J. Org. Chem. 1991, 56, 5251-5252

Kinetic Implications of Remote Participation during Photooxidation at Sulfur

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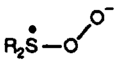
Received March 22, 1991

Summary: The kinetic behavior of 17 hydroxy-substituted sulfides in their reactions with singlet oxygen have been investigated by using a time-resolved kinetic method and by competition. A dramatic 11.6-fold rate increase in the chemical rate was observed when the hydroxy groups were separated from the sulfide reaction center by three carbon atoms, indicative of remote hydroxy participation and the presence of a sulfurane on the reaction surface.

The kinetic study of diethyl sulfide photooxidation by Foote and co-workers[1] in the early 1980s resulted in the suggestion of two mechanisms that provided elegant explanations for a large amount of experimental data. Two mechanisms, rather than one, were necessary as a result of the very different kinetic behavior observed in protic and aprotic solvents. In aprotic solvents two intermediates as depicted in Figure 1 were needed in order to explain the experimental data. The kinetic data in the protic solvent methanol, however, required only one intermediate on the reaction surface.

A variety of structures for intermediates **A** and **B** and the intermediate in methanol have been suggested and include persulfoxide **1**,[2-4] thiadioxirane **2**,[5,6] hydrogen-bonded persulfoxide **3**,[3] ion pair **4**,[7] and sulfurane **5**.[8-10]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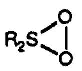
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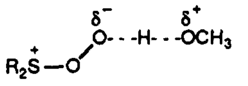
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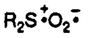
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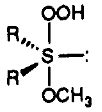
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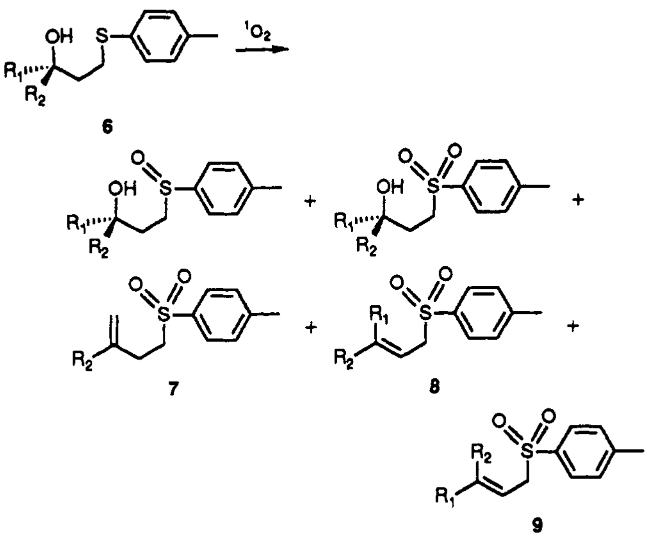
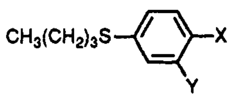
We recently reported[11] that hydroxy sulfide **6** reacted with singlet oxygen to give unusual oxidative elimination products **7**, **8**, and **9**. An ^{17}O tracer experiment also demonstrated that the hydroxy oxygen in **6** had migrated to sulfur in **7**, **8**, and **9**. The remote participation of oxygen to form a sulfurane intermediate, which subsequently decomposed, was suggested in order to rationalize the formations of these unusual olefins.



R_1 = Me; R_2 = iPr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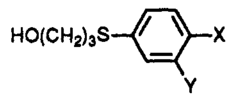
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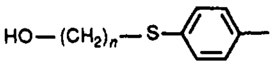
a: X = H; Y = Cl
b: X = Cl; Y = H
c: X = F; Y = H
d: X = H; Y = H
e: X = Me; Y = H
f: X = OMe; Y = H


n = 2, 4, 5, 6
12

We now report kinetic data for the 17 sulfides **6**, **10a–f**, **11a–f**, and **12** (n = 2, 4, 5, 6),[12] which provides additional support for a sulfurane intermediate. This kinetic study involves the determination of the rate constants k_T, k_q, and k_r. The rate constant k_T represents the total rate of sulfide-induced disappearance of singlet oxygen by both chemical and physical processes. The physical quenching rate constant, k_q, represents the rate of sulfide-induced removal of singlet oxygen without chemical modification of the sulfide, and the chemical quenching rate constant, k_r, represents the rate of reaction of the sulfide to form products. The total rate constant, k_T, is therefore numerically equal to the sum of the physical (k_q) and chemical (k_r) rate constants.

The Foote mechanism in Figure 1 suggests that the participation to form the sulfurane could occur in the rate-determining step and the rate enhancement affect k_T, or, alternatively, it could occur after the rate-determining step and affect the partitioning between the chemical, k_r, and physical quenching, k_q, channels.

The total rate constants, k_T, were measured by monitoring the substrate-induced decrease of singlet oxygen emission at 1270 nm in acetone as previously described.[13,14] The chemical rate constants, k_r, were also determined in acetone but by competition with limonene[15] (k_r = 1.74

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[15] The k_T values for (1*R*)-(+)-α-pinene and limonene were measure in acetone in our laboratory and set equal to k_r. Wilkinson and Brummer (Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809-999) report k_T(limonene, MeOH) = 5.9×10^4 M^{-1} s^{-1} and k_T(α-pinene, MeOH) = $(1.2-3.6) \times 10^4$ M^{-1} s^{-1}.

0022-3263/91/1956-5251$02.50/0

Table I. Kinetic Data for the Reactions of Singlet Oxygen with Aryl Alkyl Sulfides[a]

compd	σ	$k_T \times 10^{-6}$ (M^{-1} s^{-1})[b]	$k_r \times 10^{-4}$ (M^{-1} s^{-1})[b]	$k_q \times 10^{-6}$ (M^{-1} s^{-1})	(k_q/k_r)
10a	0.37	0.53			
10b	0.23	0.77			
10c	0.06	1.25			
10d	0	1.63	1.06 ± 0.03	1.62	152.8
10e	−0.17	2.83			
10f	−0.27	4.28			
11a	0.37	0.60			
11b	0.23	0.86			
11c	0.06	1.26			
11d	0	1.51			
11e	−0.17	2.29 ± 0.2 (1.5)	7.1 ± 0.3 (11.6)	2.22	31.3
11f	−0.27	4.07			
12 (*n* = 2)		1.5 ± 0.1 (1.0)	4.2 ± 0.3 (6.9)	1.46	34.8
12 (*n* = 4)		2.7 ± 0.1 (1.8)	4.1 ± 0.2 (6.7)	2.66	64.9
12 (*n* = 5)		2.9 ± 0.1 (1.9)	1.5 ± 0.1 (2.5)	2.88	192.0
12 (*n* = 6)		2.2 ± 0.1 (1.5)	0.61 ± 0.02 (1.0)	2.19	359.0
6		3.7 (2.4)	7.1 ± 0.5 (11.6)	3.63	51.1

[a] All rate constants measured in acetone at room temperature.[21] [b] Relative rates in parentheses.

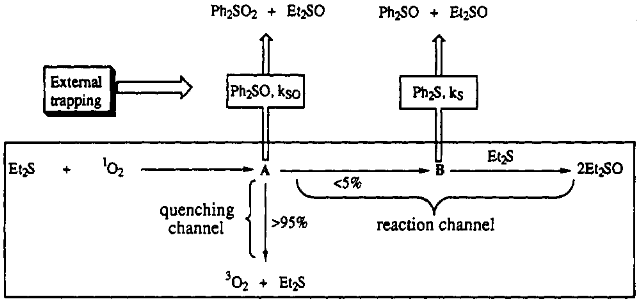

Figure 1.

(±0.13) × 10^5 M^{-1} s^{-1}) or (1*R*)-(+)-α-pinene[15] (k_r = 4.3 (±0.1) × 10^4 M^{-1} s^{-1}). The physical quenching rate constants (k_q) were determined by difference by subtracting k_r from k_T. The data are presented in Table I.

The chemical rate constants, k_r, for the reactions of **6**, **11e**, and **12**, are very sensitive to the number of intervening methylenes between the hydroxy group and the sulfur. The chemical rate constant for the reaction of **11e**, which can form an energetically favorable 5-membered ring sulfurane, is 11.6 times larger than the rate constant for the reaction of **12** (*n* = 6), which can only form an 8-membered ring sulfurane. Five-membered ring bidentate ligands are known to stabilize hypervalent species including sulfuranes.[16] We suggest that in conjunction with the previously discussed olefin formation (**7**, **8**, and **9**) the rate enhancement for **11e** in comparison to **12** (*n* = 2, 4, 5, and 6) is compelling evidence for sulfurane formation. We further suggest that a comparison of k_r for two closely related substrates, with and without a neighboring group, *can be used as a diagnostic tool to detect remote participation.* The kinetic effect of participation, [k_r(fastest) − k_r(slowest) = 6.49 × 10^4], is significantly smaller than the magnitude of k_T(≈ 10^6) or k_q(≈ 10^6). As a result of this large difference in magnitude, it is impossible to determine if the change in k_r is accompanied by an increase in k_T or by a decrease in k_q.

The k_T values for **10a–f** and **11a–f** are linearly related to the Hammett substituent constants[17] with a reaction constants (ρ) of −1.42 (r = −0.997) and −1.22 (r = −0.987), respectively. These values are very similar to the reaction constant (ρ) of −1.6 reported for the photooxidations of substituted thioanisoles.[18,19] We had anticipated that participation of the hydroxy group during photooxidations of sulfides bearing electron-withdrawing groups would result in an increase in k_T in comparison to similar substrates without the hydroxy group. Curved Hammett plots have previously been used to argue for the onset of σ or π delocalization in carbocations and has been referred to as the tool of increasing electronic demand.[20] The inability to detect curvature in the Hammett plots of **10** and **11** does not mean that participation is absent in the rate-determining step since the magnitude of the effect is small compared to the size of k_T (vide supra) and could have escaped detection.

Sulfides that we anticipate will have k_r and k_q values of comparable magnitude are currently being synthesized and will be examined in order to determine if the increase in k_r is accompanied by a decrease in k_q (competitive inhibition) or an increase in k_T (anchimeric assistance).

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for their generous support of this research.

Supplementary Material Available: Competitive kinetic plots (k_r determination) for compounds **6**, **10d**, **11e**, **12** (*n* = 2), **12** (*n* = 4), **12** (*n* = 5), and **12** (*n* = 6) (7 pages). Ordering information is given on any current masthead page.

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