

Surface-Catalyzed Transformations of Aqueous Endosulfan

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We report the effect of suspended solids on the oxidation and hydrolysis of the insecticide endosulfan (α and β isomers) and its degradation products: endosulfan diol, endosulfan sulfate, endosulfan ether, and endosulfan lactone in 0.001 M NaHCO₃ buffer (pH 8.15). Suspensions of sea sand, TiO₂, α -Fe₂O₃, α -FeOOH, Laponite, and SiO₂ all catalyzed the hydrolysis of endosulfan to the less toxic endosulfan diol. Suspended creek sediment (Bread and Butter Creek SC, 4% OC) inhibited endosulfan hydrolysis. Heterogeneous and homogeneous rate constants of endosulfan hydrolysis were measured and indicate that β -endosulfan hydrolyzes faster than α -endosulfan. This observation was explained by a more stable transition state for β -endosulfan that was confirmed with *ab initio* molecular orbital calculations (STO-6G) on the anionic intermediates of endosulfan hydrolysis. Rates of endosulfan hydrolysis over the different surfaces corresponded to their tritium-exchange site-density and suggest a mechanism involving surface coordination prior to nucleophilic attack. The oxidation of α -endosulfan and β -endosulfan to the persistent pollutant endosulfan sulfate was not observed in this study.

Introduction

Endosulfan [6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzof[dioxathiepin-3-oxide] (ES) is a cyclodiene insecticide that is applied as a mixture of isomers, α -endosulfan (α -ES) and β -endosulfan (β -ES), with similar insecticidal properties (1–3) but different physicochemical properties (4–11). Nonpoint source runoff of ES has been linked to fish kills (12–14) and decreased secondary productivity (15, 16) in several southeastern U.S. watersheds (12, 13, 16–25). Laboratory and field studies indicate that ES is volatile (Henry's law constants (HLC) at 25 °C: α -ES, 2.74×10^{-4} ; β -ES, 2.53×10^{-5}) (4, 9), has a high affinity for soils, sediments, and biota (log K_{ow} : α -ES, 3.6; β -ES, 3.83) (5, 32), and is readily dissipated in the water column. In the environment, the cyclic sulfite group of ES can be hydrolyzed to form a less toxic diol (ES diol) (1) or oxidized to the corresponding sulfate (ES sulfate) (16, 21, 23, 26–30). ES sulfate, α -ES, and β -ES are generally considered to be equally toxic and are all classified by the U.S. Environmental Protection Agency as priority pollutants (31). ES sulfate is less volatile than ES (32), is not readily hydrolyzed (33), and has a comparable affinity for soils, sediments, and biota (log K_{ow} : 3.66) (32).

Studies on the fate of ES in low moisture environments such as soils (30, 34–40) and on crops (1, 26, 41, 42) indicate that the oxidative pathway dominates. Studies on the fate of

ES in high moisture soils (34, 35), sterile aqueous systems (4, 5, 27, 32, 43), and nonsterile aqueous systems (4, 5, 7, 44–48) indicate that hydrolysis dominates and suggest that formation of ES sulfate is due to biological oxidation.

The ability of solids to catalyze the oxidation of aqueous micropollutants is well documented (49–56), suggesting that there could be surface-mediated thermal or photochemical reactions that contribute toward the formation of ES sulfate (57). Furthermore, there are reports that surfaces affect the hydrolysis rates of not only endosulfan (44, 45) but of many other hydrolyzable esters (58–67). In this paper, we report the relative contributions of homogeneous and surface-catalyzed processes toward the thermal oxidation and hydrolysis of aqueous α -ES and β -ES.

The loss of α -ES, β -ES, ES sulfate, and ES diol, endosulfan ether (ES ether), and endosulfan lactone (ES lactone) were profiled in batch experiments conducted with or without sea sand, TiO₂, α -Fe₂O₃, α -FeOOH, Laponite, SiO₂, and creek sediment suspensions in 0.001 M NaHCO₃ buffer at 28 °C, pH 8.15. The selection of these materials as potential catalytic surfaces is justified by their documented occurrence and activity in the environment (49–56, 58–70).

Experimental Section

Materials. Barnstead E-pure water (18 M Ω -cm) was used for all solutions and suspensions. Inorganic reagents were analytical grade (Fisher Scientific) unless otherwise noted. OmniSolv GC² grade methyl *tert*-butyl ether (MTBE) was purchased from EM Science (Darmstadt, GR). The internal calibration standard, 4-bromoanisole (99+%), was used as received from Aldrich. All stock solutions were prepared in analytical grade isopropyl alcohol (Mallinckrodt) and stored at 4 °C.

Technical grade ES was obtained from Hoechst Schering AgrEvo (Frankfurt, GR). ES diol, ES sulfate, ES lactone, and ES ether standards were purchased from Riedel-de-Haën (Seelze, GR). Endosulfan α -hydroxy ether (ES hydroxyether) was prepared according to the method described by Feichtinger (71).

Laponite RD, a smectite clay, was donated by Southern Clay Products, INC (Gonzales, TX). The composition of the Laponite as supplied by the producer: SiO₂, 55.6%; MgO, 25.1%; Na₂O, 3.6%; Li₂O, 0.7%; K₂O, 0.2%; TiO₂, 0.15%; Al₂O₃, 0.08%; CaO, 0.06%; Fe₂O₃, 0.04%. SiO₂, 60 Å/230–400 Mesh ASTM, was purchased from Whatman Paper Ltd. (Clifton, NJ). Goethite, α -FeOOH (99+%), was purchased from Alfa Aesar. TiO₂ (P-25; ca. 80% anatase, 20% rutile; APS 30 nm) was kindly supplied by Degussa-Hüls (Frankfurt, GR). The Laponite, α -FeOOH, TiO₂, and SiO₂ in the study were used as received. Hematite, α -Fe₂O₃, was prepared as described by Faust and co-workers (72). Transmission electron microscopy (TEM) revealed hexagonal, rhombic, and spherical particles with median diameters of 31.5 ± 18.6 nm.

Washed sea sand was obtained from Fisher Scientific and was prepared using the method of Miller and Zepp (73). Approximately 10 g of sea sand was vigorously stirred with a Pyrex stir bar in a 1 L Erlenmeyer flask containing 200 mL of water for 20 h. The resulting aqueous suspension was allowed to stand for 24 h, decanted from the settled granules, filtered with a 10–20 μ m glass frit, and dried at 225 °C for 2 h. The retained material was ground into fine grains with mortar and pestle.

Creek sediment (top 1 cm) from Bread and Butter Creek, SC was donated by Dr. G. Thomas Chandler, Department of Environmental Health Science, University of South Carolina.

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The sediment was 63 μm presieved, washed in deionized water, autoclaved, and reconstituted. Median grain diameter = 38–42 μm , organic carbon (OC) by C:H:N analysis = 3.8–4.1% (16). The creek sediment was dried at 85 °C for 24 h and ground into fine grains with mortar and pestle.

Specific surface areas (S , m^2/g) were determined by the BET method (74) on a Coulter SA 3100 surface area analyzer. The surface areas were (triplicate measurements) as follows: TiO_2 , $50.2 \pm 0.3 \text{ m}^2/\text{g}^{-1}$; $\alpha\text{-FeOOH}$, $84.5 \pm 0.6 \text{ m}^2/\text{g}^{-1}$; $\alpha\text{-Fe}_2\text{O}_3$, $46.2 \pm 0.5 \text{ m}^2/\text{g}^{-1}$; SiO_2 , $453.0 \pm 0.4 \text{ m}^2/\text{g}^{-1}$; Laponite, $386.6 \pm 0.7 \text{ m}^2/\text{g}^{-1}$; tidal creek sediment, $31.42 \pm 0.8 \text{ m}^2/\text{g}^{-1}$; ground beach sand, $28.5 \pm 0.5 \text{ m}^2/\text{g}^{-1}$.

Separation of α -ES and β -ES. Technical grade ES was separated into its α and β isomers via column chromatography utilizing a 2:8 acetone/hexane mobile phase and a SiO_2 , 60 Å/230–400 Mesh ASTM stationary phase. Isomeric identification was achieved by comparing relative thin-layer chromatographic R_f values (75) and melting points (1) of the isomeric fractions against those previously assigned to the α and β isomers. The α (mp = 108–110 °C) and β (mp = 209–213 °C) isomers were recrystallized in 2:8 acetone/hexane and stored at 4 °C. The purities of the isomeric fractions were determined to be >99.99% via GC-ECD.

Experimental Procedure. Batch reactions were conducted in a modified 140-mL Pyrex hydrogenation vessel (Ace glass # 7482-41) (Supporting Information, Figure 1) in the dark. Solids were suspended with vigorous stirring by a Teflon-coated stir bar in 80 mL of a 0.001 M NaHCO_3 buffer at 28 °C. Suspensions equilibrated for 180 min prior to substrate addition. pH was maintained at 8.15 by the dropwise addition of either 0.1 M HCl or 0.1 M NaOH and was monitored (Orion 410A) over the course of the experiment.

After equilibration, 10 μL of 1000 ng/ μL 2-propanolic stocks of the substrate was added to the suspension to afford initial ES concentrations (ca. 3×10^{-7} M) below published water solubilities (α -ES, 9.1×10^{-6} M; β -ES, 5.2×10^{-5} M) (4). 2-Propanol was employed as a carrier solvent to ensure that no ES hydrolysis had occurred prior to substrate addition.

Samples (1.5 mL) were removed from the reactor through an airtight Teflon sampling port with a spring-loaded 4-mL Manostat syringe. Samples were immediately placed in Fisherbrand 20-mL amber EPA vials that had been precharged with 1.5 mL of MTBE + internal standard (4-bromoanisole). Other investigators have reported difficulty extracting ES diol and ES hydroxyether from aqueous solution; accordingly the polar solvent, MTBE, was used as the extracting solvent (76–81). MTBE extractable analytes were removed from the samples by rapidly mixing for 2 min on a vortex Genie mixer followed by 20 min of sonication (Branson 2510). Emulsions were broken by the addition of ≈ 100 mg NaCl. The MTBE layer was transferred by Pasteur pipet to 9 mm amber crimp-top GC vials. The vials were stored at 4 °C until quantitative analysis with a GC-ECD (HP 5890 II). At the conclusion of each experiment, the remaining suspension was extracted with 2×50 mL of MTBE, concentrated to ≈ 2 mL, and qualitatively analyzed with a GC/ITMS (Varian Saturn 2000). Products were verified by matching retention times (GC-ECD and GC-ITMS) and mass spectra (GC-ITMS) against those of purchased or synthesized standards. The retention times, R_T , of the endosulfan analytes are presented in the Supporting Information (Supporting Information, Table 1). Mass spectra of all analytes are shown in the Supporting Information (Supporting Information, Figures 6–12).

Initial concentrations were measured (quadruplicate) via analogous introduction into 80 mL of MTBE + internal standard (4-bromoanisole). Samples (1.5 mL) were removed, placed in Fisherbrand 20 mL amber EPA vials, and processed as described above.

Solar Simulation. Duplicate experiments were performed under illumination at 340 nm, using an Osram (HBO 103 W/2) 100 W Hg short arc lamp with a Photon Technology International (New Brunswick, NJ) A-1010B lamp housing, 220B power supply, and a 101 grating monochromator. Slits were set at 0.6 mm with a ± 2.4 nm band-pass. The average incident light intensity ($I_{\text{av}} = 2.4 \times 10^{-6}$ eins/min) was measured by ferrioxalate actinometry as described by Taylor (82). The light source was allowed to stabilize for a least 30 min prior to use.

Batch Adsorption Studies. Solution-solid ES adsorption studies were performed using a batch equilibrium procedure. Aqueous controls and 3.125 g/L stock suspensions of TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, and SiO_2 were equilibrated as described above, however, the pH was maintained at 7. After equilibration, 8 mL of the stock suspensions were added to Fisherbrand 9-mL amber EPA vials. 2-Propanolic α -ES and β -ES were then introduced to give initial ES concentrations ranging from 4×10^{-7} M to 2×10^{-9} M ($n = 6$). After the vials were placed on a Labquake shaker for 24 h, they were centrifuged for 1 h at 5000 rpm. Supernatant samples (1.5 mL) were removed, processed, and analyzed for ES.

Gas Chromatography–Electron Capture Detector. Quantitative analysis was accomplished with a Hewlett-Packard (Palo Alto, CA) 5890 series II gas chromatograph equipped with a ^{63}Ni electron-capture detector (GC-ECD) utilizing nitrogen as the makeup gas (1.5 mL/min). Data were processed with a Shimadzu integrator.

After careful evaluation of several GC-ECD methods for ES metabolites, we found the method of Tanaka et al. (83), allowed for the quantitative detection of ES diol and ES hydroxyether without derivatization. Helium was used as a carrier gas (1.3 mL/min). Splitless injections of 1 μL were made at an injector port temperature of 200 °C, the detector temperature was maintained at 300 °C. The oven program was as follows: isothermal at 150 °C for 2 min, followed by heating from 150 °C to 290 °C at 10 °C/min, then held isothermally at 290 °C for 30 min. The analytical column was a J&W DB-1 column ($L = 30$ m, $\text{ID} = 0.53$ mm, $\text{df} = 1.5$ μm). Method detection limits for all analytes were as follows: α -ES, 1.3×10^{-11} M; β -ES, 7.3×10^{-12} M; ES sulfate, 1.0×10^{-12} M; ES diol, 7.2×10^{-10} M; ES ether, 4.3×10^{-12} M; ES lactone, 2.5×10^{-12} M; ES hydroxyether, 6.4×10^{-10} M.

Gas Chromatography–Mass Spectrometry. Qualitative analysis was achieved with a Varian 3800 gas chromatograph equipped with a Varian Saturn 2000 ion trap mass spectrometer (GC-ITMS) in electron impact (EI) ionization mode (70 eV). Full scan spectra were acquired over the ranges m/z 40–650 at 0.85 s per scan. Holox (Charlotte, NC) high purity helium was used as a carrier gas (1.4 mL/min). Splitless injections of 1 μL were made at an injector port temperature of 200 °C. The temperature program was as follows: isothermal at 90 °C for 1 min, followed by heating from 90 °C to 180 °C at 25 °C/min, then heating from 180 °C to 270 °C at 5 °C/min, and finally isothermal at 270 °C for 4 min. The analytical column was a J&W DB-5MS column ($L = 30$ m, $\text{ID} = 0.25$ mm, $\text{df} = 0.25$ μm).

Treatment of Error. The standard deviation associated with triplicate injections was used to assess error in all concentration measurements. The standard error of the mean (SEM) from quadruplicate experiments was used for all kinetic and adsorption analyses.

Extraction efficiencies (quadruplicate) from fortified aqueous solutions and suspensions were measured and are reported as average values: α -ES, $97.4 \pm 0.23\%$; β -ES, $98.8 \pm 0.32\%$; ES sulfate, $96.5 \pm 0.33\%$; ES diol, $84.2 \pm 0.47\%$; ES lactone, $96.3 \pm 0.19\%$; ES hydroxyether, $82.4 \pm 0.45\%$; ES ether, $97.2 \pm 0.34\%$.

Gas partitioning and adsorption onto reactor walls (vide supra) were treated as internally consistent sources of error

TABLE 1. Product Distribution in Relative Percentages of β -ES Loss at 300 min in 3.125 g/L Aqueous Suspensions: 0.001 M NaHCO₃ Buffer, pH 8.15, 28 °C

solid	% β -ES loss	% ES diol	% ES hydroxy ether	% ES ether	% α -ES	% ES sulfate
Laponite	73.91 $\pm$ 2.2	78.53 $\pm$ 2.4	1.87 $\pm$ 0.06	0.74 $\pm$ 0.06	1.36 $\pm$ 0.06	ND
SiO ₂	72.33 $\pm$ 3.4	78.97 $\pm$ 2.6	1.90 $\pm$ 0.10	0.78 $\pm$ 0.08	1.23 $\pm$ 0.07	-
sea sand	65.94 $\pm$ 3.4	79.68 $\pm$ 2.8	1.79 $\pm$ 0.07	0.71 $\pm$ 0.12	1.38 $\pm$ 0.08	-
α -FeOOH	65.90 $\pm$ 1.9	81.22 $\pm$ 2.6	1.84 $\pm$ 0.07	0.84 $\pm$ 0.07	1.27 $\pm$ 0.06	-
TiO ₂	62.78 $\pm$ 2.5	82.61 $\pm$ 2.0	1.94 $\pm$ 0.08	0.82 $\pm$ 0.07	1.34 $\pm$ 0.06	-
α -Fe ₂ O ₃	63.52 $\pm$ 3.2	77.87 $\pm$ 3.0	1.82 $\pm$ 0.09	0.79 $\pm$ 0.06	1.29 $\pm$ 0.09	-
homogeneous (index)	50.20 $\pm$ 3.5	79.01 $\pm$ 3.1	1.61 $\pm$ 0.06	0.55 $\pm$ 0.08	1.18 $\pm$ 0.07	-
sediment	11.19 $\pm$ 1.4	81.34 $\pm$ 2.2	2.05 $\pm$ 0.05	0.88 $\pm$ 0.04	1.24 $\pm$ 0.05	-

TABLE 2. Product Distribution in Relative Percentages of α -ES Loss at 300 min in 3.125 g/L Aqueous Suspensions: 0.001 M NaHCO₃ Buffer, pH 8.15, 28 °C

solid	% α -ES loss	% ES diol	% ES hydroxy ether	% ES ether	% ES sulfate
Laponite	59.31 $\pm$ 3.7	80.83 $\pm$ 1.5	1.91 $\pm$ 0.08	0.88 $\pm$ 0.05	ND
SiO ₂	55.56 $\pm$ 2.6	78.95 $\pm$ 3.1	1.86 $\pm$ 0.10	0.90 $\pm$ 0.04	-
α -Fe ₂ O ₃	54.58 $\pm$ 3.1	78.19 $\pm$ 2.7	1.89 $\pm$ 0.11	0.76 $\pm$ 0.07	-
α -FeOOH	54.54 $\pm$ 2.5	78.17 $\pm$ 2.5	1.82 $\pm$ 0.09	0.86 $\pm$ 0.06	-
TiO ₂	52.20 $\pm$ 3.3	82.81 $\pm$ 2.2	1.85 $\pm$ 0.03	0.82 $\pm$ 0.09	-
sea sand	49.35 $\pm$ 2.4	81.42 $\pm$ 2.4	2.02 $\pm$ 0.12	0.77 $\pm$ 0.08	-
homogeneous (index)	42.40 $\pm$ 2.7	80.16 $\pm$ 2.5	1.58 $\pm$ 0.08	0.62 $\pm$ 0.08	-
sediment	17.44 $\pm$ 2.9	79.49 $\pm$ 2.0	2.05 $\pm$ 0.10	0.93 $\pm$ 0.04	-

(with respect to the experimental design) in the quantification of α -ES and β -ES loss. Even so, based on published HLCs, we estimate that less than 0.05% total ES could have volatilized into the reactor headspace.

Results and Discussion

Loss of α -ES, β -ES, ES Sulfate, ES Diol, ES Lactone, and ES Ether in Aqueous Solution. The loss of α -ES, β -ES, ES sulfate, ES diol, ES lactone, and ES ether in 0.001 M NaHCO₃ buffer at 28 °C, pH 8.15 was measured in aqueous solution for 300 min. This data was used as a comparative data set to index the effects of suspended solids against.

Over that time scale, the hydrolytic formation of ES diol accounted for approximately 80% of α -ES and β -ES loss; no oxidative to ES sulfate was detected. ES diol (80.16%), ES hydroxyether (1.58%), and ES ether (0.62%) accounted for the 42.40% loss of α -ES at $t = 300$ min (82.36% mass balance). The loss of β -ES (50.20% at $t = 300$ min) provided a similar mass balance and product distribution; however, β -ES also isomerized to generate low yields of α -ES (1.18%).

ES sulfate was stable under our conditions through 300 min. The stability of ES sulfate in our experiments is in agreement with work by Reviejo (33) who observed no hydrolysis of ES sulfate over 80 min at 20 °C, pH 9.

The formation of ES hydroxyether and ES ether accounted for 50.51% and 4.93%, respectively, of the 9.92% ES diol loss at $t = 300$ min (65.36% mass balance). These data strongly suggest that the formation of ES hydroxyether and ES ether proceeds only after an initial hydrolysis of ES to ES diol.

ES hydroxyether was the only identified product of ES ether in 0.001 M NaHCO₃ buffer at 28 °C, pH 8.15. At $t = 300$ min, ES hydroxyether accounted for only 3.42% of the 15.28% loss of ES ether.

ES hydroxyether and ES ether were detected at trace levels, combining for 0.2% of the 98.4% loss of ES lactone at $t = 300$ min. No attempt was made to quantify other products; however, the rapid alkaline hydrolysis of five-membered lactones to their corresponding γ -hydroxy acids is well established in bicyclo[2.2.1] systems (84, 85). Readjusting the pH of the experimental solution to ~ 1 after the conclusion of the experiment resulted in the qualitative reappearance of ES lactone, which supports the hypothesis of endosulfan γ -hydroxy acid formation.

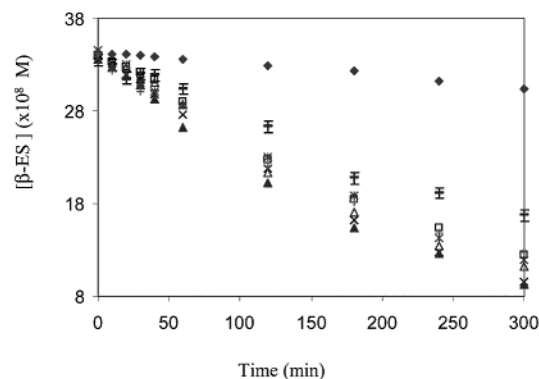


FIGURE 1. All the suspended solids (3.125 g/L) examined in this study affect the loss of β -ES in 0.001 M NaHCO₃ buffer at 28 °C, pH 8.15: α -Fe₂O₃ ($\square$), α -FeOOH ($\triangle$), SiO₂ ($\times$), tidal creek sediment ($\blacklozenge$), Laponite ($\blacktriangle$), TiO₂ ($+$), sea sand ($*$), and homogeneous solution ($-$).

Loss of α -ES, β -ES, ES Sulfate, ES Diol, ES Lactone, and ES Ether in Aqueous Suspensions. The loss of α -ES, β -ES, ES sulfate, ES diol, ES lactone, and ES ether in aqueous solution was contrasted against their loss in 3.125 g/L suspensions. Figure 1 shows the loss of β -ES through time in suspensions of sea sand, TiO₂, α -Fe₂O₃, α -FeOOH, Laponite, SiO₂, and creek sediment. Although aqueous suspensions did affect the rate of ES loss, product distributions were only slightly (<1%) affected. Table 1(α -ES) and Table 2 (β -ES) detail the product distributions in relative percentages (as a function of ES loss) at 300 min. Figure 2 shows β -ES loss and byproduct formation in a suspension of a commonly occurring material, sea sand, and its profile is typical of ES loss in solution and 3.125 g/L suspensions (Supporting Information, Figures 9–24).

ES sulfate was stable in suspensions of TiO₂, α -FeOOH, and creek sediment but did exhibit some hydrolysis ($\approx 1\%$) over SiO₂ (4.7% loss), Laponite (3.7% loss), and sea sand (2.2% loss). In aqueous suspensions, ES hydroxyether and ES ether accounted for $\approx 50\%$ and $\approx 5\%$, respectively, of the $\approx 16\%$ ES diol loss at $t = 300$ min. Although the mechanism of ES diol loss is not understood, these data indicate that suspensions affected ES diol loss without affecting its mass balance or product distribution (relative to aqueous solution). Tidal creek

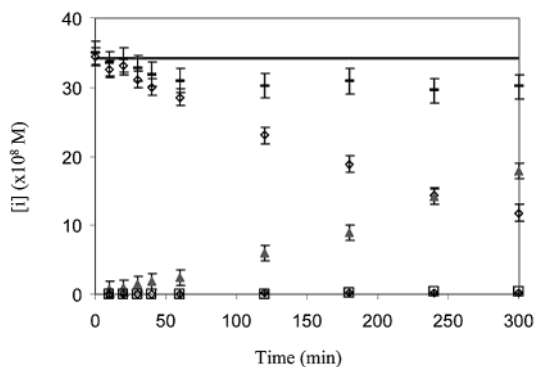


FIGURE 2. Loss of β -ES ($\blacklozenge$) in 0.001 M NaHCO_3 buffer at 28 $^\circ\text{C}$, pH 8.15, and 3.125 g/L of sea sand: ES diol ($\blacktriangle$), ES hydroxy ether ($\square$), ES ether ($+$), α -ES ($\diamond$), and mass balance ($-$).

sediment slowed ($<2\%$) the loss of ES ether and ES lactone; all other suspensions had no effect on ES ether and ES lactone loss. The losses of ES sulfate, ES diol, ES ether, and ES lactone in solution and 3.125 g/L aqueous suspensions are profiled in Supporting Information (Supporting Information, Figures 25–30).

The isomerization of β -ES to α -ES was commensurate with the overall loss of β -ES and is of particular interest. It has been demonstrated by Rice and co-workers (9, 10) that the conversion of β -ES to α -ES occurs readily at the air–water interface (α -ES to β -ES is not energetically favorable). Our data suggest that the isomeric conversion from β -ES to α -ES also occurs at the solid–water interface.

Collectively, these results indicate that the effect of suspended solids on ES loss is primarily due to the catalysis or suppression of ES hydrolysis. Figure 3 is a schematic illustration of the chemical transformations of α -ES and β -ES in aqueous solution and suspensions as indicated by this study.

Batch Adsorption Studies. The adsorption of ES onto solids (and reactor walls) was evaluated at pH 7, where ES hydrolysis is known to be very slow ($t_{1/2} \alpha = 151$ d, $t_{1/2} \beta = 88$ d) (27). In aqueous solution, we observed small losses of ES ($<3\%$) due to adsorption onto reactor walls. The experimental data for adsorption onto surfaces was fitted by the logarithmic Freundlich isotherm; constant relative

TABLE 3. Freundlich Isotherm Parameters for the Adsorption of ES on Solids (3.125 g/L) in 0.001 M NaHCO_3 Buffer at 28 $^\circ\text{C}$, pH 7

solid	adsorbate	$\log K_f \text{ (fmol m}^{-2}\text{)(nM/L)}^{-N}$	N
α -FeOOH	β	3.54 ± 0.24	0.99 ± 0.03
	α	2.83 ± 0.19	0.97 ± 0.04
α -Fe $_2$ O $_3$	β	3.77 ± 0.22	0.97 ± 0.04
	α	3.17 ± 0.14	0.96 ± 0.06
SiO $_2$	β	2.62 ± 0.33	1.02 ± 0.03
	α	1.87 ± 0.25	0.98 ± 0.05
TiO $_2$	β	3.54 ± 0.18	0.98 ± 0.05
	α	2.58 ± 0.22	1.03 ± 0.04

error was assumed (86–88).

$$\log q = \log K_f + N \log C \quad (1)$$

K_f is the Freundlich constant, N is a measure of both the relative magnitude and diversity of energies associated with a particular adsorption process (88, 90), q is the moles of adsorbate per unit surface area of sorbent (fmol m^{-2}) (87, 88), and C is the aqueous solute concentration at equilibrium (nM). A plot of $\log q$ versus $\log C$ has a slope of N and an intercept of $\log K_f \text{ ((fmol m}^{-2}\text{)(nM)}^{-N})$ (Supporting Information, Figures 37–40). Table 3 summarizes the batch adsorption data. An examination of $\log K_{f-\beta}$ versus $\log K_{f-\alpha}$ reveals that β -ES is preferentially adsorbed over α -ES on all surfaces studied. We have interpreted these observations to be a result of steric hindrance. A solvent-accessible surface area model (MM2) of ES confirms that access to the sulfonyl bond in α -ES is limited relative to β -ES. It is interesting to note that $N \approx 1$ (within a 95% confidence interval); this is consistent with other reports that used low concentrations of hydrophobic solutes and/or low sorbent loadings (91).

Kinetics. All experiments were performed in 0.001 M NaHCO_3 buffer (pH 8.15) at 28 $^\circ\text{C}$ with $[\text{ES}]_0 \approx 3 \times 10^{-7}$ M. Under these conditions (i.e. $[\text{OH}^-] \approx 10[\text{ES}]_0$) the fate of ES is dominated by specific base-catalyzed hydrolysis (1, 7, 27, 92–94) and is expressed by the differential rate equation

$$-d[\text{ES}]_{\text{aq}}/dt = k_{\text{HOM}}[\text{ES}]_{\text{aq}} \quad (2)$$

where the homogeneous rate constant of hydrolysis, k_{HOM}

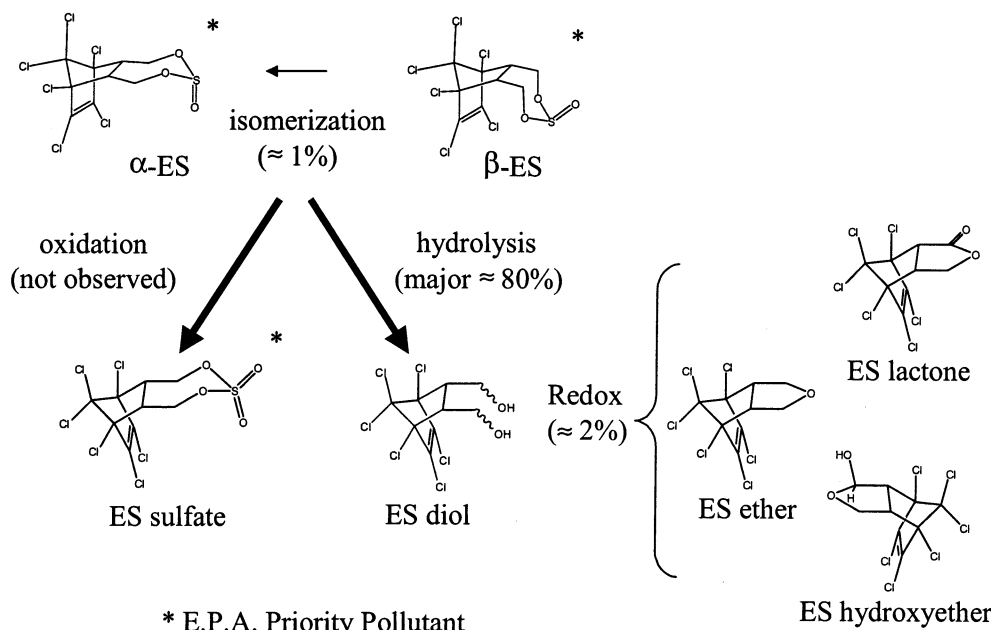


FIGURE 3. Proposed fates of α -ES and β -ES in aqueous solution and in 3.125 g/L aqueous suspensions: 0.001 M NaHCO_3 , 28 $^\circ\text{C}$, pH 8.15.

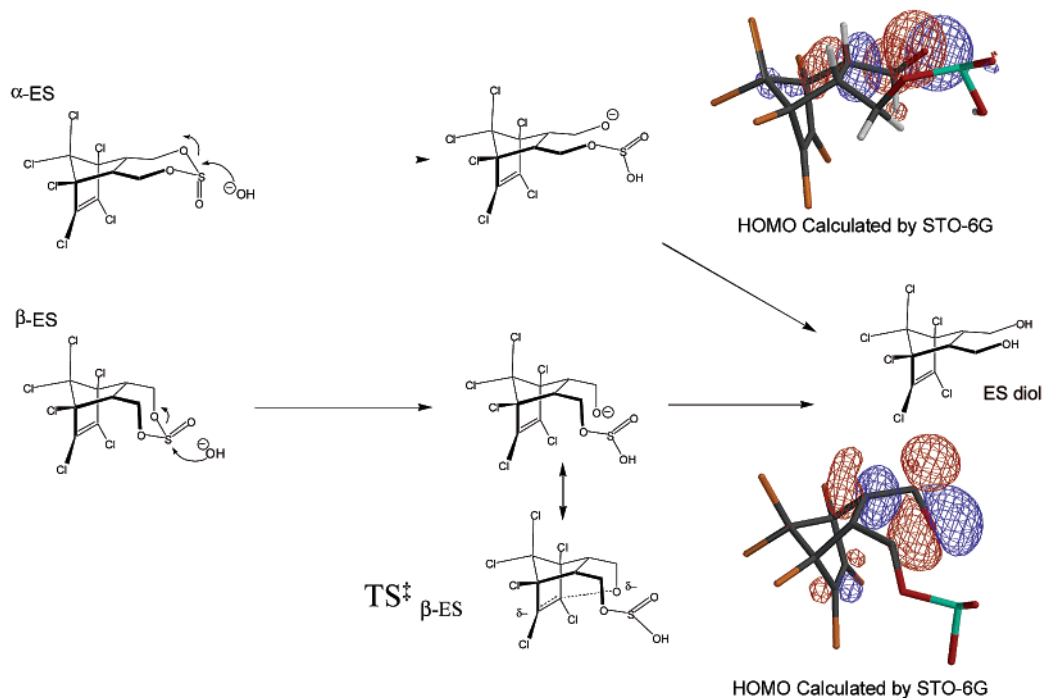


FIGURE 4. Anionic intermediates of specific base-catalyzed ES hydrolysis modeled with MacSpartan ab initio MO calculations (STO-6G).

TABLE 4. Homogeneous Rate Constants (k_{HOM}) of α -ES and β -ES Hydrolysis in 0.001 M NaHCO_3 Buffer, pH 8.15, 28 °C

	k_{HOM} (s^{-1})	$t_{1/2}$ (days)	r^2
α -ES	$(3.23 \pm 0.07) \times 10^{-5}$	0.24	0.992
β -ES	$(4.01 \pm 0.06) \times 10^{-5}$	0.20	0.982

(s^{-1}), is defined as (95, 96):

$$k_{\text{HOM}} = k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{HCO}_3^-}[\text{HCO}_3^-] \cong k_{\text{OH}^-}[\text{OH}^-] \quad (3)$$

Plots of $\ln([\alpha\text{-ES}]_t/[\alpha\text{-ES}]_0)$ and $\ln([\beta\text{-ES}]_t/[\beta\text{-ES}]_0)$ versus time were linear, indicating ES hydrolyses displayed pseudo-first-order kinetics in aqueous solution. k_{HOM} (s^{-1}), was the negative of the slope obtained by a linear least-squares analysis of the data and is presented for α -ES and β -ES in Table 4.

MacSpartan ab initio MO calculations (STO-6G) were used to model the intermediates of specific base-catalyzed ES hydrolysis. α -ES and β -ES were modeled as symmetric molecules (6). Figure 4 illustrates how, during attack by a hydroxide nucleophile, the intermediate of β -ES is stabilized relative to α -ES via neighboring-group participation (97). The proximity of the carbon-carbon π bond to the anion in β -ES allows for a delocalization of the negative charge as seen by calculations on the HOMO of the anionic intermediates of both α -ES and β -ES. The HOMO of β -ES shows electron density (partial negative charge) on the further carbon of the double bond, suggesting that the corresponding transition state ($\text{TS}^+_{\beta\text{-ES}}$) will have similar stabilization due to charge delocalization. The calculated HOMO of α -ES shows no stabilization of the anion by the double bond and justifies the slower hydrolysis of α -ES relative to β -ES.

In aqueous suspensions, the contribution of solids toward surface-catalyzed ES hydrolysis was a function of surface area (S , m^2/g) and loading (a , g/L) and is represented by the heterogeneous rate constant of hydrolysis, k_{HET} ($\text{L m}^{-2}\text{s}^{-1}$) (58). The overall rate constant, k_{OBS} (s^{-1}), is expressed by the

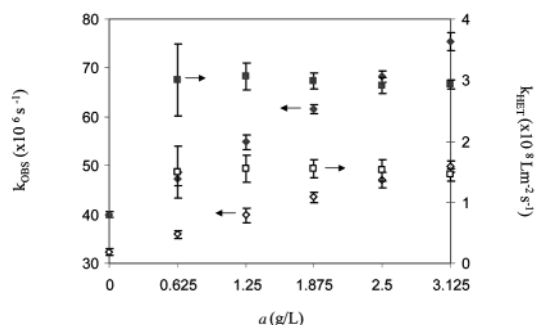


FIGURE 5. k_{OBS} and k_{HET} of α -ES and β -ES hydrolysis versus Laponite loading (a , g/L) in 0.001 M NaHCO_3 buffer at 28 °C, pH 8.15: $k_{\text{OBS-}\beta}$ ($\blacklozenge$), $k_{\text{OBS-}\alpha}$ ($\diamond$), $k_{\text{HET-}\beta}$ ($\blacksquare$), and $k_{\text{HET-}\alpha}$ ($\square$).

differential rate equation:

$$-d[\text{ES}]_{\text{aq}}/dt = k_{\text{OBS}}[\text{ES}]_{\text{aq}} = k_{\text{HOM}}[\text{ES}]_{\text{aq}} + aSk_{\text{HET}}[\text{ES}]_{\text{aq}} = (k_{\text{HOM}} + aSk_{\text{HET}})[\text{ES}]_{\text{aq}} \quad (4)$$

Plots of $\ln([\alpha\text{-ES}]_t/[\alpha\text{-ES}]_0)$ and $\ln([\beta\text{-ES}]_t/[\beta\text{-ES}]_0)$ versus time were linear for all experiments conducted in aqueous suspensions; k_{OBS} (s^{-1}) is the negative of the slope obtained by a linear least-squares analysis of the data. k_{HET} ($\text{L m}^{-2}\text{s}^{-1}$) was obtained from the following expression (58):

$$k_{\text{HET}} = (k_{\text{OBS}} - k_{\text{HOM}})/aS \quad (5)$$

k_{HET} ($\text{L m}^{-2}\text{s}^{-1}$) was determined for sea sand, TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, Laponite, and SiO_2 over a range of solid loadings (0.625–3.215 g/L). As the solid loading (a) of Laponite was changed the contribution of k_{HET} remained constant with respect toward k_{OBS} of α -ES and β -ES loss (Figure 5). Illustrations of this relationship for sea sand, TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, and SiO_2 are presented in the Supporting Information (Supporting Information, Figures 31–35). Table 5 lists k_{HET} for each solid as the grand mean $\pm$ estimated standard error based on pooling values obtained at each loading (98).

TABLE 5. Heterogeneous Rate Constants (k_{HET}) of α -ES and β -ES Hydrolysis in 0.001 M NaHCO_3 Buffer, pH 8.15, 28 °C

surface/S (m^2/g)	$k_{\text{HET}-\beta}$ ($\text{L m}^{-2} \text{s}^{-1}$)	$k_{\text{HET}-\alpha}$ ($\text{L m}^{-2} \text{s}^{-1}$)
Laponite/386.55	$(2.98 \pm 0.54) \times 10^{-8}$	$(1.51 \pm 0.26) \times 10^{-8}$
SiO_2 /453.16	$(2.13 \pm 0.43) \times 10^{-8}$	$(1.14 \pm 0.25) \times 10^{-8}$
α - Fe_2O_3 /46.18	$(1.29 \pm 0.21) \times 10^{-7}$	$(8.66 \pm 0.97) \times 10^{-8}$
α - FeOOH /84.56	$(8.05 \pm 0.99) \times 10^{-8}$	$(5.15 \pm 0.92) \times 10^{-8}$
TiO_2 /50.2	$(1.04 \pm 0.20) \times 10^{-7}$	$(6.73 \pm 1.02) \times 10^{-8}$
sea sand/37.48	$(1.69 \pm 0.24) \times 10^{-7}$	$(9.67 \pm 0.89) \times 10^{-8}$

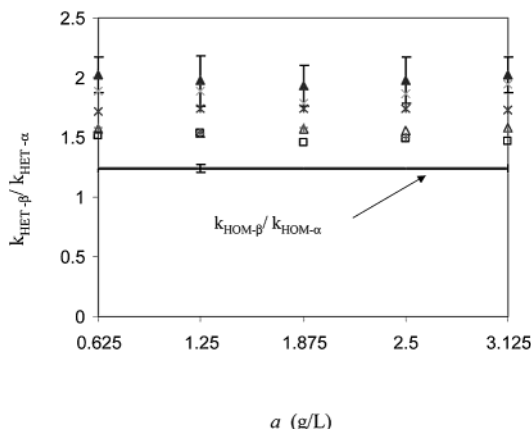


FIGURE 6. Ratios of $k_{\text{HET}-\beta}/k_{\text{HET}-\alpha}$ versus solid loading (a , g/L) in 0.001 M NaHCO_3 buffer at 28 °C, pH 8.15: α - Fe_2O_3 ($\square$), α - FeOOH ($\triangle$), SiO_2 ($\times$), Laponite ($\blacktriangle$), TiO_2 ($+$), and sea sand ($*$).

In this work, we observed an increase in the ratio of $k_{\text{OBS}-\beta}/k_{\text{OBS}-\alpha}$ as sea sand, TiO_2 , α - Fe_2O_3 , α - FeOOH , Laponite, and SiO_2 loading was increased ($k_{\text{HOM}-\beta}/k_{\text{HOM}-\alpha} = k_{\text{OBS}-\beta}/k_{\text{OBS}-\alpha}$ when $a = 0$) (Supporting Information, Figure 36). Furthermore, the ratio of $k_{\text{HET}-\beta}/k_{\text{HET}-\alpha}$ is increased relative to the ratio of $k_{\text{HOM}-\beta}/k_{\text{HOM}-\alpha}$ over the range of sea sand, TiO_2 , α - Fe_2O_3 , α - FeOOH , Laponite, and SiO_2 loading (Figure 6). These observations indicate that surface-catalyzed ES hydrolysis is not due to elevated hydroxide concentration at the outer Helmholtz plane and are consistent with reports that mechanisms of surface-catalyzed (metal oxide) hydrolyses differ from those in solution (58, 61, 63, 65, 99). Metal oxide surfaces could coordinate the sulfuryl group of ES facilitating nucleophilic attack. Additionally, metal oxide surface species in the vicinity of ES could serve as attacking nucleophiles.

The pH of zero surface charge (pH_{ZPC}) has been experimentally determined for TiO_2 , α - Fe_2O_3 , α - FeOOH , SiO_2 , and Laponite (100, 101). Under our experimental conditions (pH 8.15), the pH_{ZPC} of a metal oxide should vary inversely with the quantity of nucleophilic surface species. In this study, $k_{\text{HET}-\alpha}$ and $k_{\text{HET}-\beta}$ do not vary inversely with the respective pH_{ZPC} values. These results suggest that nucleophilic surface species may not significantly contribute to the surface-catalyzed hydrolysis of aqueous ES.

The tritium-exchange method for determining surface site-densities has been used to measure the metal oxides used in this study. Site-densities obtained by this method (100, 102–107) have been compiled by Sahai and Sverjensky (100) for α - Fe_2O_3 (22 sites· nm^{-2}), α - FeOOH (16.5 sites· nm^{-2}), TiO_2 (12.5 sites· nm^{-2}), and SiO_2 (4.6 sites· nm^{-2}). We observed that experimentally obtained values of k_{HET} ($\text{L m}^{-2} \text{s}^{-1}$) for TiO_2 , α - Fe_2O_3 , α - FeOOH , and SiO_2 correlate well (α -ES, $R^2 = 0.8229$; β -ES, $R^2 = 0.8127$) against the tritium-exchange site-density, N_s (sites· nm^{-2}) for these materials (Figure 7). Site-density measurements are known to be highly variable and are very technique dependent, yet this observation is compelling and suggests that surface coordination of ES

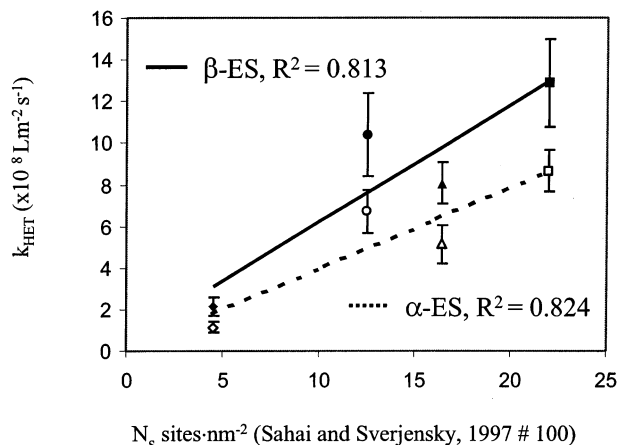


FIGURE 7. k_{HET} of ES hydrolysis (α -ES, open; β -ES, filled) versus site density, N_s (sites· nm^{-2}), in 0.001 M NaHCO_3 buffer at 28 °C, pH 8.15: α - Fe_2O_3 ($\square$, $\blacksquare$), α - FeOOH ($\triangle$, $\blacktriangle$), SiO_2 ($\diamond$, $\blacklozenge$), and TiO_2 ($\circ$, $\bullet$).

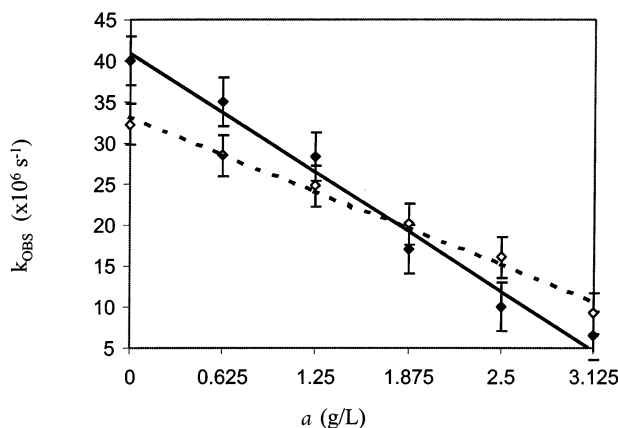


FIGURE 8. k_{OBS} (s^{-1}) of α -ES ($\diamond$) and β -ES ($\blacklozenge$) versus creek sediment (4% OC) loading (a , g/L) in 0.001 M NaHCO_3 buffer at 28 °C, pH 8.15.

occurs prior to nucleophilic attack. This mechanism is also supported by the previous observations that β -ES has a higher affinity for surfaces than α -ES and hydrolyzes more rapidly over the surfaces used in this study.

The rate of ES hydrolysis was generically slowed over natural sediment relative to the other surfaces studied (vide supra), presumably, due to the partitioning of endosulfan into nonpolar OC associated with sediment (5, 108–110). This observation and explanation are consistent with the seminal work of Macalady and Wolfe from 1985 (96), who reported that the partitioning of organophosphorothioate esters into the OC of sediment suppressed base-catalyzed hydrolysis. Further support for this hypothesis comes from the change in k_{OBS} for α -ES and β -ES loss as a function of sediment loading (Figure 8). As the sediment load increases, k_{OBS} decreases for α -ES and β -ES with a slope of -7.1 ($\text{L s}^{-1} \text{g}^{-1}$) and -11.6 ($\text{L s}^{-1} \text{g}^{-1}$), respectively. This is consistent with earlier observations that β -ES partitions more strongly into sediment than α -ES (5, 38, 108).

It was found that illumination ($\lambda_{\text{ex}} = 340 \text{ nm}$) had no statistically significant effect on ES degradation kinetics or product distributions compared to duplicate experiments performed in the dark. These results suggest that under environmental conditions, direct and indirect photolysis may have little effect on the fate of aqueous endosulfan (at least in the presence of HCO_3^-).

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Supporting Information Available

Table of GC-ECD and GC-ITMS retention times, R_T , of endosulfan analytes and mass spectra of all analytes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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