

# Supporting Information

## Nucleophilic Substitution of Phosphorothionate Ester Pesticides with Bisulfide ( $\text{HS}^-$ ) and Polysulfides ( $\text{S}_n^{2-}$ )

By Tong Wu, Qiu Gan, Urs Jans\*

(Total 13 pages, 6 figures, tables 1)

Table S-1. Calculated Sulfur Speciation at Four Different pH Values-----S2

Figure S-1. Example time courses for reactions of OPs with  $\text{HS}^-$  at 25 °C and three different pHs-----S3

Figure S-2. Plot of apparent second-order reaction rate constants,  $k'_{\text{app}}/[\text{H}_2\text{S}]_{\text{T}}$  ( $\text{M}^{-1}\text{h}^{-1}$ ), versus  $\alpha_{\text{HS}^-}$  for reactions of hydrogen sulfide/bisulfide with five OPs-----S5

Figure S-3. Temperature dependence of reactions of OPs with  $\text{HS}^-$ -----S7

Figure S-4. HPLC chromatogram and UV spectra of the last sample mixture in the reaction of parathion with thiophenol-----S9

Figure S-5a. EI total ion chromatograms (TICs) for derivatized products obtained in reaction of polysulfides with parathion-----S10

Figure S-5b. Mass spectrum (EI) for parathion and two methylated products with  $\text{CH}_3\text{I}$ -----S11

HPLC analysis methods for OPs with different nucleophiles. -----S13

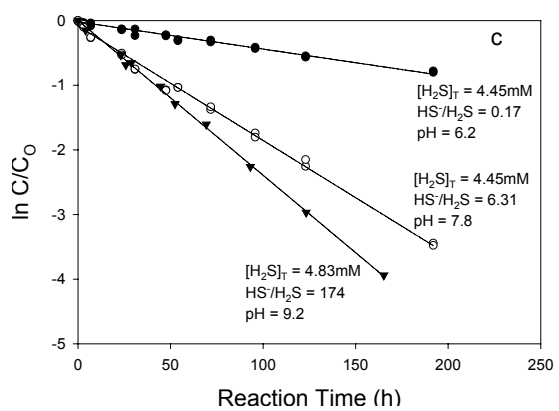
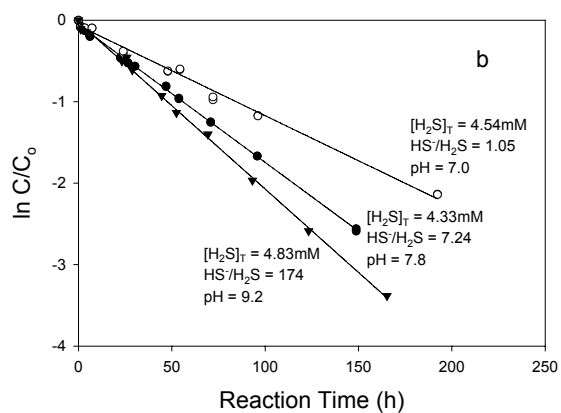
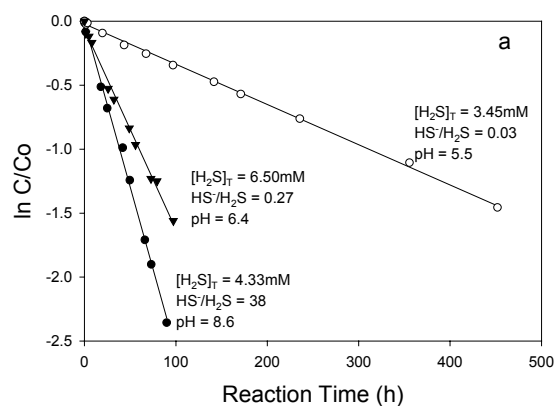
Table S-1

Table S1: Calculated Sulfur Speciation at Four Different pH Values <sup>a</sup>:

pH	S(-II) <sub>T</sub> (mM)	HS <sup>-</sup> (mM)	S <sub>4</sub> <sup>2-</sup> (mM) <sup>b</sup>	S <sub>5</sub> <sup>2-</sup> (mM) <sup>b</sup>	[S <sub>n</sub> <sup>2-</sup> ] <sub>T</sub> (mM) <sup>c</sup>	k <sub>obs</sub> (h <sup>-1</sup> ) <sup>d</sup>
8.03	1.84	1.49	0.14	0.11	0.25	2.35 (±0.20) × 10 <sup>-3</sup>
8.66	4.54	2.62	1.06	0.81	1.88	1.17 (±0.09) × 10 <sup>-1</sup>
9.02	3.12	1.18	1.09	0.83	1.94	1.33 (±0.07) × 10 <sup>-1</sup>
9.31	3.20	0.76	1.38	1.05	2.44	1.89 (±0.17) × 10 <sup>-1</sup>

<sup>a</sup> All reactions were conducted at 0.050 M sodium phosphate and sodium tetraborate buffer with ionic strength adjusted with NaCl to 0.25 equiv/L, 5% of methanol at 25.0 °C. <sup>b</sup> Polysulfides species were calculated using MacμQL for Mac based on the equilibrium constant reported by Giggenbach (1972), and the S<sup>0</sup> was assumed to be in excess. S<sub>4</sub><sup>2-</sup> and S<sub>5</sub><sup>2-</sup> are the predominate species. <sup>c</sup> [S<sub>n</sub><sup>2-</sup>]<sub>T</sub> includes all possible polysulfide species (n=2-5). <sup>d</sup> The kinetic experiment conducted for parathion-methyl.

FIGURE S-1



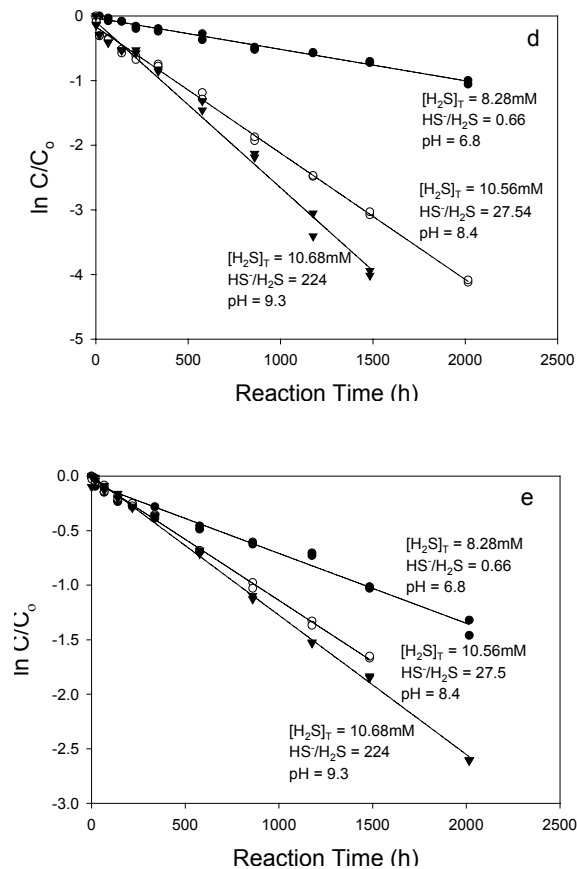
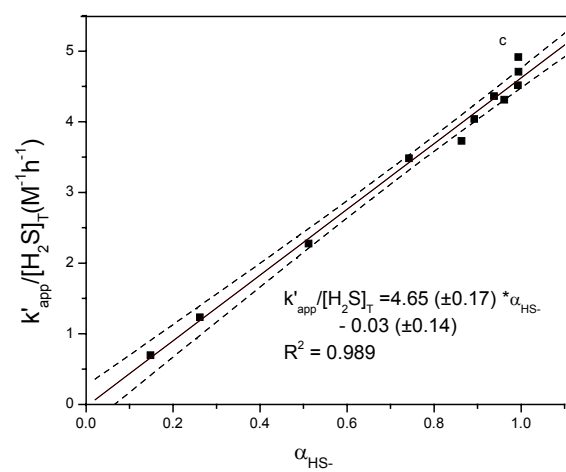
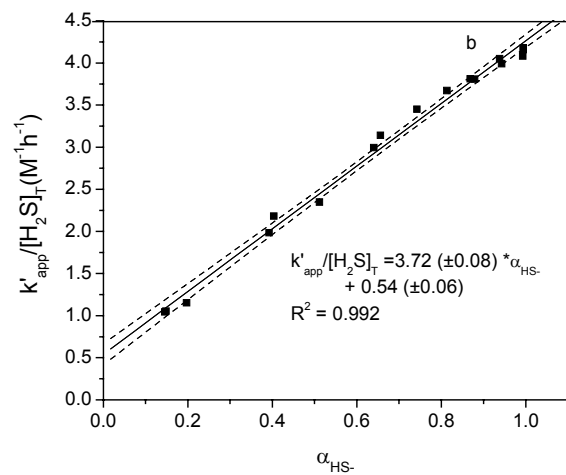
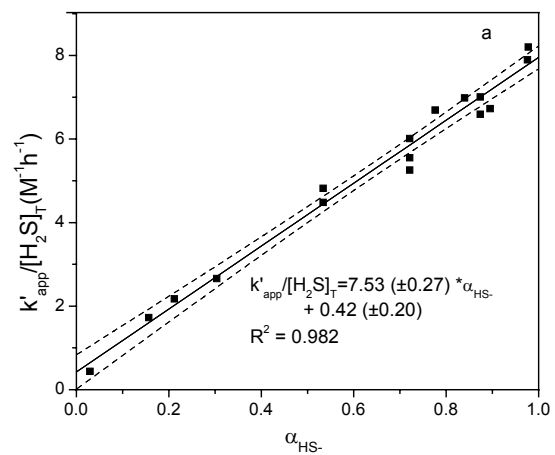


Figure S-1. Example time courses for reactions of OPs with  $HS^-$  at 25 °C and three different pHs. (a) chlorpyrifos-methyl; (b) parathion-methyl; (c) fenchlorphos; (d) chlorpyrifos; and (e) parathion. All experiments were conducted at 0.050 M sodium phosphate or 0.050 M sodium tetraborate buffer, ionic strength 0.25 equiv/L (established with NaCl), 5% methanol and 25.0 °C.

FIGURE S-2



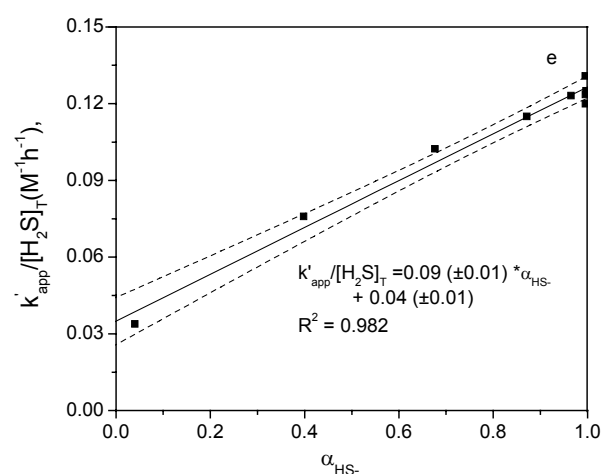
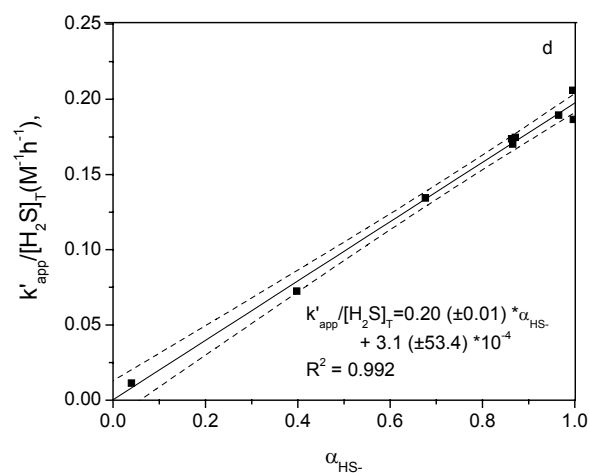
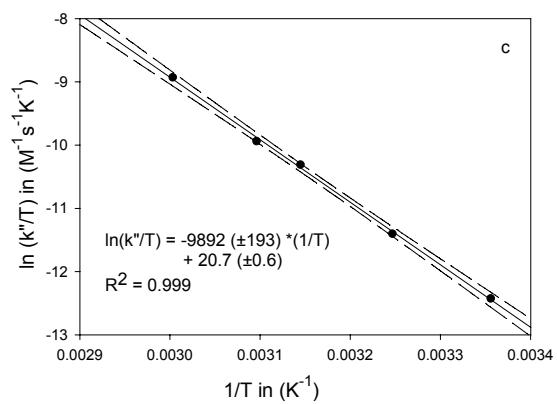
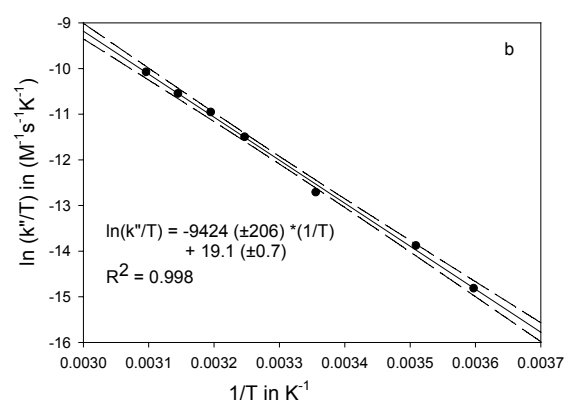
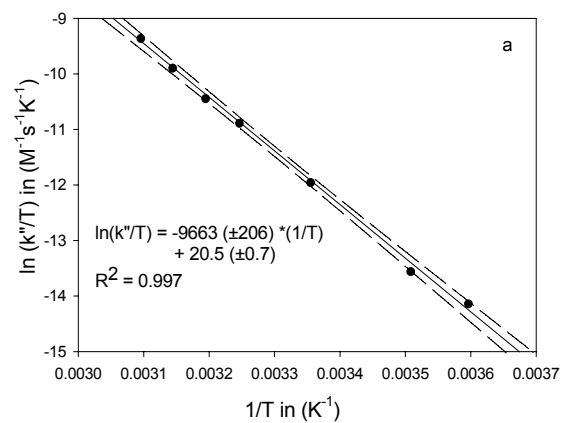


Figure S-2: Plot of apparent second-order reaction rate constants,  $k'_{app}/[H_2S]_T$  (M<sup>-1</sup>h<sup>-1</sup>), versus  $\alpha_{HS-}$  for reactions of hydrogen sulfide/bisulfide with (a) chlorpyrifos-methyl; (b) parathion-methyl; (c) fenclorphos; (d) chlorpyrifos; and (e) parathion. Solid lines represent linear regressions of  $k'_{app}$  values determined at different pHs, dashed lines represent 95% confidence intervals. Ionic strength of reaction solution is 0.25 equiv/L (established with NaCl) with 0.050 M sodium phosphate and sodium tetraborate buffer, 5 or 10% methanol and at 25.0 °C.

FIGURE S-3



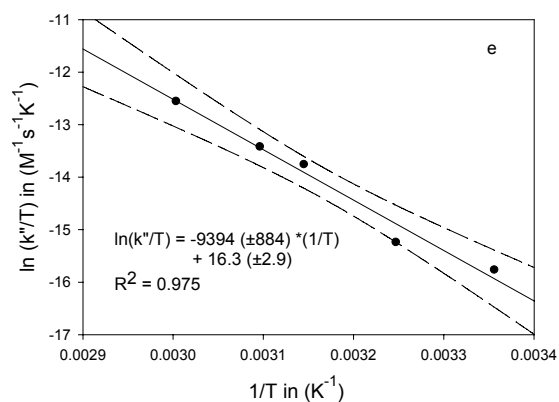
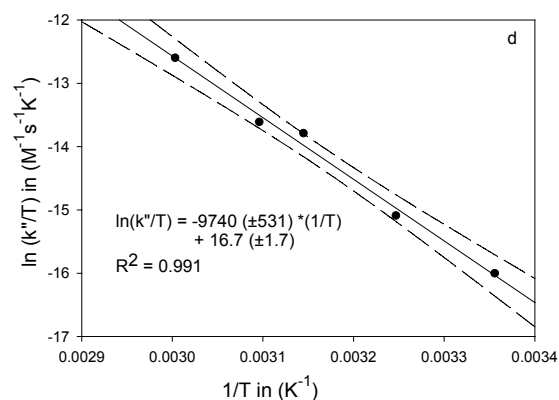


Figure S-3. Temperature dependence of reactions of OPs with  $\text{HS}^-$ . Rate constants were determined in 0.050 M sodium phosphate buffer at pH 8.4 with (a) chlorpyrifos-methyl; (b) parathion-methyl; (c) fenclorphos; (d) chlorpyrifos; and (e) parathion. Solid lines represent linear regressions of  $\ln(k''_{\text{HS}^-}/T)$  values versus  $1/T$  ( $\text{K}^{-1}$ ), dashed lines represent 95% confidence intervals. Ionic strength of reaction solution is 0.25 equiv/L (established with NaCl), 5 or 10% methanol and at 25.0 °C.



FIGURE 4

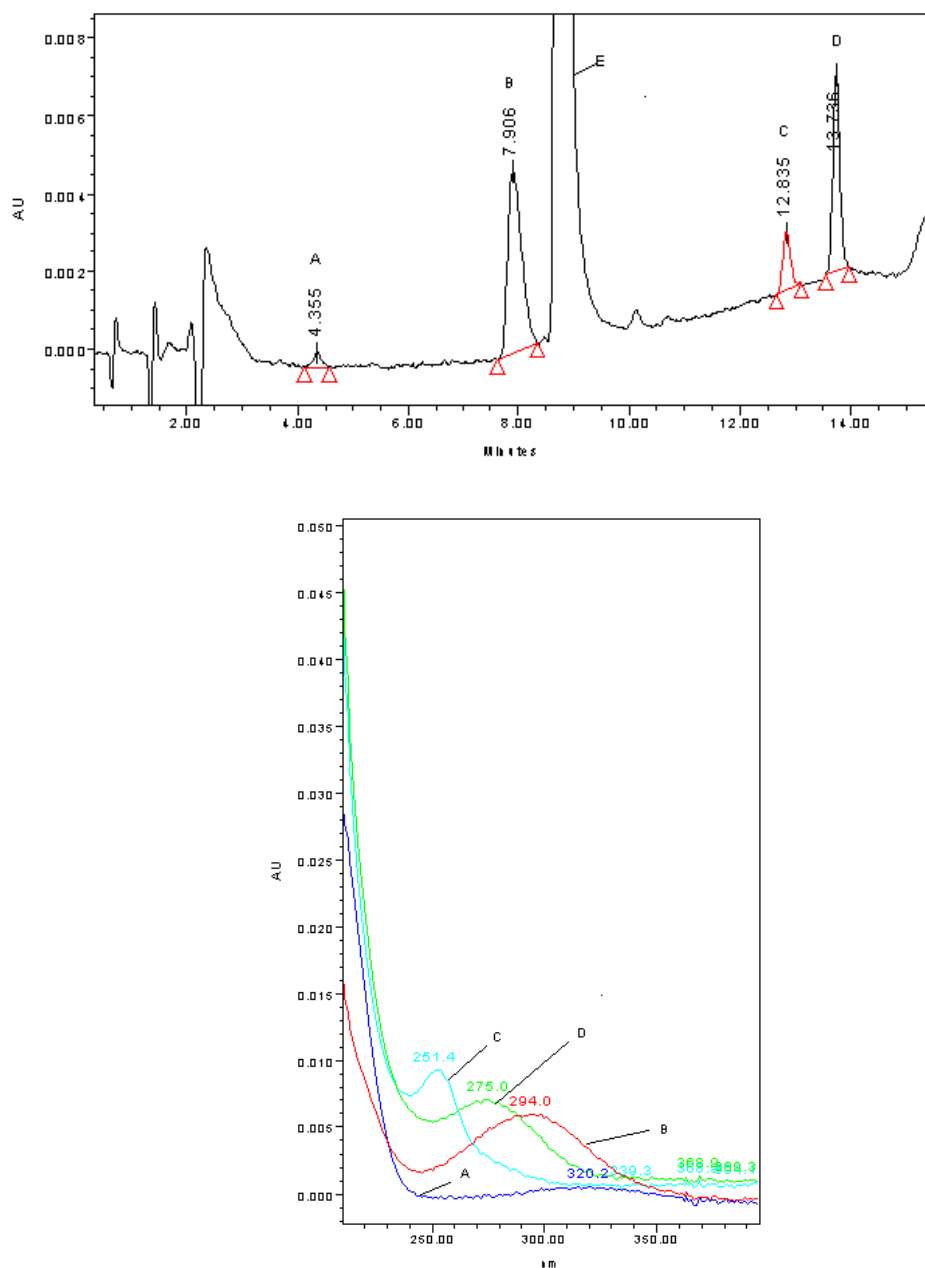


Figure S-4. HPLC chromatogram and UV spectra of a sample in the reaction of parathion with 2.28 mM of thiophenol at pH 9.1. Compounds eluted in the order of 4-nitrophenol (A), desethyl parathion (B), excess thiophenol (E), ethylthiobenzene (C), and parathion (D). The small peaks between peak E and peak C are impurities in the thiophenol.

FIGURE S-5a

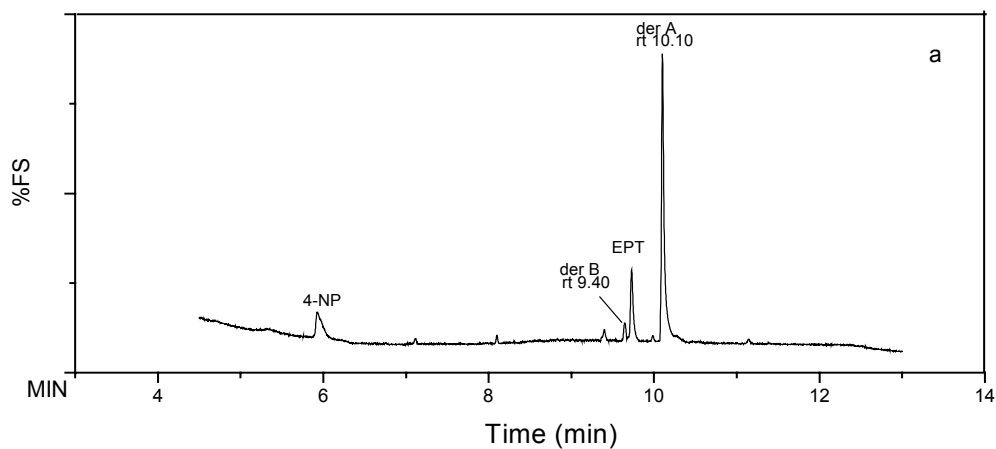
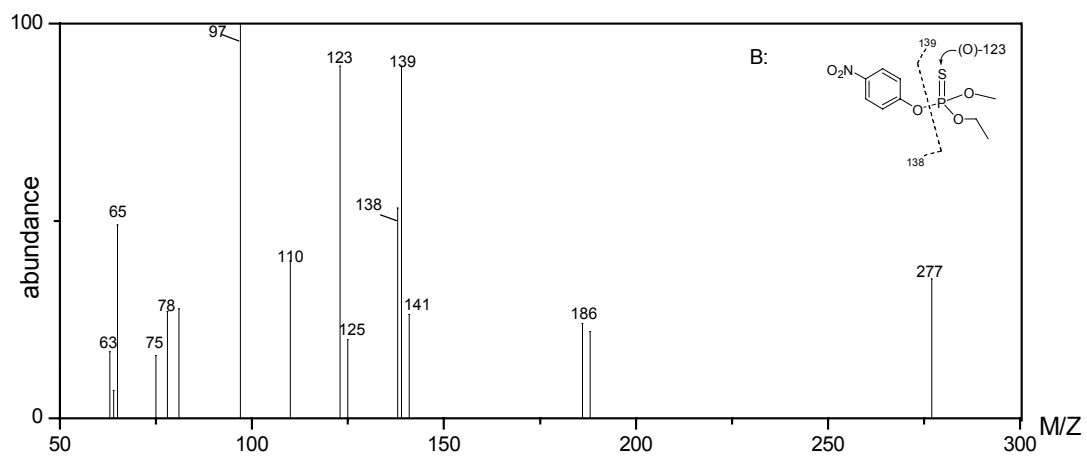
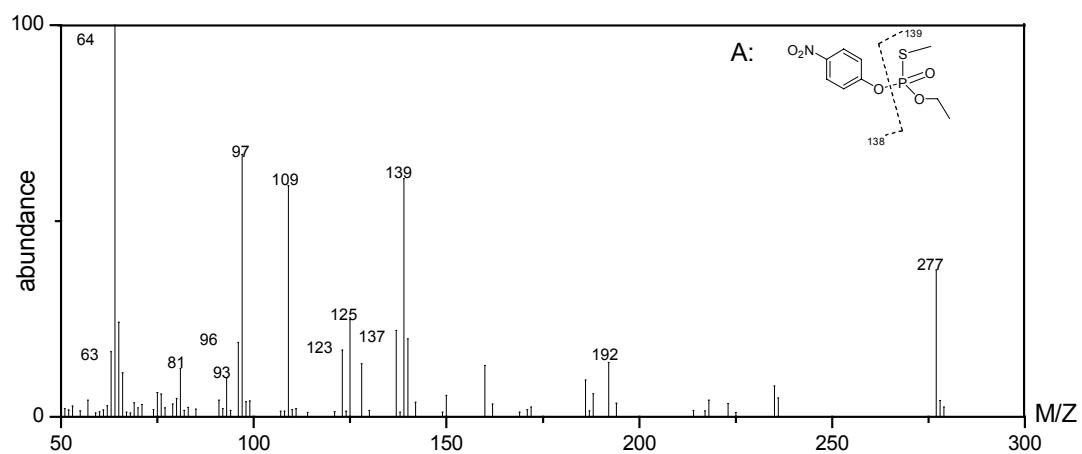


Figure S-5a: EI total ion chromatogram (TICs) for derivatized products obtained in reaction of polysulfides with parathion (parathion with 5 mM  $\Sigma[S_n^{2-}]$  at pH 9 after 120 hours, and derivatized with  $CH_3I$  at 60°C for 2 hours). The compounds eluted in the order of 4-nitrophenol (4-NP), minor methylated product with  $CH_3I$  (der B), parathion (EPT) and major methylated product with  $CH_3I$  (der A).

FIGURE S-5b



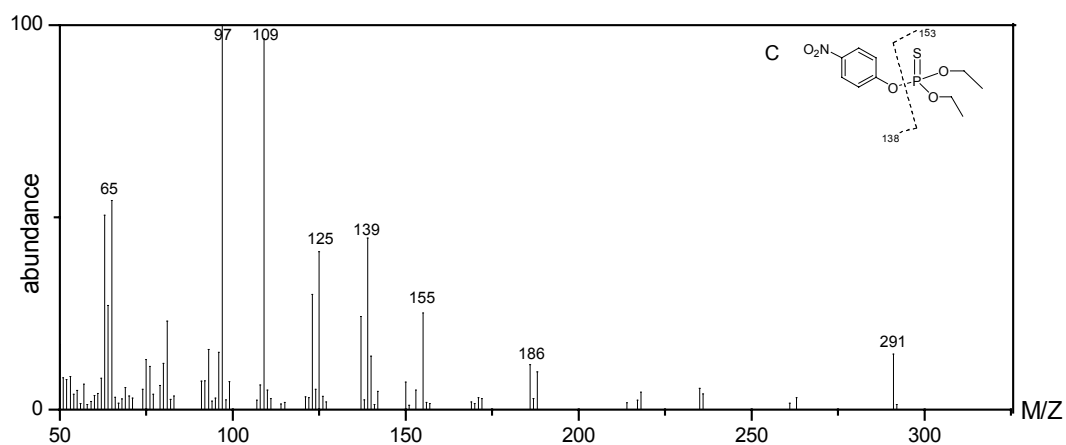


Figure S-5b. Mass spectra (EI) for major methylated product with CH<sub>3</sub>I, retention time is 10.096 min (A), minor methylated product with CH<sub>3</sub>I, retention time is 9.403 min (B), and unreacted parathion, retention time is 9.498 min (C). The major difference of (A) and (B) is the relative abundance of fragment 123.

## HPLC Analysis.

The loss of parent OPs and the formation of selected reaction products were monitored by reverse-phase HPLC with photodiode array detector. An HPLC system (Waters 2690, Waters Corp., Milford, MA) was used. A Lichrospher RP-18 column (60 Å, 5 µm, 3.0 mm×100 mm, EM Separations, Gibbstown, NJ) was used for detection of chlorpyrifos-methyl and parathion-methyl, the flow rate was set at 0.7 mL/min. An Xterra MS C<sub>18</sub> column (125 Å, 5 µm, 3.9 mm×150 mm, Waters, Milford, MA) was used for detection of chlorpyrifos, parathion and fenchlorphos, the flow rate was set at 1 mL/min. An isocratic eluent (1 mM phosphoric acid in 75% acetonitrile/25% H<sub>2</sub>O v/v) was used to monitor the reaction of chlorpyrifos-methyl, chlorpyrifos and fenchlorphos with hydrogensulfide and the hydrolysis. A gradient method was used to monitor the reaction of chlorpyrifos-methyl, chlorpyrifos and fenchlorphos with polysulfides, the mobile phase was 70% methanol and 30% 1 mM phosphoric acid to 100% methanol in 22 minutes. The injected volume was 10 µL.

For the reaction of parathion-methyl and parathion with hydrogensulfide and hydrolysis, a gradient method was used. The mobile phase was 42% methanol and 58% 1 mM phosphoric acid to 70% methanol and 30% phosphoric acid in 16 minutes. To monitor the reaction of parathion-methyl and parathion with polysulfides, the mobile phase was 42% methanol and 58% 1 mM phosphoric acid to 100% methanol in 21 minutes. The injected volume was 10 µL. Chromatographic peaks for OPs and hydrolysis products were identified by retention time comparison with authentic standards.

For selected reactions, an ion pair chromatography was used to monitor the formation of desalkyl OPs. In this case the Xterra MS C<sub>18</sub> column was used for all five OPs. The flow rate was set to 0.65 mL/min. A gradient method was used, which started from 10% of A (0.25 mM tetrabutyl ammonium sulfate in 85% acetonitrile, pH adjusted with phosphoric acid to 4) and 90% of C (0.25 mM tetrabutyl ammonium sulfate in milli-Q water, pH adjusted with phosphoric acid to 4) to 22% of A and 78% C in 14 minutes, hold for 4 minutes, then change to 25% of A and 75% of B (Milli-Q water), hold for 3 minutes and changed back to 10% of A and 90% of C. The injection volume was 10 µL.

