton, which would make the contribution from chloride ion negligible compared to hydrolysis, even at the higher temperature.

The structural difference between phorate and disulfoton, there being only one carbon between the two sulfur atoms on the thioester side chain in phorate, whereas there are two carbon atoms in disulfoton, results in a much higher reactivity of this thioacetal carbon atom in phorate than the two corresponding carbon atoms in disulfoton. Therefore, the faster hydrolysis of phorate can be explained by this structural difference. Unlike the hydrolysis of disulfoton, in which multiple pathways are present, the nucleophilic attack at the thioacetal carbon is the predominant pathway in the hydrolysis of phorate. The hydrolysis of terbufos was also investigated in pH range of 7.65–9.42 at 25 °C. The resulting hydrolysis rate constants are provided in Table S-2. The hydrolysis of terbufos was ~50% faster than the hydrolysis of phorate. The formaldehyde concentration was determined after the reaction to be 20.6 μM after 3 half-lives at pH 9.20 and 25 °C with [terbufos]_{initial} = 24.2 μM. Di-*tert*-butyl disulfide (4b, Scheme 1) was also detected as a product in the hydrolysis of terbufos. The hydrolysis rate constants for terbufos at pH 7.65–9.42 are 4.27 (±0.10) × 10⁻⁶ s⁻¹, which agree well with data reported by Hong et al. (29). As with phorate, we saw no significant influence of pH and no acceleration from Cl⁻. The higher rate constants for terbufos indicate that the *tert*-butylthio is a better leaving group than ethylthio.

Kinetics of Reaction with Reduced Sulfur Species at 25 °C. Good linearity of the semilogarithmic plots for decay of phorate and terbufos in the presence of excess sulfide species over 2–3 half-lives is indicative of a first-order dependence on the pesticide concentration. No influence of phosphate or borate buffer was observed.

The reaction of phorate with bisulfide was investigated in the pH range of 8.50–9.40. The loss of the pesticides was attributed to hydrolysis and reaction with HS⁻. H₂S is weakly reactive, and its concentration is extremely low over the pH range. The reaction order in [HS⁻] was determined by regressing log k_{corr} versus log [HS⁻]

$$\text{rate} = -d[\text{phorate}]/dt = k_{\text{obs}}[\text{phorate}]$$

$$k_{\text{obs}} = k_{\text{h}} + k_{\text{H}_2\text{S}} + k_{\text{HS}^-} \approx k_{\text{h}} + k_{\text{HS}^-}$$

$$k_{\text{corr}} = k_{\text{obs}} - k_{\text{h}} \approx k_{\text{HS}^-} = k_{\text{HS}^-}'' [\text{HS}^-]^a$$

$$\log k_{\text{corr}} = \log k_{\text{HS}^-}'' + a \log [\text{HS}^-] \quad (1)$$

where k_{h} is the observed rate constant measured in hydrolysis experiments at the same pH. The result is $a = 0.87 (\pm 0.06)$ (Figure 1b), which demonstrates that the reaction is roughly first order in [HS⁻]. Therefore, the observed reaction rate in the bisulfide solution can hence be represented as follows:

$$k_{\text{corr}} = k_{\text{obs}} - k_{\text{h}} \approx k_{\text{HS}^-} = k_{\text{HS}^-}'' [\text{HS}^-] \quad (2)$$

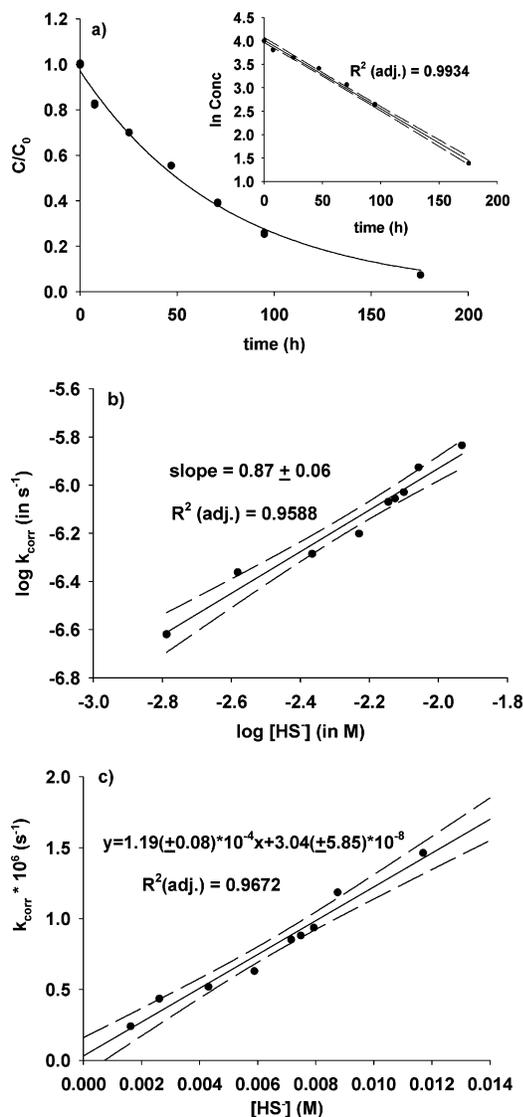


Figure 1. (a) Reaction of phorate ($[\text{phorate}]_{\text{initial}} = 52.2 \mu\text{M}$) with 8.8 mM (H_2S)_T at pH 9.42 (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) at 25 °C. Solid lines represent model fits to the data assuming exponential decay of phorate. (Inset) Data plotted in semilogarithmic form to obtain the observed pseudo-first-order reaction rate constants. (b) Plot of $\log k_{\text{corr}}$ versus $\log [\text{HS}^-]$ for the reaction of phorate with bisulfide in 50 mM phosphate/tetraborate buffer, 100 mM NaCl, and 5% methanol at 25 °C. (c) Plot of corrected reaction rate constants, k_{corr} , versus $[\text{HS}^-]$. Solid line represents linear regression of the data; dashed lines represent 95% confidence interval.

A plot of k_{corr} versus $[\text{HS}^-]$ is linear with $r^2 = 0.97$ and a slope (k_{HS^-}) of $1.2 (\pm 0.1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (**Figure 1c**). The intercept is not significantly different from zero at the 95% confidence level.

The dependence of the pseudo-first-order rate constants on $[\text{PhS}^-]$ was determined by conducting experiments at constant pH 9.2 and varying the concentrations of PhS^- at 25 °C. The kinetics for reaction with thiophenolate were also pseudo-first-order. Linear regression of $\log k_{\text{corr}}$ versus $\log [\text{PhS}^-]$ yielded a slope of $1.00 (\pm 0.03)$, which demonstrated that the reaction is also first order in $[\text{PhS}^-]$. The contribution from PhSH to k_{obs} can be neglected for the same reason as H_2S is neglected in the reaction with bisulfide. A plot of k_{corr} versus $[\text{PhS}^-]$ is linear with $r^2 = 0.98$ and a slope (k'_{PhS^-}) of $1.5 (\pm 0.1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (Figure S-2). For the reactions with thiosulfate, the intercept is also near zero. $\text{S}_2\text{O}_3^{2-}$ is known to be the only

Table 1. Second-Order Rate Constants for Reaction of Phorate and Terbufos with Reduced Sulfide Species at 25 °C^a

pesticide	k'_{HS^-} ($\text{M}^{-1} \text{ s}^{-1}$)	k'_{PhS^-} ($\text{M}^{-1} \text{ s}^{-1}$)	$k'_{\text{S}_2\text{O}_3^{2-}}$ ($\text{M}^{-1} \text{ s}^{-1}$)	$k'_{\text{S}_n^{2-}}$ ($\text{M}^{-1} \text{ s}^{-1}$)
phorate	$1.2 (\pm 0.1) \times 10^{-4}$	$2.5 (\pm 0.1) \times 10^{-4}$	$7.8 (\pm 0.6) \times 10^{-4}$	$9.0 (\pm 0.7) \times 10^{-5}$
terbufos	$1.9 (\pm 0.2) \times 10^{-4}$	$3.2 (\pm 0.3) \times 10^{-4}$	$1.0 (\pm 0.1) \times 10^{-3}$	$1.5 (\pm 0.1) \times 10^{-4}$

^a Stated uncertainties represent the 95% confidence intervals.

dominant species over the pH range of 8.5–9.2. Linear regression analysis of $\log k_{\text{corr}}$ versus $\log [\text{S}_2\text{O}_3^{2-}]$ yielded the slope of $0.93 (\pm 0.08)$. A plot of k_{corr} versus $[\text{S}_2\text{O}_3^{2-}]$ is linear with $r^2 = 0.97$ and a slope ($k_{\text{S}_2\text{O}_3^{2-}}$) of $9.0 (\pm 0.7) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (Figure S-3).

To determine kinetics of the reaction with polysulfide, experiments were conducted over a pH range of 8.85–9.30 and various concentrations of polysulfide at 25 °C. Experimental solutions contained substantial concentrations of HS^- besides polysulfide and hydropolysulfide species. The influence from hydropolysulfides, HS_n^- , was neglected due to the extremely low concentrations in the pH range investigated. Assuming all polysulfide species have the same rate constants, the rate of reaction of phorate in a polysulfide solution can be given by the expression

$$k_{\text{obs}} \approx k_{\text{h}} + k'_{\text{HS}^-} [\text{HS}^-] + k'_{\text{S}_n^{2-}} \sum [\text{S}_n^{2-}]$$

$$k_{\text{corr}} = k_{\text{obs}} - k_{\text{h}} - k'_{\text{HS}^-} [\text{HS}^-] \approx k'_{\text{S}_n^{2-}} \sum [\text{S}_n^{2-}] \quad (3)$$

Linear regression analysis of $\log k_{\text{corr}}$ versus $\log \sum [\text{S}_n^{2-}]$ yielded the slope of $0.98 (\pm 0.08)$. A plot of k_{corr} versus computed $\sum [\text{S}_n^{2-}]$ is linear with $r^2 = 0.96$ and a slope (k'_{PhS^-}) of $7.8 (\pm 0.6) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (Figure S-4). The intercept is near zero at the 95% confidence level, which agrees well with eq 3. The reactions of terbufos with HS^- , PhS^- , $\text{S}_2\text{O}_3^{2-}$, and S_n^{2-} were investigated via the same method. The kinetics of the reactions of terbufos with the sulfur species also fit a pseudo-first-order reaction model, and the reactions are all roughly first order in reduced sulfur species. All measured second-order rate constants are summarized in **Table 1**. Similar to hydrolysis, the degradation of terbufos in pH buffer containing HS^- , PhS^- , $\text{S}_2\text{O}_3^{2-}$, or S_n^{2-} was about 30–70% faster than the degradation of phorate under the same conditions. As the relative reactivity of reduced sulfur species increases, the difference between the susceptibility of phorate and terbufos to nucleophilic attack decreases. The slightly higher reactivity of terbufos is consistent with the more positive electrostatic charge at the thioacetal carbon atom of terbufos than phorate in the ground state computed by Spartan '04 using a B3LYP density functional model with 6-31G*. The difference stems from the presence of the *tert*-butyl group in terbufos rather than the ethyl group in phorate.

Our data indicate that the reduced sulfur species react with phorate and terbufos via a $\text{S}_{\text{N}}2$ mechanism. The Swain–Scott relationship also allows us to evaluate the relative nucleophilicities of these important environmental sulfur nucleophiles (40). The Swain–Scott equation is given as

$$\log \left(\frac{k'_{\text{Nuc}}}{k'_{\text{H}_2\text{O}}} \right) = sn \quad (4)$$

where k'_{Nuc} is the second-order rate constant for the nucleophilic displacement by a nucleophile, $k'_{\text{H}_2\text{O}}$ is the second-order rate constant for nucleophilic attack by water, n is the nucleophilicity of the nucleophile reacting with CH_3Br , and s reflects

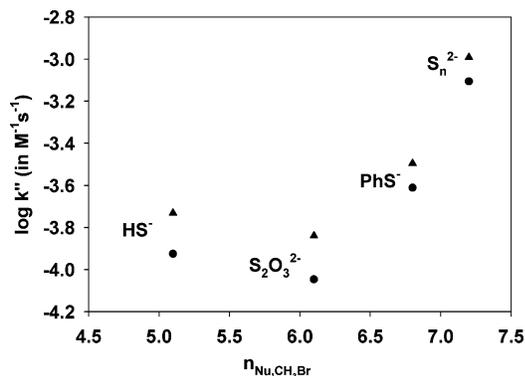


Figure 2. Logarithm of rate constants for reaction of phorate (●) and terbufos (▲) with various reduced sulfur nucleophiles versus $n_{\text{Nu,CH}_3\text{Br}}$.

the sensitivity of substrate to nucleophilic attack ($s = 1$ for $\text{CH}_3\text{-Br}$). Application of the Swain–Scott equation to the rate constants listed in **Table 1** (**Figure 2**) demonstrates that the relative order of k''_{Nuc} values for reaction of phorate and terbufos tends to parallel that previously reported for $\text{S}_{\text{N}}2$ reactions of methyl bromide (41, 42). Observed deviations from linearity are likely caused by steric hindrance, which is responsible for the lower reactivity to phorate and terbufos of the larger thiosulfate and thiophenolate nucleophiles. Similar observations for relative reactivity orders are reported for thiometon in our previous study (31) and were also reported by Lippa and Roberts (13) for the nucleophilic substitution reactions of chloroacetanilide herbicides and by Wu and Jans (43) for chlorpyrifos-methyl. A similar trend of the reaction rate constants of phorate with reduced sulfur species to the reaction rate constants of terbufos with reduced sulfur species would likely suggest similar susceptibilities of phorate and terbufos to the individual reduced sulfur species.

Product Analyses. Product identification is a very important tool for the elucidation of reaction mechanisms. Because the possible transformation products in the reactions of phorate and terbufos with thiophenolate should be readily extracted into an organic solvent and analyzed by GC-MS, the reaction with thiophenolate was chosen as a model to investigate the possible degradation products and the reaction pathways in reactions with reduced sulfur species. As our results show, the reaction of phorate with 3.2 mM $(\text{PhSH})_{\text{T}}$ at pH 9.16 was 30% faster than hydrolysis. The time course of the sample reaction of phorate with 3.2 mM $(\text{PhSH})_{\text{T}}$ at pH 9.16 with $[\text{phorate}]_{\text{initial}} = 52.2 \mu\text{M}$ is shown in **Figure 3**. The concentrations of hydrolysis products were predicted on the basis of the control experiment in pH 9.2 buffer in the absence of sulfur species. After the completion of the reaction, the sample was derivatized with PFBHA·HCl. The concentration of formaldehyde was determined to be $40.2 \mu\text{M}$, which was slightly lower than [formaldehyde] in the hydrolysis control experiment at pH 9.20. Traces of ethyl phenyl sulfide (**3**, **Scheme 1**) were detected as a degradation product during the reaction of phorate and PhS^- , which accounted for <10% of the initial phorate concentration after 2 half-lives. The rate constants for the loss of phorate (k_{obs}) and formation of ethyl phenyl sulfide (k_{PhSEt}) were calculated to be 0.013 and 0.001 h^{-1} , respectively, by simultaneously fitting the data for phorate and ethyl phenyl sulfide to a numerically integrated solution of the system of governing the differential rate expression. The rate constant for the hydrolysis of phorate at pH 9.2 in the control experiment was 0.0098 h^{-1} . The minor formation of ethyl phenyl sulfide was attributed to nucleophilic attack by PhS^- at the ethoxy group, which is similar to observations in the reaction of disulfoton with PhS^- (31).

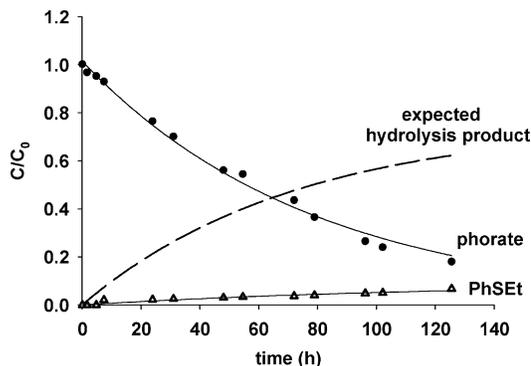


Figure 3. Degradation of phorate ($[\text{phorate}]_{\text{initial}} = 52.2 \mu\text{M}$) at pH 9.16, 3.2 mM $(\text{PhSH})_{\text{T}}$ (50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol) at 25 °C, indicating the degradation of phorate (●, $k_{\text{obs}} = 0.0127 \text{ h}^{-1}$), the formation of ethyl phenyl sulfide (△, 0.001 h^{-1}), and predicted hydrolysis products (—, 0.0099 h^{-1} , assumed to be equal to k_{obs} in hydrolysis experiments). Solid lines represent model fits to the data assuming exponential decay of phorate to degradation product ethyl phenyl sulfide and hydrolysis product simultaneously.

Hydrolysis and nucleophilic attack from PhS^- at the ethoxy group accounted for ~80% of k_{obs} in the degradation of phorate in the presence of 3.2 mM $(\text{PhSH})_{\text{T}}$ at pH 9.16. For the remaining 20% of k_{obs} , there exists the possibility of the nucleophilic attack of PhS^- at the thioacetal carbon. However, the expected product, 2-(ethylthio)methyl phenyl sulfide (**2a**, **Scheme 1**), was not detected, which may be due to the instability at pH 9.2 due to its fast hydrolysis. Ethyl phenyl disulfide (**5a**, **Scheme 1**) was detected in the reaction, which results from the oxidation of PhS^- and EtS^- . The EI mass spectrum is shown in Figure S-5a. Unfortunately, like diethyl disulfide, the concentration of ethyl phenyl disulfide could not be determined exactly because it is unstable in the presence of oxygen. Similar observations were obtained for terbufos. In the reaction of terbufos and PhS^- , the formation of ethyl phenyl sulfide accounted for only <10% of k_{obs} (Figure S-6). The mass balance suggests the presence of other pathways in addition to hydrolysis and the nucleophilic attack of PhS^- at the ethoxy group. *tert*-Butyl phenyl disulfide (**5b**, **Scheme 1**) was detected in the reaction of terbufos and PhS^- (Figure S-5b). The formation of ethyl phenyl disulfide or *tert*-butyl phenyl disulfide in the reaction of phorate and terbufos with PhS^- , along with the formation of diethyl disulfide or di-*tert*-butyl disulfide in the hydrolysis, implies that the thioacetal carbons of phorate and terbufos are very prone to nucleophilic attack from $\text{H}_2\text{O}/\text{OH}^-$ and the reduced sulfur nucleophile due to their high reactivity. The high reactivity of phorate and terbufos might explain the rather low selectivity toward attacking nucleophiles. Although the presence of reduced sulfur species promoted the degradation of phorate, the contributions from the reduced sulfur species (excluding polysulfides) to the degradation of phorate were not as important as in the degradation of thiometon due to fast hydrolysis rate of phorate. The high reactivity of polysulfides relative to bisulfide was discussed in the previous work (31). Because the polysulfides are much more reactive than HS^- , $\text{S}_2\text{O}_3^{2-}$, and PhS^- , the significant increase in the degradation rate was expected and also observed in the degradation of phorate and terbufos in the presence of polysulfides.

Activation Barriers (ΔH^\ddagger and ΔS^\ddagger) for the Reaction with HS^- . Statistically, some differences in the second-order rate constants were observed between phorate and terbufos. The reactivity of terbufos is 60% greater than that of phorate for reaction with HS^- . To explore whether this difference in

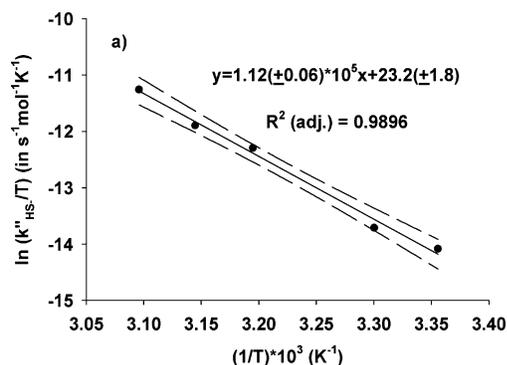


Figure 4. Temperature dependence of the reactions of phorate with bisulfide. The experiments were conducted in pH 9.20, 5.12 mM (H₂S)_T, 50 mM tetraborate buffer, 100 mM NaCl, and 5% methanol over 25–50 °C. Solid line represents linear regression of data; dashed lines represent the 95% confidence level.

Table 2. Calculated Activation Barriers for Hydrolysis and Reaction of Phorate and Terbufos with Bisulfide^a

pesticide	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol·K)	ΔG^\ddagger (kJ/mol)
phorate	92.6 (±4.7)	-4.5 (±15.2)	94.0 (±4.6)
terbufos	92.5 (±6.0)	-5.2 (±19.3)	94.1 (±5.9)

^a Stated uncertainties represent the 95% confidence intervals. ^b Calculated at 298.15 K.

reactivity results from enthalpic or entropic effects, the temperature dependence of k''_{HS^-} was explored in buffered solutions (pH 9.20) over the temperature range of 25–50 °C. Control experiments at pH 9.20 in the absence of bisulfide were also carried out over a comparable time period over the same temperature range. Data for phorate and terbufos were plotted as shown in **Figure 4** according to a linearized version of the Eyring equation (44)

$$\ln(k''_{\text{HS}^-}/T) = \ln(k/h) - \Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad (5)$$

where k is Boltzmann's constant, h is Planck's constant, R is the gas constant, T is the temperature in Kelvin, and ΔH^\ddagger and ΔS^\ddagger are the enthalpic and entropic contributions to the overall activation barrier ΔG^\ddagger , respectively. Linear regression analysis of the data yielded ΔH^\ddagger and ΔS^\ddagger , as summarized in **Table 2**. Thermodynamic studies can be useful in estimating the relative contributions of each pathway when multiple reaction pathways are present. Although a difference was detected between k''_{HS^-} for phorate and terbufos, there is no significant difference in the activation parameters, which is not surprising considering their similar structures. This tends to support that similar reaction pathways are present and that the relative significance of the individual pathways is similar. Activation entropy reflects the loss or gain of degrees of freedom between the starting compounds and the transition states. Because multiple pathways may simultaneously contribute to the reactions of phorate and terbufos with bisulfide, the magnitude and the sign of ΔS^\ddagger can be used to evaluate the relative significance of the individual pathways. According to our recent investigation of the nucleophilic reaction of chlorpyrifos and parathion with bisulfide, in which nucleophilic attack of sulfur species at the α -carbon of ethoxy group is the only pathway, the ΔH^\ddagger and ΔS^\ddagger attributed to the nucleophilic attack of bisulfide at the ethoxy group were measured to be 81.0 (±4.5) kJ/mol and -59.1 (±14.0) J/mol·K for chlorpyrifos and 79.8 (±7.4) kJ/mol and -62.4 (±23.3) J/mol·K for parathion, respectively (18); these are much different

from the measured ΔH^\ddagger and ΔS^\ddagger for the reaction of phorate and terbufos with bisulfide. This could be explained by multiple pathways rather than the sole pathway in the reaction of phorate and terbufos with bisulfide. Next to the nucleophilic attack at ethoxy group, nucleophilic substitution occurring at the thioacetal carbon (pathway III) might be much more important in the reaction with bisulfide, which might lead to the less negative ΔS^\ddagger value.

Conclusions. Our results show that the presence of the reduced sulfur species accelerates the loss of phorate and terbufos from the aquatic environment. Understanding of chemical fate in sulfidic environment is important not only for hypoxic coastal marine environments in which the reduced sulfur species are present at high concentrations but also for agricultural soil. Phorate and terbufos are moderately persistent in the soil and bind to the soil organic matter and clay particles. Polysulfides are actually applied as a 30% aqueous solution in commercial preparations used for agricultural soil conditioning and for fungal, mite, and insect control (45). Elemental sulfur is also added to soil due to its fungicidal qualities as well as its role as an essential nutrient. Under anoxic conditions, this elemental sulfur could undergo dissimilatory reduction by microorganisms to produce polysulfides and bisulfide (46). Therefore, abiotic reactions with reduced sulfur species may also represent important reactions in agricultural soils.

Considering the hydrolysis rates of phorate and terbufos, the half-lives of phorate and terbufos at pH 7.0 in the absence of sulfur species at 25 °C can be calculated to be 70 and 45 h, respectively. On the basis of the measured second-order rate constants listed in **Table 1**, we can predict the persistence of phorate and terbufos under environmentally relevant sulfidic conditions. Half-lives for phorate and terbufos in marine porewaters containing reduced sulfur species were calculated by multiplying second-order rate constants by maximum concentrations of [HS⁻] and $\Sigma[S_n^{2-}]$ reported by MacCrehan (7). The results indicate that the calculated half-lives of phorate and terbufos at pH 7.0, 5.6 mM HS⁻, and 0.33 mM S_n^{2-} at 25 °C are 52 and 34 h, respectively, which are ~30% shorter than those through only hydrolysis. In particular, although the polysulfide concentration is much lower than that of bisulfide, the contribution from polysulfide is still important due to its high reactivity. Hence, our results demonstrate that reduced sulfur species at environmentally relevant concentration may influence the chemical fate of phorate and terbufos in coastal marine environments.

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Supporting Information Available: Hydrolysis rate constants of phorate and terbufos at 25 °C, scheme and procedure for derivatization of formaldehyde with PFBHA, EI mass spectrum of the derivatized sample of hydrolysis of phorate, plots of log k_{corr} versus log([PhS⁻], [S₂O₃²⁻] or $\Sigma[S_n^{2-}]$) and plots of k_{corr} versus [PhS⁻], [S₂O₃²⁻] or $\Sigma[S_n^{2-}]$ for phorate to determine the second-order rate constants at 25 °C, EI mass spectrum of the products obtained in the reaction of phorate and terbufos with PhS⁻ and time course of degradation of terbufos at pH 9.26, 3.6 mM (PhSH)_T (50 mM tetraborate buffer containing 100 mM NaCl, and 5% methanol) at 25 °C, temperature dependence of the reactions of terbufos with bisulfide in pH 9.20, 5.12 mM (H₂S)_T, 50 mM tetraborate buffer, 100 mM NaCl

and 5% methanol over 25 – 50 °C are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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