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The reactions of singlet oxygen with β-chlorosulfides. The role of hydroperoxy sulfonium ylides in the oxidative destruction of chemical warfare simulants

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Abstract

The reactions of singlet oxygen with 2-chloroethyl ethyl sulfide and 3-chlorothiane are reported. In both cases elimination of HCl to produce α,β-unsaturated sulfoxides is observed. The experimental results implicate a hydroperoxy sulfonium ylide as a transition state or intermediate in an E2 or E1cb elimination, respectively.

The destruction of chemical weapon stockpiles poses a significant challenge to the chemical community which must design environmentally benign processes to achieve this internationally agreed upon goal. The destruction of mustard gas has previously focused on oxidative and/or hydrolytic processes.[1] We report here an alternative process which involves the use of singlet oxygen as a decontaminant. Singlet oxygen is a potent oxidant which is known to react with sulfides to produce both sulfoxides and sulfones.[2] We demonstrate its use with two mustard gas simulants, **1** and **3**, and we provide experimental details which have a direct bearing on the proper description of the sulfide singlet oxygen reaction surface.[3]

Irradiation of $CDCl_3$ solutions containing 2-chloroethyl ethyl sulfide, **1**, and 10^{-4} M tetraphenylporphyrin under a constant stream of O_2 with a 600 W tungsten lamp at 25°C through a saturated $NaNO_2$ filter solution resulted in formation of **1SO** and ethyl vinyl sulfoxide, **2**. The formation of **2** provides compelling confirmation for the recent suggestion that the hydroperoxy sulfonium ylide (**B** in Scheme 1) is a precursor to sulfoxide.[4]

In the absence of a β-leaving group hydroperoxy sulfonium ylide, **B**, reacts with starting material to generate the sulfoxide product. During photooxidation of **1**, however, rapid loss of chloride generates ion pair **C** which ultimately acts as an oxidant towards **1** to give a 1:1 mixture of **1SO** and **2**. This scenario was experimentally confirmed when the reaction was carried out in the presence of Na_2CO_3 as shown in Table 1. In the absence of an acid trap **1SO** was increased at the expense of **2** and the photooxidation was more efficient. This is consistent with protonation of the persulfoxide, **A**, by adventitious HCl to give

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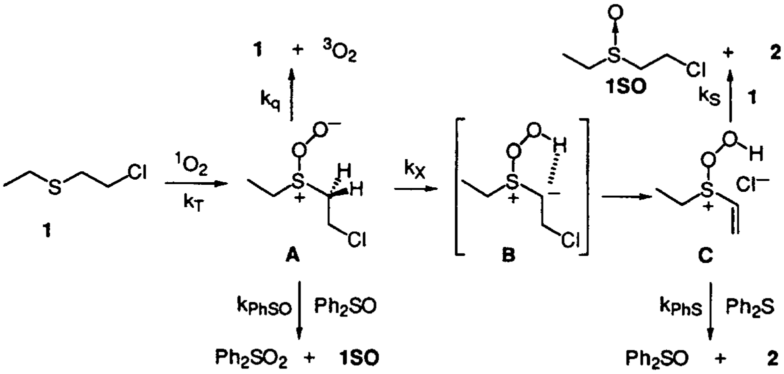


Scheme 1.

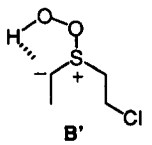
Table 1
Reaction of **1** with singlet oxygen[a]

[1], moles/l	Irradiation time, s	% conversion	% 1SO	% 2
0.051	210	64.0	87.4	12.6
0.051[b]	210	31.0	50.7	49.3
0.061[b]	300	47.0	51.7	48.3
0.27[b,c]	300	24.3	54.7	45.3
0.54[b,c]	300	14.9	54.7	45.3

a. In $CDCl_3$ at 25°C. b. In a Na_2CO_3 slurry. c. A small amount (<5%) $ClCH_2CHClSEt$ formed.

$RR'S^+$-OOH which acts as an oxidant towards **1** ultimately suppressing both physical quenching, k_q, and formation of **2**.[5]

Formation of hydroperoxy sulfonium ylide, **B′**, by hydrogen abstraction from the ethyl group is unlikely to be competitive with formation of **B** because of the greater acidity of hydrogens adjacent to chlorine and is consequently not depicted in Scheme 1. Reaction of **1** with Cl_2 or *N*-chlorosuccimide also generates the ylide adjacent to chlorine giving >80% 1,2-dichloroethyl ethyl sulfide and <20% 1-chloroethyl 2-chloroethyl sulfide.



B'

The mechanism in Scheme 1 also predicts that trapping of persulfoxide **A** with Ph_2SO would enhance the formation of **1SO** as given by Eq. 1. On the other hand, trapping of ion pair **C** would lead to enhanced formation of **2** as given by Eq. 2. Both predictions were experimentally verified as shown in Fig. 1. The value of k_{PhS}/k_S of 0.11 derived from the slopes of the Ph_2S trapping plot reflects the diminished nucleophilicity of Ph_2S in comparison to **1** and can be attributed to both steric and electronic factors.

$$\frac{[1SO]}{[2]} = \frac{k_{PhSO}}{k_X}.[Ph_2SO] + 1 \qquad (1)$$

$$\frac{[2]}{[1SO]} = \frac{k_{PhS}}{k_S}.\frac{[Ph_2S]}{[1]} + 1 \qquad (2)$$

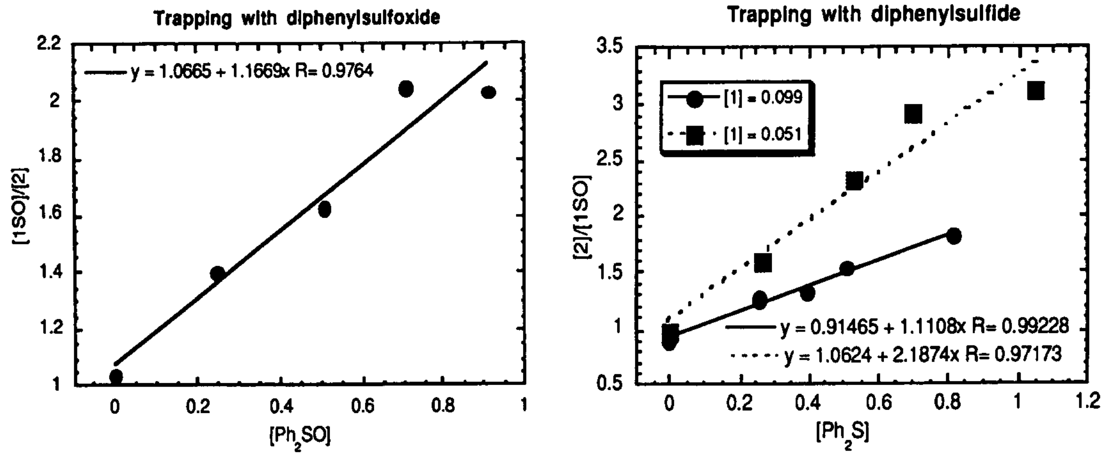


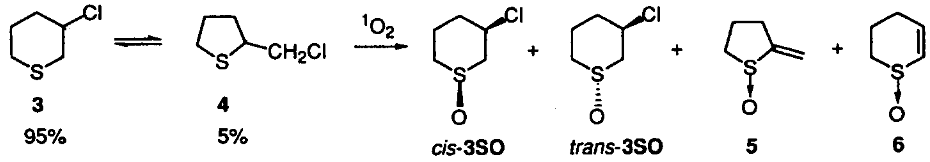
Figure 1.

Table 2
Reaction of **3** with singlet oxygen[a]

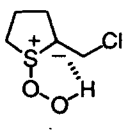
Irradiation time (m)	%Conversion	% *cis*-3SO	% *trans*-3SO	% 5	%6
10	5	39	28	33	-
30	14	31	37	25	7
60	23	30	39	21	10
90	28	27	41	20	12
120[b]	36	28	42	16	14
180[b]	44	28	42	14	16

a. Photooxidation of 0.1M **3** in a $CDCl_3/Na_2CO_3$ slurry at 25°C. b. A small amount (< 3%) of 3-chlorothiane-dioxide forms at long irradiation times.

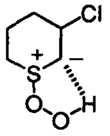
3-Chlorothiane, **3**, exists in equilibrium with a small amount of 2-(chloromethyl)thiolane, **4**. Photooxidation of this mixture under the same conditions utilized for photooxidation of **1** generated four major products in the ratios given in Table 2.[6] The formation of the α,β-unsaturated sulfoxides, 2-methylenethiolane-oxide, **5**, and dehydrothiane oxide, **6**, is compelling evidence for participation of hydroperoxy sulfonium ylides in this complicated reaction.



The absence of **4SO** in the **3/4** photooxidation reaction mixture suggests that hydroperoxy sulfonium ylide **D** undergoes elimination to give **5** more rapidly than it can be reduced with either **3** or **4**. In stark contrast, the observation that ([**5**]+[**6**])<([*cis*-**3SO**]+[*trans*-**3SO**]) suggests that hydroperoxy sulfonium ylide **E** undergoes a slow elimination relative to reduction. This is a consequence of the preference for the equatorial disposition of the chloride in **E** placing it in an unfavorable geometry for elimination.



D



E

In conclusion, an examination of the reactions of $^{1}O_2$ with two chemical warfare simulants has resulted in the discovery of a new singlet oxygen 'oxidative elimination' reaction to give α,β-unsaturated sulfoxides. It also provides an example of a new reaction channel available to hydroperoxy sulfonium ylides.

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6. *trans*-3-Chlorothiane-*S*-oxide (*trans*-**3SO**). White crystals, mp 62–63°C. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.75–3.45 (m, 8H), 4.69 (tt, $^{3}J_{H\text{-}H}$=11.3 Hz, $^{3}J_{H\text{-}H}$=3.7 Hz, 1H, C*H*Cl). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 17.48(C-5), 35.87(C-4), 45.49(C-6), 51.02(C-3), 53.45(C-2). Anal. calcd for C_5H_9ClOS: C, 39.35; H, 5.94. Found: C, 39.11; H, 5.96. *cis*-3-Chlorothiane-*S*-oxide (*cis*-**3SO**). White crystals, mp 95–96°C. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.56–3.79 (m, 8H), 3.93 (tt, $^{3}J_{H\text{-}H}$=11.8 Hz, $^{3}J_{H\text{-}H}$=3.7 Hz, 1H, C*H*Cl). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 19.91(C-5), 35.36(C-4), 50.80(C-6), 51.21(C-3), 59.70(C-2). Anal. calcd for C_5H_9ClOS: C, 39.35; H, 5.94. Found: C, 39.54; H, 6.06. 3-Chlorothiane-*S,S*-dioxide. White crystals, mp 78–79°C. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.75–3.45 (m, 8H), 4.26 (tt, $^{3}J_{H\text{-}H}$=11.9 Hz, $^{3}J_{H\text{-}H}$=3.8 Hz, 1H, C*H*Cl). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 21.6(C-5), 34.63(C-4), 50.18(C-6), 52.12(C-3), 59.37(C-2). 2-Methylenethiolane-*S*-oxide (**5**). Colorless liquid. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.15–3.03 (m, 6H), 5.79 (s, 1H, =CH*H*), 5.96(s, 1H, =C*H*H). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 23.32(C-4), 30.45(C-3), 53.38(C-5), 120.21(CH_2=), 145.81(C-2). Anal. calcd for C_5H_8OS: C, 51.69; H, 6.94. Found: C, 51.76; H, 7.04.