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Isotope Effects as Mechanistic Probes in Solution and in Intrazeolite Photooxygenations. The Formation of a Hydroperoxysulfonium Ylide

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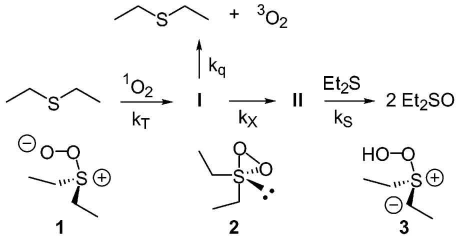
The reactions of singlet oxygen with 2,2,6,6-tetradeuterio-1,4-dithiane have been examined in acetone and methanol, and in the interior of the zeolite NaY. The product isotope effects k_H/k_D have been measured for sulfoxide and, when possible, for sulfone formation. The results provide evidence for a hydroperoxysulfonium ylide intermediate in acetone, a hydrogen bonded or sulfurane intermediate in methanol, and an interesting equilibrium between two complexed forms of the substrate in NaY.

Introduction

The current mechanistic understanding of the reaction of singlet oxygen, $^1O_2$, with sulfides is in large part a result of seminal work conducted by the Foote group in the 1970s, which culminated in 1983 in what is now a classic paper describing the mechanism of diethyl sulfide, Et_2S, photooxygenation.[1] The key feature of the Foote proposal was that the $Et_2S/^1O_2$ reaction occurred in polar aprotic solvents via two distinct intermediates, **I** and **II** (Scheme 1). Intermediate **I** partitions between interconversion to **II** and decomposition to Et_2S and triplet oxygen via a physical quenching channel, k_q. As a result of this physical quenching pathway the reaction is very inefficient and less than 5% of the $^1O_2$ is incorporated into the sulfoxide product. This basic 2-intermediate reaction surface has withstood the test of time and has been shown to be valid for a structurally diverse set of sulfides.[2−7] Persulfoxide, **1**, has received widespread support as the structure of intermediate **I**. However, the structural identity of **II** has been the source of a lively debate with a growing consensus that thiadioxirane, **2**, and hydroperoxysulfonium ylide, **3**, are the two most likely candidates.[8−10]

SCHEME 1. Mechanism of Sulfide Photooxygenation



In this paper we report product isotope effects observed during photooxygenations of 2,2,6,6-tetradeuterio-1,4-dithiane, **4-d₄**, under a variety of conditions. These results provide the first experimental evidence for hydroperoxysulfonium ylide, **3**, as precursor **II** during photooxygenation of a simple dialkylsulfide.[11] They also provide unique insight into subtle environmental effects on the choice of mechanistic pathway.

Results and Discussion

Acetone-d_6 solutions 0.04 M in **4** and 1×10^{-3} M in Rose Bengal were presaturated with oxygen for 15 min and then irradiated for 1 h at room temperature with a 600-W tungsten−halogen lamp through 1 cm of a 12 M $NaNO_2$ filter solution (cutoff 400 nm) under a continuous oxygen flow. Photooxygenations to low conversions (≤25%) produced sulfoxide, **4SO**, and a trace of sulfone, **$4SO_2$**, as the only products.

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[11] An isotope effect has previously been reported during photooxidations of 1,3-dithianes. However, the protons attached to the carbon between the two sulfur atoms in the persulfoxide intermediates formed in these reactions are significantly more acidic than those in simple sulfides. Consequently, the observed isotope effects do not provide general evidence for a hydroperoxysulfonium ylide intemediate. Toutchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, *64*, 5620−5625.

10.1021/jo034426i CCC: $25.00

TABLE 1. Product Ratios and Isotope Effects in the Photooxygenations of $\mathbf{4d_4}$ in Acetone-d_6

	experiment no.						
	1	2	3	4	5	6	average
% conversion	22.96	22.35	19.70	25.78	21.06	28.01	23.31 ± 4.70
% sulfoxide	96.97	96.50	96.65	96.30	96.21	96.50	96.52 ± 0.45
% sulfone	3.02	3.50	3.35	3.71	3.79	3.50	3.48 ± 0.46
% **4SO-βd$_4$**	50.21	50.07	49.79	49.61	49.88	50.06	49.94 ± 0.33
% **4SO-αd$_4$**	46.76	46.43	46.86	46.69	46.33	46.44	46.59 ± 0.27
% **4SO$_2$-βd$_4$**	1.57	1.82	1.76	1.93	1.98	1.80	1.81 ± 0.24
% **4SO$_2$-αd$_4$**	1.45	1.68	1.59	1.78	1.81	1.70	1.67 ± 0.22
k_H/k_D(SO)[a]	1.15	1.16	1.13	1.13	1.16	1.16	1.15 ± 0.02
k_H/k_D(SO$_2$)[b]	1.08	1.09	1.11	1.08	1.10	1.06	1.09 ± 0.03

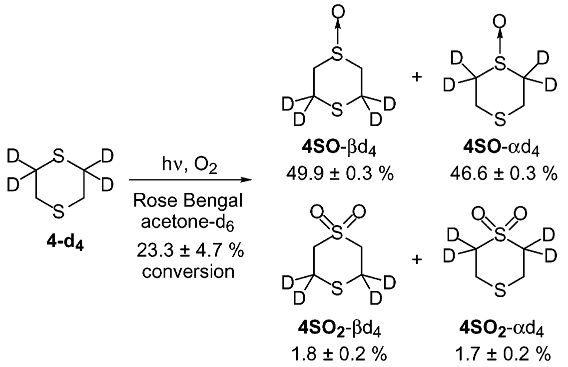
[a] Calculated according to eq 5 as described in the text. [b] Ratio of % **4SO$_2$-βd$_4$**/% **4SO$_2$-αd$_4$**.

The total rate constant for removal of $^1O_2$ from solution by **4**, k_T (4.83×10^6 M^{-1} s^{-1}), was measured by monitoring the time-resolved quenching of its emission at 1270 nm. The rate constant for product formation, k_r (2.4×10^5 M^{-1} s^{-1}), was measured by the competition method of Higgins, Foote, and Cheng[12] relative to that of 2,5-dimethyl-2,4-hexadiene ($k_r = 7.4 \times 10^5$ M^{-1} s^{-1}).[13] The rate constant for physical quenching of $^1O_2$ by **4**, k_Q (4.71×10^6 M^{-1} s^{-1}), was determined by difference, using the equation $k_T = k_Q + 0.5k_r$.[14] These phenomenological rate constants are related to the microscopic rate constants shown in Scheme 1 by eqs 1 and 2. Typical of many sulfide photooxidations this reaction has a very low quantum yield as revealed by the microscopic rate constant ratio k_X/k_q (0.026), which is $^1/_2$ of the k_r/k_Q ratio (see eqs 1 and 2).

$$k_r = 2k_T\left(\frac{k_X}{k_X + k_q}\right) \tag{1}$$

$$k_Q = k_T\left(\frac{k_q}{k_X + k_q}\right) \tag{2}$$

Photooxygenation of **4-d$_4$** in acetone-d_6 with use of conditions identical to those used for **4** resulted in the formation of the four products shown in eq 3. The product



(3)

ratios were determined by integration of the proton NMR spectra of the reaction mixtures and represent the average of 6 independent experiments. A representative example of the typical NMR spectrum is given in Figure 1. In addition, the raw experimental data derived from these spectra are given in Table 1.

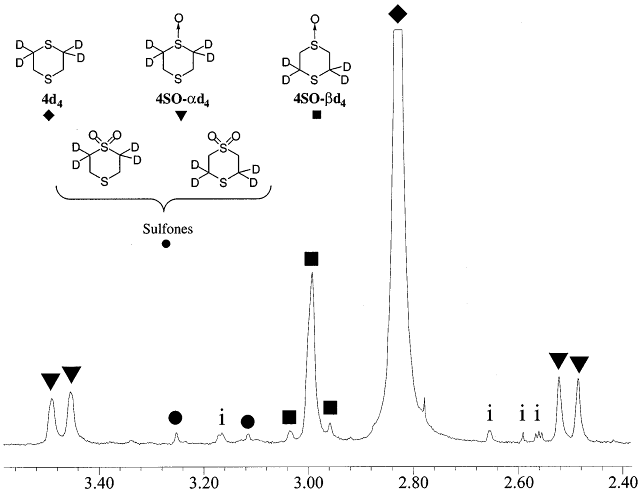


FIGURE 1. Typical proton NMR spectra of the photooxidation of **4d$_4$**: (▼) **4SO-αd$_4$**; (●) sulfones; (■) **4SO-βd$_4$**; (◆) **4d$_4$**; and (**i**) impurity.

Examination of the data in eq 3 reveals a [**4SO-βd$_4$**]/[**4SO-αd$_4$**] ratio of 1.07 ± 0.01. This is consistent with cleavage of the C$_\alpha$−isotope bond in the product-determining step and with formation of **3** as an intermediate in this reaction. Abstraction of hydrogen in step k_X can compete with k_q more effectively than abstraction of deuterium and as a consequence **4SO-βd$_4$** formation is more rapid. This can be expressed mathematically in terms of the microscopic rate constants in Scheme 1 and an adjusted product ratio, [**4SO-βd$_4$**]^A/[**4SO-αd$_4$**]^A, by eq 4 (see Experimental Section for derivations). This equation can be simplified to give eq 5 since k_q is more than 40 times larger than k_X (vide supra) and $k_q{}^H$ and $k_q{}^D$ are expected to exhibit little if any isotope effect. The isotope effect derived from eq 5, $k_X{}^H/k_X{}^D = 1.15 \pm 0.02$, is considerably smaller than those observed in the reactions of 1,3-dithaines (1.31−1.62) and reflects a smaller degree of bond cleavage in the transition state for removal of the less acidic C-hydrogen in the hydroperoxysulfonium ylide formed in the reaction of **4**.[11] However, the magnitude of this primary isotope effect is

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TABLE 2. Product Ratios and Isotope Effects in the Photooxygenations of $4d_4$ in Methanol

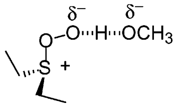
	experiment no.					
	1	2	3	4	5	average
% conversion	28.36	26.43	27.56	29.21	25.94	27.50 ± 1.71
% **$4SO$-βd_4**	49.84	50.09	50.05	50.28	50.10	50.07 ± 0.23
% **$4SO$-αd_4**	50.16	49.91	49.95	49.72	49.90	49.93 ± 0.23
$k_H/k_D(SO)$	0.994	1.004	1.002	1.011	1.004	1.003 ± 0.009

similar to those observed in other singlet oxygen reactions including the singlet oxygen ene reaction.[15]

$$\frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{k_X{}^H(k_X{}^D + k_q{}^D)}{k_X{}^D(k_X{}^H + k_q{}^H)} \tag{4}$$

$$\frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{k_X{}^H}{k_X{}^D} \tag{5}$$

In contrast to acetone, photooxygenation of **4-d₄** in methanol (Table 2) did not exhibit an isotope effect ($[k_H/k_D(SO) = \mathbf{4SO\text{-}\beta d_4}/\mathbf{4SO\text{-}\alpha d_4} = 1.003 \pm 0.009]$). This is consistent with previous reports that in methanol a hydrogen-bonded persulfoxide, **5**,[16,17] or a sulfurane, **6**,[18-20] rather than a hydroperoxysulfonium ylide is the key intermediate.



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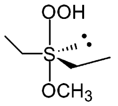

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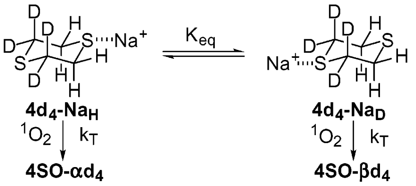
Photoxygenation of zeolite Y encapsulated **4-d₄** was conducted by adding 300 mg of dry NaMBY (zeolite Y containing on average of 1 molecule of methylene blue per 100 supercages; $\langle S \rangle = 0.01$) to 5 mL of a 0.02 M oxygen saturated hexane solution of **4-d₄** and irradiation for 30 min under continuous oxygen agitation with a 600-W tungsten−halogen lamp through 1 cm of a 12 M $NaNO_2$ solution filter (cutoff 400 nm). Under these conditions 100% of **4-d₄** migrated into the zeolite to give an average occupancy ($\langle S \rangle$) of 0.5 molecules of **4-d₄** per supercage.

The reaction of **4-d₄** in NaMBY generated (89.8 ± 0.4)% of **4SO-d₄** and (10.2 ± 0.5)% of **$4SO_2$-d_4**. The isotope effects, $k_H/k_D(SO) = \mathbf{4SO\text{-}\beta d_4}/\mathbf{4SO\text{-}\alpha d_4}$ and $k_H/k_D(SO_2) = \mathbf{4SO_2\text{-}\beta d_4}/\mathbf{4SO_2\text{-}\alpha d_4}$, were measured by both proton and deuterium NMR to give 1.15 ± 0.01 and 1.14 ± 0.02, respectively.

Previous studies of the photooxygenations of sulfides have demonstrated that these reactions are much faster in NaY than in solution. A detailed kinetic study revealed that the origin of this rate enhancement was complete suppression of physical quenching, k_q, in the intrazeolite reaction.[21] This phenomenon was attributed to stabilization of the persulfoxide by complexation with the interstitial sodium cations. Consequently, since both $k_q{}^H$ and $k_q{}^D$ are both small relative to $k_X{}^H$ and $k_X{}^D$ then $k_H/k_D(SO)$ should be equal to 1 (see eq 4), in dramatic contrast to the experimental observations reported above.

SCHEME 2. Kinetic Model for Reaction of $^1O_2$ with Coordinated $4d_4$



In the zeolite **4-d₄** can exist in two coordinated forms as shown in Scheme 2. As a consequence of the population of these two species two limiting cases can potentially explain the unanticipated isotope effect: (1) Physical quenching is suppressed in the zeolite (i.e. $k_q{}^H \ll k_X{}^H$ and $k_q{}^D \ll k_X{}^D$) to give the isotope effect expressed mathematically by eq 6. (See the Experimental Section for the derivation of this equation and eq 7 vide infra.) (2) Physical quenching is dominant in the zeolite (i.e. $k_q{}^H \gg k_X{}^H$ and $k_q{}^D \gg k_X{}^D$) because the sodium is not available to stabilize the persulfoxide since it is complexed to the remote sulfur to give the isotope effect expressed mathematically by eq 7. K_{eq} is likely to be greater than 1.0 since deuterium is electron donating[22] relative to hydrogen and the C−D bond is sterically less demanding than the C−H bond.[23] As a result, both limiting cases will give isotope effects greater than 1.0 consistent with the experimental results.

$$\frac{k_H}{k_D}(SO) = \frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = K_{eq} \tag{6}$$

$$\frac{k_H}{k_D}(SO) = \frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{K_{eq}k_X{}^H}{k_X{}^D} \tag{7}$$

Conclusion

These examples provide compelling evidence that isotope effects (i.e. **4d₄)** can provide otherwise difficult to obtain insight into environment effects on sulfide photooxygenations. They also provide the first evidence that a hydroperoxysulfonium ylide is an intermediate on the sulfoxide-forming reaction surface for simple dialkyl sulfides. This new reaction of hydroperoxysulfonium ylides can now take its place along with Pummerer rearrangements,[24-27] conversions to sulfones,[28] and epoxi-

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dations[29] as well-established reactions of this fascinating intermediate.

Experimental Section

1,4-Dithiane-1-oxide, 4SO.[30] A solution of 2.56 g of $NaIO_4$ in 26 mL of water was added dropwise to 1.44 g (12 mmol) of 1,4-dithiane in 35 mL of acetone at room temperature over a 15-min period. This mixture was stirred for 24 h and then extracted with chloroform (3 × 50 mL). The combined extracts were washed with aqueous sodium bisulfite and then dried over anhydrous sodium sulfate. After removal of the solvent the residue was purified with a silica gel column, using chloroform followed by a chloroform:methanol mixture (8:1) as eluents. A 38.3% yield of pure 1,4-dithiane oxide (0.625 g) was obtained. Mp 123.5−124 °C (lit.[2] mp 125.5−127 °C). MS *m*/*e* 136. ^1H NMR ($CDCl_3$) δ 2.58 (m, 2H), 3.03 (m, 2H), 3.14 (m, 2H), 3.61 (m, 2H). ^1H NMR (acetone-d_6)[31] δ 2.52 (m, 2H, J = 15, 3, 2 Hz), 2.98 (m, 2H, J = 13.98, 2, 2 Hz), 3.01 (m, 2H, J = 13.98, 12, 3 Hz), 3.56 (m, 2H, J = 15, 12, 2 Hz).

2,2,6,6-Tetradeuterio-1,4-dithiane-1-oxide, 4SO-αd$_4$.[30] 1,4-Dithiane-1-oxide (162 mg) in 2 mL of D_2O was added to 3 mL of 40% sodium deuterium oxide solution (99.9% deuterium). This mixture was stirred under a nitrogen atmosphere at 60 °C for 14 h and then extracted with four 15-mL portions of chloroform. The combined organic phase was dried over anhydrous magnesium sulfate and the solvent removed to give 161.2 mg of **4SO-αd$_4$** as a white solid. The deuterium content by NMR was greater than 95% but could be increased to 100% by repeating the procedure 2 or 3 times. Mp 123−124 °C. MS *m*/*e* 140. ^1H NMR ($CDCl_3$) δ 2.52 (d, J = 14.7 Hz, 2H), 3.56 (d, J = 14.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 17.4 (s), 45.2 (pen, J = 21.3 Hz).

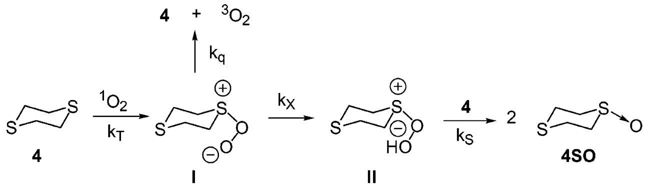
2,2,6,6-Tetradeuterio-1,4-dithiane, 4d$_4$.[30] A 130-mg portion of $LiAlH_4$ was added to a solution of **4SO-d$_4$** (120 mg) in 30 mL of anhydrous ethyl ether (treated with metallic sodium prior to use). After the mixture was refluxed for 16 h, 20 mL of 1.5 M $NaOH_{aq}$ and 50 mL of chloroform were added. The layers were separated and the aqueous layer extracted with three 20-mL portions of chloroform. The combined organic phase was then dried over anhydrous magnesium sulfate followed by careful removal of the solvent. The product was purified by silica gel chromatography, using chloroform as eluent, to obtain 50 mg (47.2% yield) of white crystals. MS *m*/*e* 124. ^1H NMR (acetone-d_6) δ 2.83 (s, 4H).

Photooxygenations of 4d$_4$ in Acetone-*d*$_6$. Acetone-d_6 solutions 0.04 M in **4d$_4$** and 1×10^{-3} M in Rose Bengal were saturated with oxygen for 15 min and then irradiated under continuous oxygen agitation with a 600-W tungsten−halogen lamp for 1 h through 1 cm of a 11.5 M $NaNO_2/H_2O$ filter solution (cutoff 400 nm) at room temperature. The proton NMR was then taken immediately to give the data shown in Table 1. A representative NMR spectrum that was used to determine the product ratios (i.e. isotope effects) is shown in Figure 1.

Photooxygenations of 4d$_4$ in Methanol. Methanol solutions 0.01 M in **4d$_4$** and 1×10^{-5} M in methylene blue were saturated with oxygen for 15 min and then irradiated under continuous oxygen agitation with a 600-W tungsten−halogen lamp for 4 min through 1 cm of a 11.5 M $NaNO_2/H_2O$ filter solution (cutoff 400 nm). The methanol was carefully removed by rotoevaporation and the residue added to acetone-d_6 for NMR analysis. The data for five independent experiments are listed in Table 2.

Photooxygenations of 4d$_4$ in NaMBY. A 300-mg portion of NaMBY ($\langle S\rangle_{MB} = 0.01$) was added to 5 mL of a 0.0183 M hexane solution of **4d$_4$**. The hexane slurries were then saturated with oxygen and stirred for 15 min. GC analysis of the hexane demonstrated that this was sufficient time for 100% migration of the substrate into the zeolite. This corresponds to a loading of $\langle S\rangle = 0.49$ (molecules of **4d$_4$** per supercage). Each sample was then irradiated for 30 min under continuous oxygen agitation with a 600-W tungsten−halogen lamp through 1 cm of a 11.5 M $NaNO_2/H_2O$ solution filter (cutoff 400 nm). After irradiation the zeolite was extracted six times by stirring the powder with 5 mL of acetonitrile for 3 h. The reactions were monitored by both proton and deuterium NMR to give the isotope effects. Run 1: 58.8% conversion, 89.4% sulfoxide, 10.6% sulfone. Run 2: 61.2% conversion, 90.3% sulfoxide, 9.7% sulfone. The mass balances were (75 ± 2)%.

Derivations of Equations 1 and 2. These derivations are based on the mechanism given in the following scheme.



Equation 1:

$$d[\mathbf{4SO}]/dt = 2k_S[\mathbf{4}][\mathbf{II}]$$

Using the steady-state approximation on **II** gives:

$$d[\mathbf{II}]/dt = 0 = k_X[\mathbf{I}] - k_S[\mathbf{4}][\mathbf{II}]$$

$$[\mathbf{II}] = k_X[\mathbf{I}]/k_S[\mathbf{4}]$$

$$d[\mathbf{4SO}]/dt = 2k_X[\mathbf{I}]$$

Using the steady-state approximation on **I** gives:

$$d[\mathbf{I}]/dt = 0 = k_T[^1O_2][\mathbf{4}] - k_q[\mathbf{I}] - k_X[\mathbf{I}]$$

$$[\mathbf{I}] = \frac{k_T[^1O_2][\mathbf{4}]}{k_X + k_q}$$

$$\frac{d[\mathbf{4SO}]}{dt} = \frac{2k_Tk_X[^1O_2][\mathbf{4}]}{k_X + k_q} = k_r[^1O_2][\mathbf{4}]$$

where k_r is the rate constant for product formation given by:

$$k_r = 2k_T\left(\frac{k_X}{k_X + k_q}\right) \qquad (1)$$

Equation 1 is two times the rate constant for the disappearance of singlet oxygen multiplied by the partitioning ratio along the reaction channel.

Equation 2:

$$d[^3O_2]/dt = k_q[\mathbf{I}]$$

Using the steady-state concentration of **I** given above you get:

$$\frac{d[^3O_2]}{dt} = \frac{k_Tk_q[^1O_2][\mathbf{4}]}{k_X + k_q} = k_Q[^1O_2][\mathbf{4}]$$

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[31] Coupling constants were obtained by computer simulation of the 4-spin system.

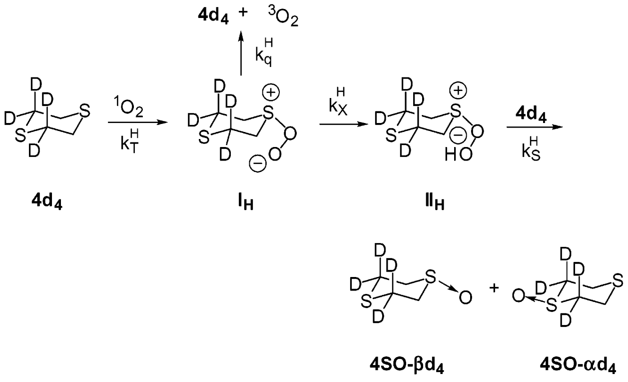
where k_Q is the rate constant for physical quenching given by:

$$k_Q = k_T\left(\frac{k_q}{k_X + k_q}\right) \tag{2}$$

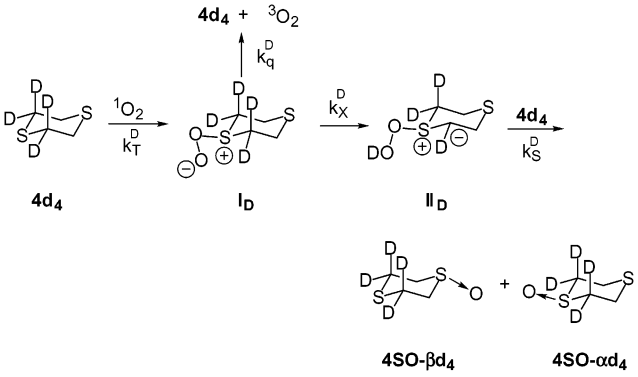
Equation 2 is the rate constant for disappearance of singlet oxygen times the partitioning ratio along the physical quenching channel.

Derivations of Equations 4 and 5. These derivations are based on the fact that two simultaneous processes, attack at the sulfur adjacent to the CD_2 and adjacent to the CH_2 groups, both occur. These are shown below in the scheme along with the associated microscopic rate constants. The α and *β* in the product labels refer to the location of the oxidized sulfur relative to the CD_2 group.

Process 1



Process 2



The isotope effect k_X^H/k_X^D is given by the ratio of $\mathbf{II_H}/\mathbf{II_D}$. An expression for the rate of formation of $\mathbf{II_H}$ in Process I can be derived as shown below.

$$d[\mathbf{II_H}]/dt = k_X^H[\mathbf{I_H}]$$

Using the steady-state approximation on $\mathbf{I_H}$ gives:

$$d[\mathbf{I_H}]/dt = k_T^H[\mathbf{4d_4}][^1O_2] - k_q^H[\mathbf{I_H}] - k_X^H[\mathbf{I_H}]$$

$$[\mathbf{I_H}] = \frac{k_T^H[\mathbf{4d_4}][^1O_2]}{k_X^H + k_q^H}$$

$$\frac{d[\mathbf{II_H}]}{dt} = \frac{k_T^H k_X^H[\mathbf{4d_4}][^1O_2]}{k_X^H + k_q^H} \tag{A}$$

An analogous expression can be derived for $d[\mathbf{II_D}]/dt$ from process 2 as shown below.

$$\frac{d[\mathbf{II_D}]}{dt} = \frac{k_T^D k_X^D[\mathbf{4d_4}][^1O_2]}{k_X^D + k_q^D} \tag{B}$$

The ratio of eqs A and B at low conversions is given by:

$$\frac{[\mathbf{II_H}]}{[\mathbf{II_D}]} = \frac{k_T^H k_X^H(k_X^D + k_q^D)}{k_T^D k_X^D(k_X^H + k_q^H)}$$

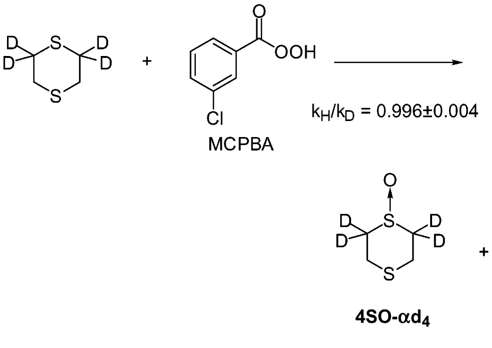
Since no isotope carbon bond is broken in the addition of singlet oxygen to sulfur $k_T^H = k_T^D$ and

$$\frac{[\mathbf{II}_H]}{[\mathbf{II_D}]} = \frac{k_X^H(k_X^D + k_q^D)}{k_X^D(k_X^H + k_q^H)}$$

The ratio $[\mathbf{II_H}]/[\mathbf{II_D}]$ is not directly related to experimental value of [**4SO-*β*d$_4$**]/[**4SO-αd$_4$**] since **4SO-*β*d$_4$** and **4SO-αd$_4$** are also formed indirectly (i.e. not via $\mathbf{II_H}$ or $\mathbf{II_D}$) from **4d$_4$** when it reacts as a reducing agent in the last step, k_S^H and k_S^D of the mechanism. Consequently the [**4SO-*β*d$_4$**]/[**4SO-αd$_4$**] ratio must be adjusted to account for the amount of products formed from the **4d$_4$** acting as a reducing agent. Fortunately, it is possible to make this adjustment because of the following:

For every molecule of product produced from **II** one molecule of product is produced from **4d$_4$** in the last step of the reaction (i.e. 50% of the sulfoxide produced in the reaction never existed as a hydroperoxysulfonium ylide, **II**).

The [**4SO-*β*d$_4$**]/[**4SO-αd$_4$**] produced from **4d$_4$** acting as a reducing agent is 1.0. This contention is supported by using MCPBA (see below) as a mimic for **II** in the oxidation of **4d$_4$**. In three experiments using a 5-fold excess of **4d$_4$** the ratio of [**4SO-*β*d$_4$**]/[**4SO-αd$_4$**] was 0.996 ± 0.004.



Consequently, an adjusted product ratio, [**4SO-*β*d$_4$**]^A/[**4SO-αd$_4$**]^A, which would be equal to $[II_H]/[II_D]$ (see eq 4), can be determined by first subtracting one-half of 50% of the total sulfoxide yield from the percent of **4SO-*β*d$_4$** and **4SO-αd$_4$** formed in the reaction (i.e., [**4SO-*β*d$_4$**]^A = % of [**4SO-*β*d$_4$**] − $^1/_2$(50% × % of sulfoxide). An example calculation for experiment 1 (Table 1) is given below.

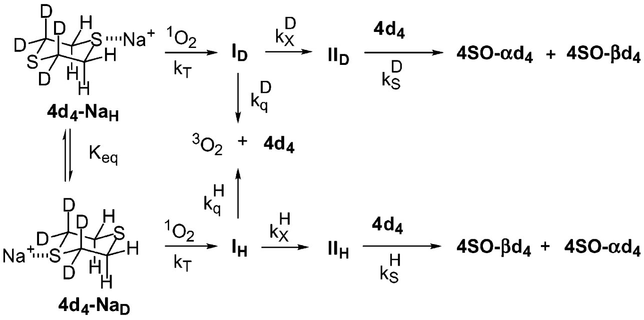
$$\frac{[\mathbf{4SO}\text{-}\boldsymbol{\beta}\mathbf{d_4}]^A}{[\mathbf{4SO}\text{-}\boldsymbol{\alpha}\mathbf{d_4}]^A} = \frac{k_X^H(k_X^D + k_q^D)}{k_X^D(k_X^H + k_q^H)} \tag{4}$$

In solution physical quenching dominates and $k_q{}^D \gg k_X{}^D$ and $k_q{}^H \gg k_X{}^H$ and no isotope effect is expected on the rate constants for physical quenching since hydrogen abstraction is not involved (i.e., $k_q{}^D = k_q{}^H$). Consequently this equation reduces to:

$$\frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{k_X{}^H}{k_X{}^D} \tag{5}$$

Example Calculation of Adjusted Concentrations and Isotope Effect ($k_X{}^H/k_X{}^D$) for Experiment 1. Product composition of analyzed reaction mixture: $\mathbf{4d_4}$, 77.04%; $\mathbf{4SO\text{-}\beta d_4}$, 11.53%; $\mathbf{4SO\text{-}\alpha d_4}$, 10.74%; $\mathbf{4SO_2\text{-}\beta d_4}$, 0.36%; $\mathbf{4SO_2\text{-}\alpha d_4}$, 0.33%; $[\mathbf{4SO\text{-}\beta d_4}]^A = 11.53 - {}^1/_2[{}^1/_2(11.53 + 10.74)] = 5.9625$; and $[\mathbf{4SO\text{-}\alpha d_4}]^A = 10.74 - {}^1/_2[{}^1/_2(11.53 + 10.74)] = 5.1725$. $k_X{}^H/k_X{}^D = 5.9625/5.1725 = 1.15$.

Derivations of Equations 6 and 7. These derivations are based on the premise that singlet oxygen only reacts with the uncomplexed rather than with the complexed less nucleophilic sulfur atom of the zeolite bound substrate. A scheme with the microscopic rate constants used in the derivation is shown below.



An expression for the rate of formation of $\mathbf{II_H}$ is given below:

$$\mathrm{d}[\mathbf{II_H}]/\mathrm{d}t = k_X{}^H[\mathbf{I_H}]$$

Using the steady-state approximation on $\mathbf{I_H}$ gives:

$$\mathrm{d}[\mathbf{I_H}]/\mathrm{d}t = k_T[\mathbf{4d_4\text{-}Na_D}][{}^1O_2] - k_q{}^H[\mathbf{I}_H] - k_X{}^H[\mathbf{I_H}]$$

$$[\mathbf{I_H}] = \frac{k_T[\mathbf{4d_4\text{-}Na_D}][{}^1O_2]}{k_q{}^H + k_X{}^H}$$

$$\frac{\mathrm{d}[\mathbf{II_H}]}{\mathrm{d}t} = \frac{k_T k_X{}^H[\mathbf{4d_4\text{-}Na_D}][{}^1O_2]}{k_q{}^H + k_X{}^H} \tag{I}$$

A similar equation can be derived for $\mathrm{d}[\mathbf{II_D}]/\mathrm{d}t$:

$$\frac{\mathrm{d}[\mathbf{II_D}]}{\mathrm{d}t} = \frac{k_T k_X{}^D[\mathbf{4d_4\text{-}Na_H}][{}^1O_2]}{k_q{}^D + k_X{}^D} \tag{II}$$

Taking the ratio of these two expressions, I and II, gives:

$$\frac{[\mathbf{II_H}]}{[\mathbf{II_D}]} = \frac{k_T k_X{}^H[\mathbf{4d_4\text{-}Na_D}][{}^1O_2]}{k_q{}^H + k_X{}^H} \cdot \frac{k_q{}^D + k_X{}^D}{k_T k_X{}^D[\mathbf{4d_4\text{-}Na_H}][{}^1O_2]}$$

$$\frac{[\mathbf{II_H}]}{[\mathbf{II_D}]} = \frac{k_X{}^H(k_q{}^D + k_X{}^D)[\mathbf{4d_4\text{-}Na_D}]}{k_X{}^D(k_q{}^H + k_X{}^H)[\mathbf{4d_4\text{-}Na_H}]}$$

Since:

$$K_{eq} = \frac{[\mathbf{4d_4\text{-}Na_D}]}{[\mathbf{4d_4\text{-}Na_H}]}$$

$$K_{eq}[\mathbf{4d_4\text{-}Na_H}] = [\mathbf{4d_4\text{-}Na_D}]$$

and the ratio $[\mathbf{II_H}]/[\mathbf{II_D}]$ is equal to ratio of adjusted concentrations of the sulfoxide products as described above:

$$\frac{k_H}{k_D} = \frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{K_{eq} k_X{}^H(k_q{}^D + k_X{}^D)}{k_X{}^D(k_q{}^H + k_X{}^H)} \tag{III}$$

Using eq III and the boundary value conditions for the two limiting cases gives the following.

Case A: Physical quenching is suppressed in the zeolite (i.e. $k_q{}^D \ll k_X{}^D$ and $k_q{}^H \ll k_X{}^H$)

$$\frac{k_H}{k_D}(\mathrm{SO}) = \frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = K_{eq} \tag{6}$$

Case B: Physical quenching predominates (i.e. $k_q{}^D \gg k_X{}^D$ and $k_q{}^H \gg k_X{}^H$)

$$\frac{k_H}{k_D}(\mathrm{SO}) = \frac{[\mathbf{4SO\text{-}\beta d_4}]^A}{[\mathbf{4SO\text{-}\alpha d_4}]^A} = \frac{K_{eq} k_X{}^H}{k_X{}^D} \tag{7}$$

Acknowledgment. We thank the National Science Foundation for their generous support of this research.

Supporting Information Available: Proton NMR spectra of $\mathbf{4d_4}$ and its synthetic precursor $\mathbf{4SO\text{-}\alpha d_4}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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