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Photooxidation of Sulfenic Acid Derivatives. 3.[1,2] Oxygen Isotopic Tracer Evidence for the Origin of the Sulfonyl Products

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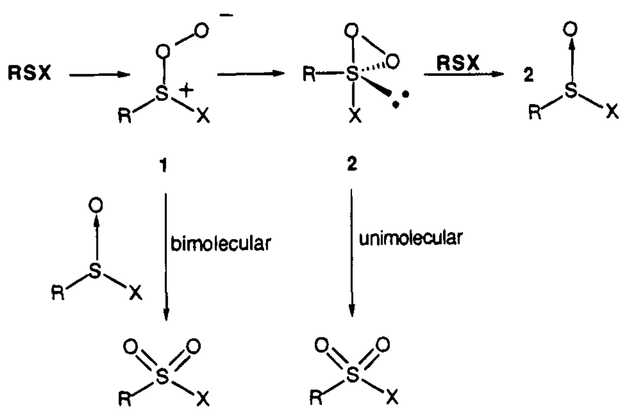
Summary: Isotopic labeling studies with $^{32}O_2/^{36}O_2$ mixtures during photooxidations of sulfides, sulfenamides, sulfenate esters, and disulfides reveal that the oxygens in the sulfonyl products (R_2SO_2) are from different oxygen molecules except in the case of disulfides which implicates a new mechanism for the photooxidations of disulfides involving a novel intramolecular cleavage of the sulfur−sulfur bond in a perthiolsulfinate intermediate.

Photooxidations of sulfenic acid derivatives can result in formations of sulfinyl (RSOX) and/or sulfonyl (RSO_2X) products.[1−9] The origin of the sulfone (R_2SO_2) in the photooxidations of sulfides has been actively debated, but a consensus opinion on the mechanism does not exist.[10,11] The sulfonyl products can potentially form either by bimolecular trapping of a persulfinyl intermediate, **1**, or by unimolecular decomposition of a thiadioxirane, **2**[12] (Scheme 1). Sawaki and co-workers have suggested that the sulfone formed in the photooxidation of phenyl methyl sulfide is primarily formed via a unimolecular route.[13] On the other hand, Jensen questions that conclusion and reports that he is unable to locate an ab initio transition state for unimolecular decomposition of dimethyl thiadioxirane.[14]

Unimolecular but not bimolecular formation of the sulfonyl product requires that both oxygen atoms come from the same oxygen molecule. Consequently, we report here the results of oxygen labeling studies conducted during the photooxidations of sulfenamides ($R'SNR_2$), disulfides (RSSR), sulfenate esters (RSOR′), and sulfides (RSR) which have a direct bearing of the question of molecularity and which provide unique insight into the mechanisms of these reactions.

Photooxidations in the presence of a 1.3/1 mixture of $^{32}O_2/^{36}O_2$ (ICON Services Inc. Summit , NJ) were conducted by irradiation of benzene solutions 0.05 M in the sulfenic acid derivative and 5×10^{-5} M in the sensitizer TPP with a 650 W tungsten−halogen lamp through 1 cm of a 11 M sodium nitrite filter solution. In each case the isotopically enriched oxygen was introduced into the reaction vessel after a series of freeze−pump−thaw cycles on samples which had been presaturated with gaseous nitrogen. Three independent isotopic labeling experiments were conducted for each sulfenic acid derivative, and the experimental $(M)/(M+2)/(M+4)$ ratios were determined by GC/MS immediately after completion of the photooxidations. These experimental peak ratios were then corrected for contributions from other isotopes (e.g., ^{34}S) and compiled in Table 1. The relative abundances of the isotopic sulfinyl products ($RS^{16}OX/RS^{18}OX$) served as an independent check of the $^{32}O_2/^{36}O_2$ ratio and provided verification of the efficiency of the degassing procedure. Independent control studies also verified the absence of disproportionation and the structural integrities of the products under the gas chromatographic conditions.

Scheme 1



The calculated values of the sulfonyl $(M)/(M+2)/(M+4)$ ratio for a $^{32}O_2/^{36}O_2$ ratio of x/y are $x^2/2xy/y^2$ for a 100% bimolecular and $x/0/y$ for a 100% unimolecular reaction pathway. These calculated values for a $^{32}O_2/^{36}O_2$ ratio of 1.324/1 are reported in Table 1 for comparison to the corrected $(M)/(M+2)/(M+4)$ ratios measured for the sulfonyl products. The fraction of the sulfonyl product formed via the bimolecular (f_{BM}) and unimolecular (f_{UM}) pathways were calculated from the corrected $(M+2)/(M+4)$ ratios using eq 1 which simplifies to eq 2 since $y = 1$ and $f_{BM} + f_{UM} = 1$.

$$\frac{M+2}{M+4} = \frac{(f_{BM})(2xy) + (f_{UM})(0)}{(f_{BM})(y^2) + (f_{UM})(y)} = (f_{BM})(2xy) \tag{1}$$

$$f_{BM} = \frac{[M+2]}{[M+4](2x)} \tag{2}$$

Sulfenamides. In general, sulfenamides react with singlet oxygen to give exclusively sulfinamides ($RSONR_2$).[1] Sulfenamides **3** and **4**, however, bearing an electron-withdrawing *p*-ClPh− and a sterically demanding *tert*-

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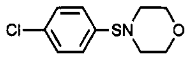
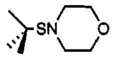
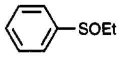
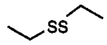
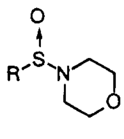
Table 1. Oxygen Labeling Studies[a]

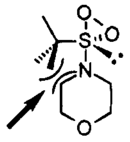
	oxygen isotopic contribution to				
compd[b,c]	M	$M+2$	$M+4$	% UM[e]	% BM[d]
	1.753	2.648	1		100
	1.324	0	1	100	
 **3**	1.79 ± 0.05	2.67 ± 0.04	1		100 ± 2
 **4**	1.75 ± 0.07	2.60 ± 0.05	1		98 ± 2
Et_2S **5**	1.70 ± 0.05	2.49 ± 0.06	1		101 ± 2
 **6**	1.66 ± 0.07	2.56 ± 0.05	1		102 ± 3
 **7**	1.39 ± 0.04	0.078 ± 0.009	1	97 ± 2	
 **8**	1.46 ± 0.01	0.50 ± 0.03	1	80 ± 2	

[a] In benzene using 5 × 10^{-5} M TPP as sensitizer.[26] [b] Percent conversions: **3**, 100%; **4**, 100%; **5**, 5–10%; **6**, 50–96%; **7**, 87–92%; **8**, 3–42%. [c] The $RS^{16}OX/RS^{18}OX$ ratios revealed that the isotopic compositions of O_2 changed slightly in each experiment as a result of inadvertent introduction of traces of atmospheric O_2: $^{32}O_2/^{36}O_2$ **3** (1.324/1); **4** (1.324/1); **5** (1.231/1); **6** (1.264/1); **7** (1.220/1); **8** (1.2/1). [d] Percent bimolecular formation of the sulfonyl product according to eq 2. (% BM = $f_{BM}100$ and $f_{BM} = (M+2)/[(2x)(M+4)]$). [e] Percent unimolecular formation of the sulfonyl product (% UM = 100 − % BM).

butyl− group are exceptional and react with singlet oxygen to give 16% and 11% of the sulfonamide (RSO_2NR_2), respectively. Examination of Table 1 reveals that these sulfonamides are formed exclusively via bimolecular trapping with the sulfinamide formed during the reaction. The formation of the sulfonamide in the reaction of **3** can consequently be attributed to enhanced trapping ability of the sulfinamide intermediate, **11**, in comparison to less electron poor analogues. A similar explanation, however, is not adequate to explain sulfonamide formation in the reaction of **4** since it is unlikely that **12** is a better trapping agent than less sterically hindered but electronically similar analogues. As an alternative explanation, we suggest that trapping in the photooxidation of **4** is a result of a suppressed rate of interconversion of intermediate **1** to **2** (Scheme 1) reflecting destabilizing steric interactions in the thiadioxirane intermediate, **13**. Steric interactions between apical and equatorial substituents are well documented in the formations of σ-sulfuranes[15] and σ-dialkoxyphosphoranes.[16]



11 R = pClPh
12 R = tBu



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Sulfides and Sulfenate Esters. Diethyl sulfide, **5**, and ethyl phenylsulfenate, **6**, both react with $^1O_2$ in benzene-d_6 to give the sulfinyl derivative as the major and the sulfonyl derivative as the minor product. The sulfinate/sulfonate product ratio of 2.2 ± 0.1 formed in the reaction of **6** was conveniently measured by integration of the methylene region of the ^1H NMR which exhibited two doublets of quartets (δ 3.47 (J = 7.0, 9.9 Hz), 3.96 (J = 7.0, 9.9Hz)) for the sulfinate and a solitary quartet (δ 3.80 (J = 7.0 Hz)) for the sulfonate product. Examination of Table 1 also reveals that the sulfonyl product in both reactions forms exclusively via a bimolecular pathway.

Disulfides.[17] In dramatic contrast to the other sulfenyl derivatives, thiolsulfonates rather than thiolsulfinates are the major products formed in the photooxidations of disulfides in benzene.[2] In addition, oxygen labeling results (Table 1) reveal that the thiolsulfonates are formed primarily by a unimolecular process. Rather than invoke a unique ability of these thiadioxiranes (X = S) to decompose by O−O scission we suggest that an alternative mechanism similar to those depicted in Scheme 2 is responsible for the unusual behavior of disulfides. Ample precedent exists for both nucleophilic attack on thiosulfonium ions[18] (process a in Scheme 2) and dimerization of sulfenate radicals[19,20] similar to **14**. The four-centered transition state for rearrangement of perthiolsulfinate **15** precludes a classical backside S_N2 displacement mechanism. Nucleophilic displacement could be circumvented by cleavage of **15** to an ion pair followed by recombination. However, a similar nonlinear nucleophilic displacement at trivalent phosphorus, via a hypervalent transition state and/or intermediate, is supported by the results of an endocyclic restriction test.[21] In addition, Akasaka and Ando[22] have reported that

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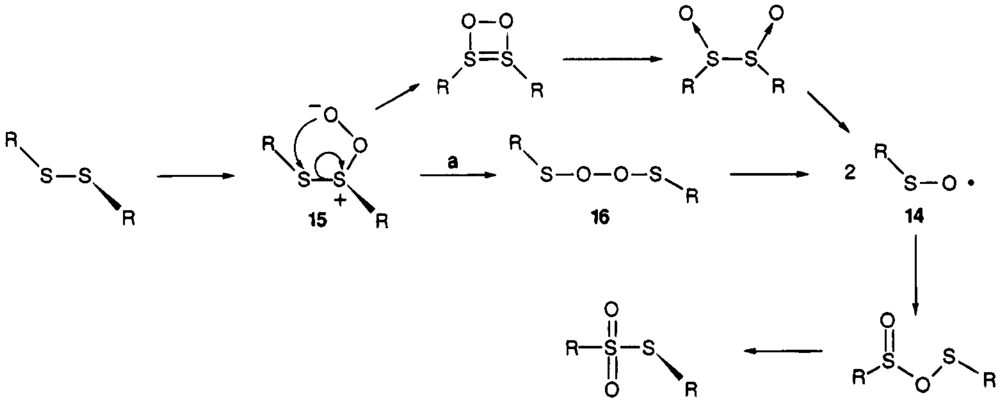
Scheme 2



triazolinediones insert into the sulfur–sulfur bond of disulfides to give the nitrogen analogue of **16**.

Control reactions suggest that the 20% contribution to the bimolecular pathway in the photooxidation of **8** in comparison to **7** appears to be a result of a slow disproportionation[23,24] of the thiolsulfinate rather than an enhanced ability to trap a thiolpersulfinate intermediate, **15**.[25]

Conclusion. The results presented here suggest that at moderate to high substrate conversions the unimolecular cleavage of a thiadioxirane does not compete effectively with either bimolecular trapping and/or its reactions with sulfur nucleophiles. In addition, these results have implicated a new mechanism for the photooxidations of disulfides.

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Supplementary Material Available: Experimental procedures and characterization data (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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