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First Experimental Evidence for the Formation of a Silicate Anion by Intramolecular Addition of a Persulfoxide to a Trimethylsiloxy Group.

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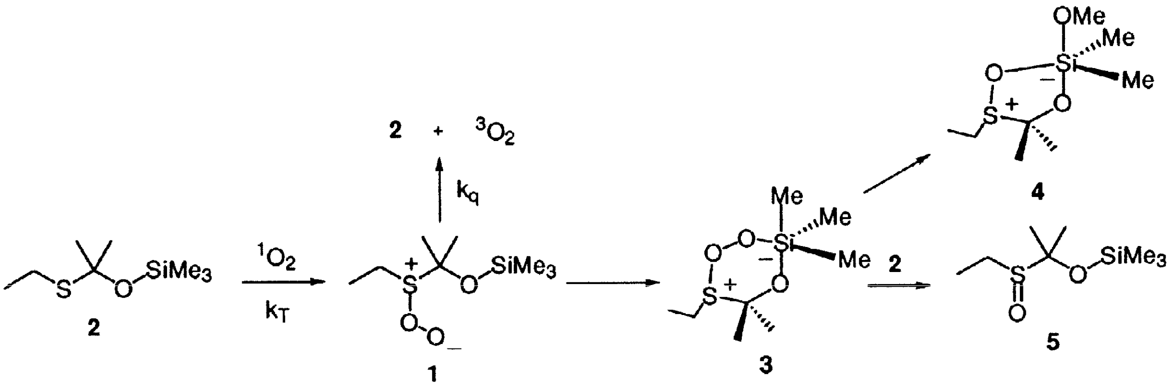
Abstract: The photooxidation of an α-trimethylsiloxysulfide has been studied. The reaction generates a persulfoxide which can be trapped by diphenylsulfoxide, decompose to generate triplet oxygen and substrate, or rearrange to a silicate product via a silicate intermediate.

Persulfoxides, (e.g. **1** in the Scheme), were first suggested as discrete bound species by Schenck and Krausch[1] during their pioneering study of the photooxidations of dialkyl sulfides. Subsequent computational[2] and experimental studies[3,4] have verified this suggestion and have provided compelling evidence that **1** is a ubiquitous intermediate in the reactions of singlet oxygen with a wide range of organosulfur compounds.[5-7] Persulfoxides have never been directly observed at room temperature as a result of the availability of several facile inter- and intramolecular reaction pathways.[7-12] We now report that the photooxidation of [1-(ethylthio)-1-methylethoxy]trimethylsilane, **2**, provides the first compelling evidence for the formation of silicate intermediate, **3**, and silicate product **4**, via a persulfoxide as depicted in the following Scheme.



Scheme

Irradiation of an oxygen saturated 0.012 M solution of 2, 0.3 M pyridine, and 1 x 10^{-4} M tetraphenylporphyrin (TPP), in toluene-d_8 at -60°C for 20 minutes through 1cm of a saturated sodium nitrite

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filter solution resulted in the complete disappearance of **2**, formation of acetone, a trace of diethyldisulfide, several unidentified products, and **4** as the major product. Conspicuously absent were the sulfoxide **5** and the corresponding sulfone. Participation of singlet oxygen in these reactions was verified by demonstrating that **2** quenched the emission of $^1O_2$ at 1270nm, that 5 x 10^{-3} M DABCO completely quenched the reaction, and that the rate of the reaction was much faster in toluene-d_8 than in toluene-h_8.

In order to verify the absence of either sulfoxide **5** or the corresponding sulfone, **6**, they were independently synthesized by treatment of **2** at -60°C with one or two equivalents of MCPBA in the presence of pyridine, respectively. Their structures were verified by both low temperature ^{1}H and ^{13}C NMR. [**5** ^{1}H NMR (toluene-d_8) δ 0.06(s, 9H), 1.15(t, J = 7Hz, 3H), 1.29(s, 3H), 1.30(s, 3H), 2.15(m, 1H), 2.24(m, 1H), ^{13}C NMR ($CDCl_3$) δ 2.0, 8.3, 20.7, 26.0, 38.6, 88.2; **6** ^{1}H NMR (toluene-d_8) δ 0.10(s, 9H), 1.10(t, J = 7Hz, 3H), 1.34(s, 6H), 2.42(q, J = 7Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 1.9, 5.3, 23.7, 39.0, 92.0]. Sulfoxide, **5**, decomposes at temperatures at or above -20°C in a clean first order process with activation barriers at the 95% confidence level of $\Delta H^{\neq} = 19.6 \pm 2.3$ kcal/mol, $\Delta S^{\neq} = -6 \pm 8$ cal mol^{-1} K^{-1}, and $\Delta G^{\neq}(298.16) = 21.3 \pm 4.6$ kcal/mol.

The identity of silicate **4** was established by a combination of ^{1}H NMR, ^{13}C NMR, DEPT, and C,H-COSY experiments (Figure 1). The observation of a methoxy peak at 3.27 ppm in the proton NMR which correlated to a methyl peak at 49.7 ppm in the ^{13}C NMR was especially revealing. In addition, the observation of overlapping gem-dimethyl groups in the ^{1}H NMR which are well separated in the ^{13}C NMR, two very closely spaced Si-Me groups in the ^{1}H and ^{13}C NMR's, and a quaternary carbon at 88.0 ppm in the ^{13}C NMR, are compelling evidence for the structure of **4**.

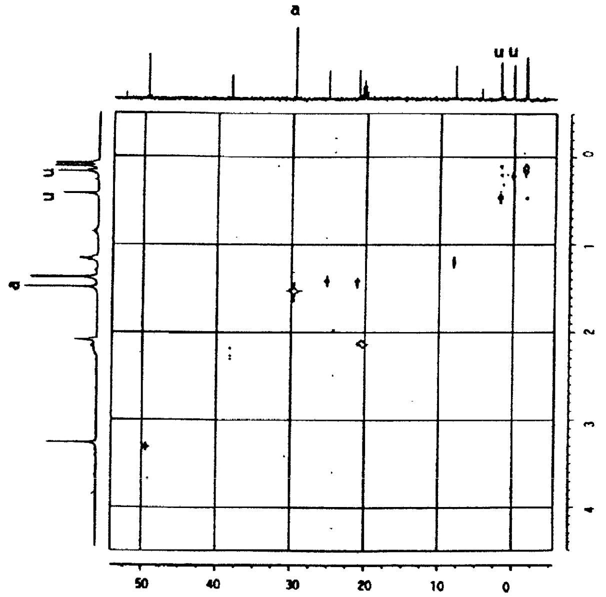

FIGURE 1. C,H - COSY of the reaction mixture from photooxidation of **2** at -60°C in toluene-d_8. a-acetone; u-unknown

Two intermediates formed prior to the silicate, **4**, are also required by the following experimental evidence. Incrementally increasing the concentration of **2** in this experiment from 0.002 molar to 0.3 molar, resulted in the appearance and increase of sulfoxide **5**. However, silicate **4** is unreactive towards **2** as demonstrated by addition of authentically prepared **2** at the end of the photooxidation. Consequently, a fleeting intermediate trapped by **2** must have been intercepted. We suggest that this trapped intermediate is silicate **3**. The peroxide unit in silicate **3** is likely to be susceptible to nucleophilic attack by **2** and its rearrangement by migration of an apical methyl group to form **4** has ample precedent in migrations from silicon to carbon.[13] Increasing the concentration of **2** from 0.01 to 0.50 M had no effect on the extent of non productive physical quenching. (i.e. **2** does not trap an intermediate which dissociates to starting material and $^3O_2$ since this would increase the efficiency of the reaction)[2] The extent of physical quenching was determined by comparing the rate constant for chemical reaction of **2**, k_r, which was measured by NMR in $CDCl_3$ in competition with tetramethylethylene using the method of Higgins, Foote, and Cheng,[14] to the rate constant for disappearance of singlet oxygen, k_T, which was measured by examining the ability of **2** to quench the time-resolved emission of singlet oxygen at 1270 nm as described earlier.[15] The ratio $k_r/k_T = [(1.46 \pm 0.62) \times 10^6 M^{-1}s^{-1}]/[(2.67 \pm 0.30) \times 10^6 M^{-1}s^{-1}]$ reveals that k_r is only 55% of k_T and is independent of concentration. Consequently, nonproductive physical quenching must account for 45% of all interactions of singlet oxygen with **2** over the entire range of 0.01 to 0.50M. Considerable precedent exists which suggests that it is decomposition of a persulfoxide (k_q in the Scheme) which is responsible for the inefficiency of sulfide photooxidations.[2,3]

Additional evidence for the persulfoxide was obtained by cophotooxidation of **2** and diphenylsulfoxide (Ph_2SO). An intermediate is implicated since Ph_2SO is unreactive in the absence of **2**, but is converted to diphenylsulfone (Ph_2SO_2) when cophotooxidized with **2**. In addition, bis-(p-chlorophenyl)sulfoxide, $(pClPh)_2SO$, is approximately 3 times more reactive than Ph_2SO consistent with the nucleophilic character of the persulfoxide but inconsistent with the anticipated electrophilic character of **3**.

The persulfoxide in the reaction of **2** was 10 times more difficult to trap than the persulfoxide formed in the photooxidation of diethylsulfide. In addition, physical quenching accounts for 95% of the interactions of singlet oxygen with diethylsulfide but only 45% of the interactions with **2**. Both these observations point to a reduced lifetime of the persulfoxide formed in the reaction of **2** in comparison to diethylpersulfoxide. This suggests that formation of **3** is considerably more rapid than formation of the putative second intermediate in diethylsulfide photooxidation.

In conclusion, the photooxidations of appropriately substituted sulfides can now be added to a growing list of reactions which have been demonstrated to proceed via hypervalent silicon intermediates.[16] In addition, the formation of **4** and the absence of rearrangement of **5** to its silicate isomer reveals a remarkable stabilization of the trigonal bypyramidal structure by the apocophilic methoxy group.

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