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Temperature, Solvent, and Substituent Effects on the Singlet Oxidations of Allylic Phenyl Sulfoxides, Sulfones, and Sulfides

Edward L. Clennan* and Xiangning Chen

Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071. *Received April 10, 1989*

Abstract: The reactions of singlet oxygen with a series of allylic sulfoxides, sulfones, and sulfides have been examined as a function of extent of reaction, temperature, and solvent. Hydroperoxy groups but not alkyl, hydrogen, or hydroxyl on chiral carbons β to sulfide sulfur induce diastereoselective sulfoxide formations. Evidence is presented that suggests that the oxidation at sulfur occurs with anchimeric assistance from the hydroperoxy group via a favorable sulfurane-like transition state.

In the past 25 years the reactions of singlet oxygen with a wide variety of sulfur-containing compounds including dialkyl sulfides,[1] aryl sulfides,[2] vinyl sulfides,[3] disulfides,[4] thiophenes,[5] thioketones,[6] and sulfur ylids[7] have been reported. The multiple-oxidation states available to sulfur, and the ability of both the substrate and oxidized products to intercept labile intermediates on the reaction surfaces, have complicated the examinations of these important reactions. Despite these complexities, substantial progress toward a mechanistic understanding of several of these reactions has been made.[8]

In 1983[9] Foote and co-workers, reported detailed kinetic studies of the reaction of singlet oxygen with diethyl sulfide. These kinetic studies, which involved competitive trapping experiments with diphenyl sulfide and diphenyl sulfoxide,[10] were conducted in both protic (methanol) and nonprotic (benzene and acetonitrile) solvents. In nonprotic solvents the presence of two kinetically distinguishable intermediates was demonstrated. In the protic solvent, methanol, however, the kinetic results could be accommodated with only one intermediate. No structural information on these intermediates was presented that allowed a distinction to be made between probable candidates, tight ion pair **1**,[11] persulfoxide **2**, thiadioxirane[12] **3**, hydrogen-bonded persulfoxide **4**, or sulfurane **5**. Recently,[13] however, we reported a remarkable diastereoselective photooxidation of allylic sulfide **6b**, which we suggested provided the first experimental evidence for the formation of a sulfurane intermediate (eq 1). We now report additional examples of this diastereoselective photooxidation and the results of a study of the effect of temperature and solvent on the reactions of sulfides **6a–d**, **7–9**, sulfoxides **10a–d**, and sulfones **11b** and **c**. We also discuss the mechanistic implications of these results.

$Et_2S^{\bullet +}O^{\bullet -}_2$

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$Et_2S^+{-}O{-}O^-$

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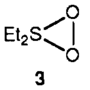

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$Et_2S^+{-}O{-}O^-\cdots H\cdots OMe$

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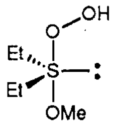

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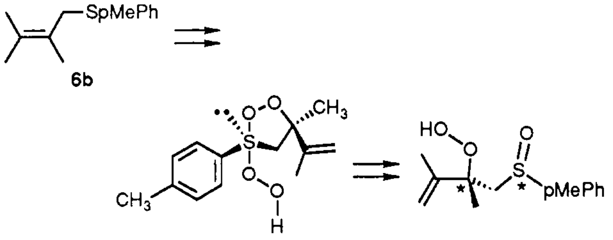

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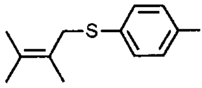
Results

The sulfides, sulfoxides, and sulfones **6–11** were photooxidized in oxygen-saturated deuterated solvents in 5-mm NMR tubes.



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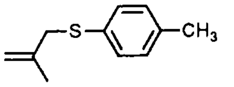

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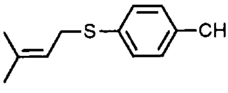

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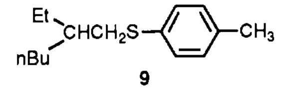

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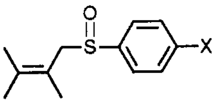

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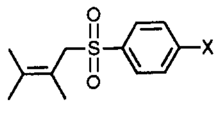

11

a, X = OMe
b, X = Me
c, X = H
d, X = NO_2

Both the substrate concentrations (2–5 × 10^{-2} M) and dye concentrations (1–2 × 10^{-5} M) were kept low in order to prevent substrate dye interactions. The reaction mixtures were also saturated with oxygen for 20 min prior to irradiation to maximize oxygen–dye interactions. The irradiations were conducted under continuous oxygen agitation with a 750-W projection lamp through a 1-cm 0.5% potassium dichromate filter solution.[14] The temperatures of the reaction mixtures were maintained within ±1 °C and the progress of the reactions monitored by ^1H NMR. Identical product mixtures were obtained with either Rose Bengal or tet-

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Table I. ^1H NMR Data for Sulfoxide Oxidation Products **12**[a]

	chemical shifts (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
12a	1.21 1.45	3.60 (13) 3.74 (13)	5.37 (2) 5.49		7.16 (9) 7.72 (9)	11.09	3.89
12a′	1.32	3.60 (13) 3.87 (13)	4.78 5.20		7.12 (9) 7.68 (9)		3.87
12b	1.23 1.46	3.58 (13) 3.77 (13)	5.38 (2) 5.49		7.44 (8) 7.67 (8)	10.9	2.43
12b′	1.33 1.35	3.58 (13) 3.91 (13)	4.80 5.21		7.4 (9) 7.7 (9)	4.1	2.4
12c	1.23 1.45	3.61 (13) 3.82 (13)	5.38 (2) 5.49		7.6–7.9	10.86	
12c′	1.33	3.59 (13) 3.93 (13)	4.78 5.20		7.5–7.7		
12d	1.28 1.44	3.70 (13) 3.96 (13)	5.39 5.51		8.08 (9) 8.48 (9)	10.73	
12d′	1.33 1.36	3.69 (13) 4.03 (13)	4.84 5.24		7.98 (9) 8.43 (9)		

[a] In acetone-d_6 referenced to TMS. See eq 2 for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent.

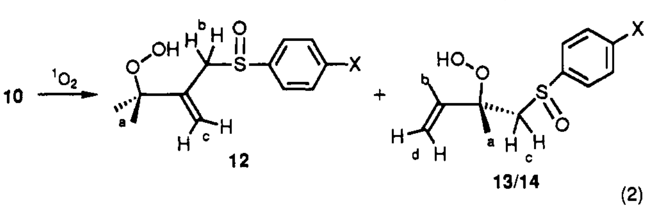
Table II. ^1H NMR Data for Sulfoxide Oxidation Products **13**[a]

	chemical shift (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
13a	1.53	1.84	3.2–3.4	4.85 4.91	7.2 (9) 7.7 (9)	10.62	3.87
13a′	1.57	1.88	2.95 (14) 3.13 (14)	4.87 5.19	7.1 (9) 7.6 (9)		3.87
13b	1.54	1.84	3.3–3.4	4.85 4.91	7.4 (8) 7.6 (8)	10.61	2.41
13b′	1.57	1.81	2.95 (14) 3.14 (14)	4.88 5.20	7.4 (8) 7.6 (8)	4.70	2.40
13c	1.56	1.85	3.3–3.5	4.87 4.92	7.5–7.8	10.60	
13c′	1.57	1.81	2.96 (14) 3.17 (14)	4.88 5.21	7.5–7.8	4.77	
13d	1.58	1.86	3.58 (14) 3.74 (14)	4.89 4.94	8.01 (9) 8.41 (9)	10.54	
13d′	1.55	1.84	3.12 (13) 3.31 (13)	4.93 5.24	8.0 (9) 8.4 (9)	4.25	

[a] In acetone-d_6 referenced to TMS. See eq 2 for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent.

raphenylporphyrin, providing verification of singlet oxygen involvement.

Sulfoxides. Acetone-d_6 solutions of allylic sulfoxides **10a–d** were photooxidized under these carefully controlled conditions at −78 °C. In each case only allylic hydroperoxy sulfoxide **12** and diastereomers **13** and **14** were formed (eq 2). The product ratios were independent of extent of reaction. The sensitive hydroperoxides were not isolated directly but were quantitatively reduced to a mixture of allylic alcohols **12′**, **13′**, and **14′** with triphenylphosphine. The alcohols were separated and purified by thin-layer chromatography. The ^1H NMR spectral assignments in Tables I–III, which were made with the aid of single-frequency decoupling experiments, provide compelling evidence for the structures of these alcohols and their hydroperoxide homologues.



(2)

Sulfones formed by oxidation at sulfur or by intramolecular trapping of a perepoxide intermediate[15] were not observed even under photolysis conditions, which resulted in complete conversion of **10** to **12–14**. The inability, at high effective molarity, of all the sulfoxide groups and in particular the *p*-nitro-substituted allylic sulfoxide, to trap the perepoxide is indicative of the elusive character of this highly reactive intermediate. Clearly, only very rapid reactions[16] can compete with the collapse of the perepoxide to the ene product. This elusive character is consistent with the observation[17] that an interaction between the allylic hydrogens and the pendant oxygen of the perepoxide has already developed in the transition state for its formation.

Table III. ^1H NMR Data for Sulfoxide Oxidation Products **14**[a]

	chemical shift (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
14a	1.47	1.86	3.2–3.4	5.02 5.08	7.2 (9) 7.7 (9)	10.83	3.88
14a′	1.37	1.88	2.90 (13) 3.17 (13)	4.99 5.27	7.13 (9) 7.6 (9)		3.87
14b	1.48	1.86	3.3–3.4	5.03 5.08	7.4 (8) 7.6 (8)	10.80	2.40
14b′	1.38	1.88	2.91 (13) 3.18 (13)	4.99 5.28	7.4 (8) 7.6 (8)	4.80	2.40
14c	1.50	1.87	3.3–3.5	5.03 5.09	7.5–7.8	10.70	
14c′	1.39	1.89	2.92 (13) 3.22 (13)	5.00 5.28	7.5–7.8	4.77	
14d	1.54	1.86	3.37 (14) 3.50 (14)	5.02 5.05	8.01 (9) 8.41 (9)	10.57	
14d′	1.47	1.88	3.05 (13) 3.33 (13)	4.99 5.27	8.0 (9) 8.4 (9)	4.25	

[a] In acetone-d_6 at −78 °C. See eq 2 for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent.

Table IV. Product Ratios in the Reactions of Sulfoxides **10**[a]

compd	**12**	**13 + 14**	**13/14**
10a	73.9	26.1	1/1.2
10b	75.2	24.8	1/1.3
10c	76.2	23.8	1/1.3
10d	78.4	21.6	1/1.4

[a] In acetone-d_6 at −78 °C using Rose Bengal as sensitizer.

Table V. Temperature Effects in the Photooxidation of Sulfoxide **10b**[a]

T, °C	**12b**	**13b + 14b**	**13b/14b**
20	66.7	33.3	1/1.3
−3	67.9	32.1	1/1.2
−31	70.8	29.2	1/1.3
−55	72.4	27.6	1/1.2
−77	75.2	24.8	1/1.3

[a] Temperature ±1 °C.

The para substituents on **10a–d** have minor but noticeable effects on the ratios of the regioisometric allylic hydroperoxides (Table IV). In contrast, the diastereoselectivities **13/14** (1/1.3) are insensitive to the electronic character at sulfur. Temperature has a similar effect on the reactions of **10b** (Table V). Decreasing temperature favors abstraction of the geminal hydrogens but has little or no effect on diastereoselectivity. Solvents, on the other hand, have no effect on the singlet oxidations of **10**. Identical regio- and stereoisomer ratios were obtained in the reactions of **10b** in acetone-d_6, $CDCl_3$, and methanol-d_4.

The alcohols **13d′** and **14d′** were solids, but all attempts to obtain a crystal suitable for X-ray diffraction work failed. Consequently, the relative configurations of the chiral centers in the diastereomers are not known with certainty. We tentatively assign the minor diastereomer, **13**, the R^*S^* configuration and the major diastereomer, **14**, and R^*R^* configuration by comparing the ^1H NMR's of **13** and **14** to the NMR's of chiral β-hydroxy sulfoxides isolated by Solladie[18] and co-workers.

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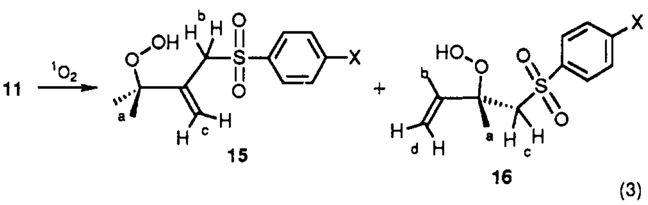
Table VI. ^{1}H NMR Data for Sulfone Oxidation Products **15** and **16**[a]

	chemical shifts (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
15b	1.29	4.04	5.39 5.45		7.48 (9) 7.85 (9)	10.29	2.46
15b′	1.28	4.10	5.10 5.36		7.45 (9) 7.82 (9)		2.45
15c	1.28	4.08	5.40 5.46		7.6–7.8	10.29	
15c′	1.27	4.12	5.10 5.36		7.6–7.8		
16b	1.58	1.76	3.74	4.90 4.93	7.45 (9) 7.85 (9)	10.20	2.45
16b′	1.44	1.65	3.48 (14) 3.65 (14)	4.78 5.13	7.45 (9) 7.82 (9)		2.44
16c	1.59	1.76	3.77	4.90 4.93	7.6–8.0	10.22	
16c′	1.44	1.64	3.50 (15) 3.69 (15)	4.78 5.13	7.6–7.8		

[a] In acetone-d_6 at −78 °C. See eq 3 for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent.

Sulfones. The sulfones **11b** and **c** were also photooxidized in acetone-d_6 at −78 °C. In a very similar reaction to that observed with the sulfoxides **10**, only two regioisomeric ene products **15** and **16** were obtained (eq 3). The ratio **15**/**16** remained constant as a function of extent of reaction. The hydroperoxides were not isolated directly but were first quantitatively reduced with triphenylphosphine to a mixture of the corresponding alcohols **15′** and **16′**. The alcohols were separated by thin-layer chromatography and the spectra of both alcohols and hydroperoxide precursors were assigned with the aid of single-frequency decoupling experiments (Table VI).



(3)

Photooxidations at −78 °C produced a ratio **15**/**16** of 83/17 for both **11b** and **c**. The predominate formation of **15** was previously attributed to a conformational effect in **11**, which places the carbon–hydrogen bond on the methyl group geminal to the sulfonyl group nearest to the preferred perpendicular arrangement relative to the olefinic plane.[19] This reaction complements the irradiation of oxygenated solutions of allyl sulfones in the presence of $Pd(OCOCF_3)_2$, which also results in allylic oxidation and migration of the double bond but with formation of the vinyl sulfone.[20]

Sulfides. Sulfides **6a–d**, **7**, and **8** have two seats of potential reactivity toward singlet oxygen, the sulfur atom and the double bond. The similar rates of reaction of singlet oxygen with substituted thioanisoles[21] (p-OMe, 7.6×10^6; p-Me, 3.1×10^6; p-H, 2.3×10^6 M^{-1} s^{-1}) and with 2,3-dimethyl-2-butene[22] (3.0×10^7 M^{-1} s^{-1}) suggested that oxidation at sulfur and the olefinic linkage would be competitive. This suggestion was verified by examinations of the photooxidations of **6a–d** at low conversions at −80 °C in acetone-d_6.

Table VII. Product Ratios in the Photooxidation of **6b** as a Function of Temperature

		yields[b]		
T, °C	extent of reaction[a]	**17**	**18**	**10**
14	7.9	4.04 (51.1)	3.87 (48.9)	0
−6	19.2	10.6 (55.0)	8.60 (45.0)	0
−29	15.0	8.70 (58.0)	6.30 (42.0)	0
−55	13.7	7.90 (57.5)	4.80 (35.0)	1.0 (7.3)
−78	8.9	3.90 (44.0)	2.20 (24.4)	2.8 (31.6)

[a] % starting material consumed. [b] % of total product in parentheses.

Table VIII. ^{1}H NMR Data for Sulfide Oxidation Products **17**[a]

	chemical shifts (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
17a	1.39	3.68	5.09 5.15		6.9 (9) 7.4 (9)		3.78
17a′	1.37	3.66	4.97 5.20		6.9 (9) 7.4 (9)		3.78
17b	1.39	3.77	5.17 5.20		7.1 (8) 7.3 (8)	10.25	2.30
17b′	1.38	3.74	5.07		7.1 (8) 7.3 (8)		2.3
17c	1.41	3.81	5.20 5.25 (1)		7.1–7.4	10.30	
17c′	1.39	3.78	5.10 (1) 5.22 (1)		7.1–7.4		
17d	1.44	3.99	5.26 5.34		7.54 (9) 8.12 (9)		
17d′	1.42	3.97	5.19 5.28		7.53 (9) 8.12 (9)	4.08	

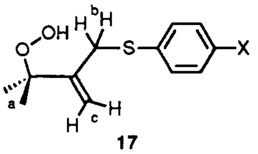
[a] In acetone-d_6 at −78 °C. See structure **17** in the text for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent.

Table IX. ^{1}H NMR Data for Sulfide Oxidation Products **18**[a]

	chemical shifts (δ)[b]						
compd	H_a	H_b	H_c	H_d	H_{Ar}	Y[c]	X[d]
18a[e]				4.95	6.9 (9) 7.4 (9)		3.78
18a′[e]	1.41				6.9 (9) 7.4 (9)		3.78
18b	1.43	1.75	3.26 (12) 3.32 (12)	4.96 5.02	7.1 (8) 7.3 (8)	10.28	2.3
18b′	1.40	1.76	3.17 (12) 3.25 (12)	4.82 5.11	7.1 (8) 7.3 (8)	3.81	2.3
18c	1.43	1.76	3.31 (12) 3.37 (12)	4.97 5.04	7.1–7.4	10.32	
18c′	1.42	1.77	3.20 (12) 3.29 (12)	4.84 5.12	7.1–7.4		
18d	1.49	1.85	3.53 (12) 3.58 (12)	5.00 5.09	7.57 (9) 8.13 (9)		
18d′	1.48	1.82	3.36 (12) 3.44 (12)	4.88 5.17	7.56 (9) 8.12 (9)		

[a] In acetone-d_6 at −78 °C. See structure **18** in the text for proton labeling. [b] Coupling constants in parentheses. [c] Y = OOH or OH. [d] Para substituent. [e] Compound not isolated, NMR taken in reaction mixture, and some peaks obscured.

At less than 10% conversion, photooxidation of the p-Me-substituted **6b** resulted in 68% reaction at the double bond and 32% at sulfur. The reaction at sulfur in comparison to the reaction at the double bond became less important as the temperature of the photooxidation increased (Table VII). This is consistent with the previous observation that with increasing temperature physical quenching of singlet oxygen by sulfides occurs at the expense of chemical reaction. The ene products **17b** and **18b** formed at low conversion were not isolated directly but were reduced with triphenylphosphine to a mixture of the alcohols **17b′** and **18b′**. The alcohols were separated and purified by preparative thin-layer chromatography. Their structures are consistent with their ^{1}H NMR spectra (Tables VIII and IX).



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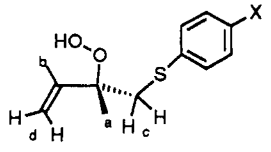

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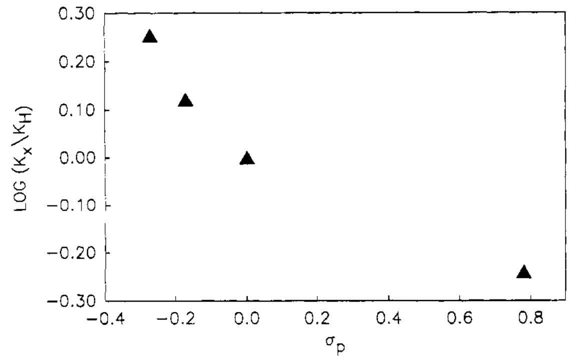


Figure 1. Hammett plot for the reactions of **6** with singlet oxygen.

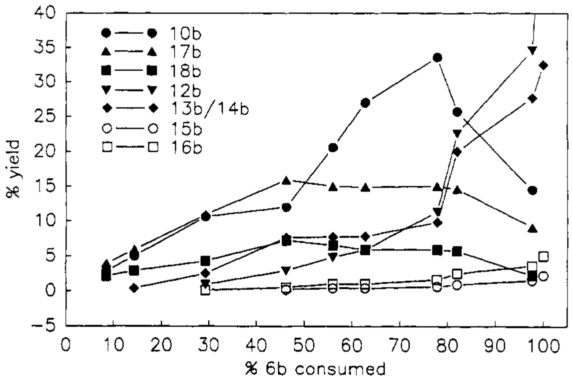


Figure 2. Evolution of reaction components in the reaction of **6b** at −78 °C as a function of **6b** consumed.

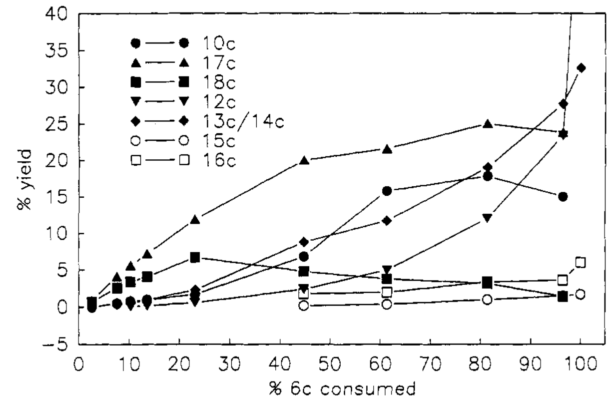


Figure 3. Evolution of reaction components in the reaction of **6c** at −78 °C as a function of **6c** consumed.

Examination of the reaction mixture of the most electron-rich allylic sulfide, **6a**, at 16% conversion revealed that reaction at sulfur increased to approximately 60% with only 40% of the reaction occurring at the double bond. In contrast, photooxidations of the less electron-rich sulfides **6c** and **6d**, at less than 10% conversion, proceeded entirely at the double bond. The nonlinear Hammett plot (Figure 1) for the reactions of these sulfides with singlet oxygen provides additional evidence for the dual reactivity of these substrates.

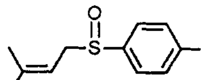
All of the allylic sulfides except for those formed in the reaction of **6d** were susceptible to reaction with a second molecule of singlet oxygen. The *p*-nitro-substituted hydroperoxy sulfides **17d** and **18d** were inert, and oxidation at sulfur was not observed even after 2 h of continuous irradiation. The products of exhaustive photooxidations of the sulfides susceptible to multiple oxidations, **6a–c**, were hydroperoxy sulfoxides **12–14** and hydroperoxy sulfones **15** and **16**. The assignment of all the NMR peaks, before and after reduction with PPh_3, in these complex reaction mixtures was made possible by comparison to the hydroperoxides and isolated alcohols produced in the photooxidations of allylic sulfoxides **10** and sulfones **11**.

In contrast to the reactions of allylic sulfoxides **10** the diastereomer ratios **13/14** in photooxidations of sulfides **6a–c** were a function of extent of reaction. Early in the reaction the diastereomer ratio was greater than 10/1 for **6a**, 13/1 for **6b**, and 20/1 for **6c**. In each case as the reaction proceeded, the diastereomer ratio decreased. Clearly, the immediate precursors to **13** and **14** are the hydroperoxy sulfides **18** rather than allylic sulfoxides **10**, which must produce diastereomer ratios of approximately 1/1.3. Photooxidation of the pure alcohol **18b′** rather than the hydroperoxide **18b** resulted in a remarkable reversal and dramatic decrease in diastereoselectivity (**13b′**/**14b′** = 1/2.3). Photooxidation of sulfide **9**, which also contains a chiral center *β* to sulfur, formed 95% sulfoxide with little diastereoselectivity (1/1.3) and 5% sulfone.

The evolution of the reaction components as a function of percent of **6b** consumed at −78 °C in acetone-d_6 is shown graphically in Figure 2. At the beginning of the reaction only the sulfoxide **10b** and hydroperoxy sulfides **17b** and **18b** were present. As the reaction proceeded the concentrations of the diastereomeric hydroperoxy sulfoxides **13b/14b** increased rapidly despite the fact that isomeric hydroperoxy sulfoxide **12** was the major product upon exhaustive photooxidation.[23] A very similar reaction profile was observed for the reaction of **6c** (Figure 3). The concentrations of the diastereomeric hydroperoxy sulfoxides **13c/14c** increased rapidly, and the concentration of their precursor sulfide, **18c**, peaked early in the reaction.

Increasing reaction temperatures during oxidations of **6** were accompanied by decreasing diastereoselectivity. For example, at −60 °C in $CDCl_3$, acetone-d_6, and CD_3OD, the diastereoselectivity in the reaction of **6b** decreased to 5/1, 7/1, and 2.9/1, respectively. At −29 °C, in acetone-d_6, the diastereoselectivity continued to degrade to 2.7/1, and hydroperoxy sulfoxides **12b** and **13b/14b** were produced at similar rates (see the supplementary material).

Sulfide **7** reacted exclusively at sulfur to give the allylic sulfoxide. Reaction at the electron-poor disubstituted double bond did not occur even after 4 h of irradiation. The trisubstituted double bond in sulfide **8**, however, did react but only after total conversion to the allylic sulfoxide **19**. The ene products **20**, **21**, and **22/23** were formed in the reaction of **19** in a 31/3/66 ratio. Formation of diastereomers **22/23** occurred with little diastereoselectivity (1.2/1) as expected based on our previous work with sulfoxides **10**. The stereochemical assignments of double bond configurations in **20** and **21** were based on the size of the vinyl coupling constants.



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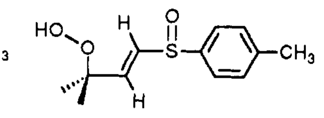

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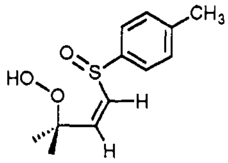

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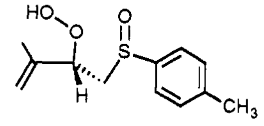

22/23

Discussion

The salient discoveries in this work, which must be explained by any acceptable mechanism for sulfide photooxidation, are the remarkably high diastereoselective oxidations of **18a–c**. The mechanism proposed by Foote[9] to explain the photooxidation of diethyl sulfide in benzene is depicted in Figure 4. The structures of intermediates A and B are not known with certainty; however, trapping experiments demonstrate that A appears to be more nucleophilic than B. It has been suggested that likely candidates for A and B are persulfoxide **2** and thiadioxirane **3**, respectively. Both of these intermediates are chiral,[24] and as a result the

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(23) At −78 °C, sulfide **1b** upon exhaustive photooxidation produced 60.3% **12**, 32.5% **13/14**, 2.2% **16**, and 5.0% **17**.

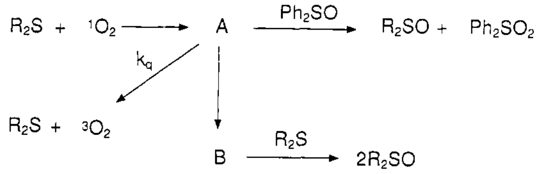


Figure 4.

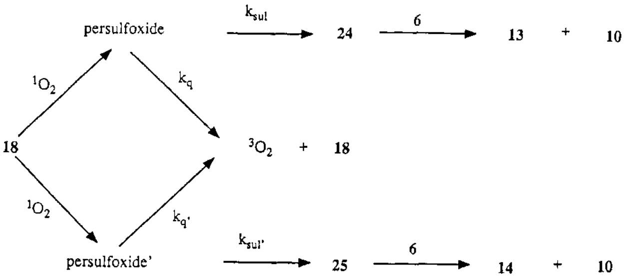
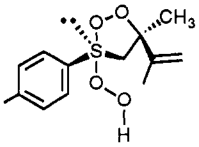


Figure 5.

diastereoselectivity observed during photooxidation of **18a–c** could reflect energy differences in diastereomeric intermediates A and/or B or in the transition states for their formation or reaction.

The dramatic decrease in magnitude and reversal of diastereoselectivity in the alcohol **18b′** in comparison to hydroperoxide **18b** is difficult to rationalize within the context of the Foote mechanism. We suggest that the unique feature of the hydroperoxide is its ability to form energetically very favorable 5-membered ring sulfuranes **24** and **25**. The diastereoselection observed in the reactions of **18** reflect the energy difference between **24** and **25**. Sulfurane **24** upon reaction with a reducing agent would produce the predominant stereoisomer formed in the photooxidation of **18**, the R^*S^* diastereomer **13**. Examination of molecular models demonstrates that only in **24** is it possible to simultaneously place the large phenyl and isopropenyl in unencumbered positions in an envelopelike conformation. The greater stability of **24**, with the large phenyl and isopropenyl groups cis, is also consistent with thermochemical data,[25] which indicate that cis 1,3-disubstituted cyclopentanes are more stable than their trans isomers. Pseudorotation of **24** to form **25** is expected to be energetically inaccessible.[26] This conformational interconversion must proceed via an unstable sulfurane with an apical lone electron pair.



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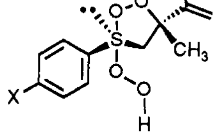

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Two mechanisms of sulfide photooxidation that utilize these sulfuranes as key intermediates warrant discussion. The first mechanism, depicted in Figure 5, is a stepwise mechanism involving initial formation of diastereomeric persulfoxides, which collapse to the sulfuranes in competition with loss of oxygen. The second mechanism, depicted in Figure 6, invokes single-step or concerted formations of the sulfuranes.

In both mechanisms reduction of the sulfuranes convert these intermediates into the hydroperoxy sulfoxide products. In the very early stages of the photooxidation, when the very high diastereoselectivities are observed, the most predominate reducing agent in solution is starting sulfide **6**. Conversion of **6** in this process to sulfoxide **10** is ultimately responsible for the degrading diastereoselectivity as the reaction proceeds. At the same time, however, the abundance of sulfide **6** prevents the potentially nondiastereoselective reduction with **18** (Figure 6) from occurring.

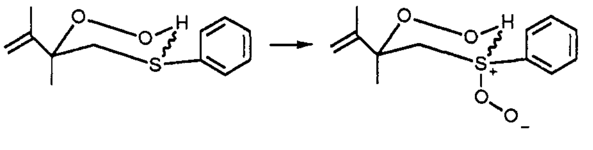
The absence of substantial diastereoselectivity in the reactions of hydroxy sulfide **18b′** and sulfide **9** with singlet oxygen and the large distance between the chiral center and sulfur suggest that formations of persulfoxides are not selective. Therefore, if the stepwise mechanism (Figure 5) is operating, diastereoselectivity relies on the differential partitioning of the two persulfoxides toward loss of oxygen and sulfurane formation. If $k_{\mathrm{sul}}/k_{\mathrm{q}} = k_{\mathrm{sul}'}/k_{\mathrm{q}'}$ or if $k_{\mathrm{q}} = k_{\mathrm{q}'} = 0$, no diastereoselectivity would be observed. Since it is likely that $k_{\mathrm{q}} = k_{\mathrm{q}'}$, the diastereoselectivity is a function of the relative magnitudes of steric interactions in the transition states for sulfurane formation. In order for the concerted mechanism (Figure 6) to be diastereoselective, the rates of formation k_{csul} and $k_{\mathrm{csul}'}$ must be different. In the concerted mechanism physical quenching to recycle one of the diastereomers does not need to occur.

The observation of diastereoselectivity at low temperatures were physical quenching is expected to be unimportant argues for the concerted mechanism. Anchimerically assisted oxidation of **18** is also consistent with the rapid formation of hydroperoxy sulfoxides **13**/**14** from **18** in comparison to the rather slow formation of hydroperoxy sulfoxide **12** from **17**.

The decrease in diastereoselectivity with increasing temperature can either reflect (1) convergence of the rates of sulfurane formation at higher temperatures (Reactions with rate ratios of 20/1 and 13/1 at −80 °C would have rate ratios of approximately 7/1 and 5/1, respectively, at 25 °C.) or (2) the unfavorable entropy of activation for sulfurane formation. Akasaka and Ando[27] used an oxygen-18 tracer study to demonstrate that at room temperature an intermediate in the oxidation of dimethyl sulfoxide by dimethyl persulfoxide did not form a cyclic sulfurane intermediate.

The larger decrease in diastereoselectivity at −60 °C in CD_3OD in comparison to acetone-d_6 and $CDCl_3$ is the result expected in a hydroxylic solvent if external anchimeric assistance competes with internal assistance from the hydroperoxy group.

An alternative explanation that the diastereoselectivity is a result of hydrogen bond directed oxidation (eq 4) is unlikely. An intramolecular hydrogen bond would decrease the electron density on sulfur and would be expected to slow down the reaction of singlet oxygen with **18** in comparison to **17**, contrary to what is experimentally observed. Formation of the much stronger[28] intermolecular hydrogen bond with acetone-d_6 is also expected to occur in preference to formation of the weaker intramolecular O···H···S[29] hydrogen bond. The downfield chemical shift of the hydroperoxy proton in **18b** (δ 10.28) is consistent with a strong hydrogen bond. That this hydrogen bond is not intramolecular is verified by observing a 1.17 ppm upfield shift for the hydroperoxy proton in $CDCl_3$ (δ 9.11) where intramolecular hydrogen bonding is still possible.[30] In addition, the very similar diast-



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[24] The thiadioxirane 3 is chiral if the oxygens occupy one apical position and one equatorial position in a trigonal-bipyramidal structure, as seems likely.

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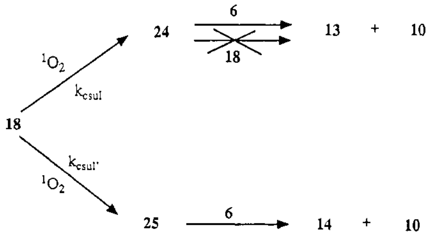

Figure 6.

ereoselectivities observed in the oxidation of **6b** at −60 °C in $CDCl_3$ and acetone-d_6 is inconsistent with an important role for hydrogen bonding.

Conclusion

Diastereoselective singlet oxidations of several sulfides are reported when a hydroperoxy group is attached to a chiral center β to sulfur. Hydrogen, alkyl, or hydroxyl groups bound to the β carbon, however, are unable to stereoselectively direct oxidation at sulfur. The unique behavior of the hydroperoxy group is attributed to its ability to anchimerically assist oxidation at sulfur via a favorable sulfurane-like transition state.

Work is currently in progress to provide additional examples of anchimerically assisted photooxidations at sulfur with other heteroatoms.

Experimental Section

Preparative gas chromatographic separations were carried out on a GOW-MAC Series 550 thermal conductivity gas chromatograph utilizing a 0.25 in. × 10 ft column packed with 20% Carbowax 20M on NAW Chromosorb W 80/100. Chromatographic separations were carried out on a Harrison Research Model 7624T chromatotron using plates coated with EM Science 7749 silica gel $60PF_{254}$.

^1H and ^{13}C NMR spectra were obtained on a JEOL FX270 at 270 and 67.83 MHz, respectively, and the chemical shifts, referenced to Me_4Si. Product ratios in Table IV, V, and VII and in Figures 2 and 3 were determined by cutting and weighing expanded portions of the NMR reaction mixtures. These values are accurate to within ±3%.

Rose Bengal, tetraphenylporphyrin, 2-ethylhexyl bromide, 1-bromo-3-methyl-2-butene, CD_3OD, *N*-bromosuccinimide, triphenylphosphine, isobutenyl chloride, *p*-methylthiophenol, thiophenol, *p*-methoxythiophenol, *p*-nitrothiophenol, *m*-chloroperbenzoic acid, and tetramethylethylene were obtained from Aldrich and used without further purification. Reagent-grade benzoyl peroxide was obtained from Fisher Scientific and used as received. The sodium salts were prepared according to a literature procedure.[31] $CDCl_3$ (99.8% atom D) and acetone-d_6 were obtained from Aldrich Chemical Co. and were dried over 4A molecular sieves before use. CCl_4 was purified by distillation from P_2O_5 and hexane and ethyl acetate by simple distillation.

1-Bromo-2,3-dimethyl-2-butene, 2,3-dimethyl-2-butenyl *p*-methylphenyl sulfide (**6b**), 1-[(4-methylphenyl)sulfinyl]-2,3-dimethyl-2-butene (**10b**), and 1-[(4-methylphenyl)sulfonyl]-2,3-dimethyl-2-butene (**11b**) were made as previously reported.[13]

2,3-Dimethyl-2-butenyl *p*-methoxyphenyl sulfide (6a) was synthesized by the method previously reported for **6b**.[13] It was purified by preparative gas chromatography; 87% yield. ^1H NMR ($CDCl_3$): δ 1.41 (s, 3 H), 1.62 (s, 3 H), 1.77 (s, 3 H), 3.46 (s, 2 H), 3.79 (s, 3 H), 6.80 (d, J = 9 Hz, 2 H), 7.33 (d, J = 9 Hz, 2 H).

2,3-Dimethyl-2-butenyl phenyl sulfide (6c) was synthesized by the method previously reported for **6b**.[13] It was purified by vacuum distillation prior to final purification by preparative gas chromatography; bp 91 °C (0.4 mmHg), 92% yield. ^1H NMR ($CDCl_3$): δ 1.56 (s, 3 H), 1.65 (s, 3 H), 1.78 (s, 3 H), 3.58 (s, 2 H), 7.14–7.36 (m, 5 H).

2,3-Dimethyl-2-butenyl *p*-nitrophenyl sulfide (6d) was synthesized by adding 165 mg (1.01 mmol) of tetramethylethylene bromide to a solution of 155 mg (1.00 mmol) of *p*-nitrophenol and 54 mg (1.00 mmol) of sodium methoxide in 10 mL of absolute ethanol. This solution was stirred for 1 h at room temperature. The solvent was removed at reduced pressure, and the residue was dissolved in ether, washed with water, and dried over $MgSO_4$. The compound was purified by recrystallization from hexane; mp 67–68 °C; 85% yield. ^1H NMR ($CDCl_3$): δ 1.71 (s, 3 H), 1.75 (s, 3 H), 1.80 (s, 3 H), 3.71 (s, 2 H), 7.32 (d, J = 9 Hz, 2 H), 8.11 (d, J = 9 Hz, 2 H).

2-Ethylhexyl 4-methylphenyl sulfide (9) was synthesized by adding 1.13 g (5.8 mmol) of 2-ethylhexyl bromide to a solution of 1.03 g (7.1 mmol) of sodium 4-methylthiophenoxide in 20 mL of absolute ethanol. This mixture was stirred and refluxed for 1 h followed by removal of the solvent at reduced pressure. The product was dissolved in 30 mL of ether, washed with water, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give 1.28 g, 93% yield, of product. The product was purified by preparative gas chromatography (column temperature 190 °C, He flow rate 80 mL/min, retention time 22 min). ^1H NMR: δ 0.86 (t, J = 7 Hz, 3 H), 0.88 (t, J = 7 Hz, 3 H), 1.27 (m, 4 H), 1.43 (m, 4 H), 1.53 (m, 1 H), 2.31 (s, 3 H), 2.86 (d, J = 6 Hz, 2 H), 7.08 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 10.7 (q, J = 125 Hz), 14.1 (q, J = 124 Hz), 21.0 (q, J = 125 Hz), 23.0 (t, J = 125 Hz), 25.5 (t, J = 125 Hz), 28.7 (t, J = 123 Hz), 32.2 (t, J = 125 Hz), 38.8 (t, J = 138 Hz), 38.9 (d, J = 125 Hz), 129.4 (d, J = 160 Hz), 129.5 (d, J = 160 Hz), 133.8 (s), 135.6 (s).

2-Methyl-2-propenyl 4-methylphenyl sulfide (7) was synthesized by the method of Kwart and Johnson.[32] ^1H NMR ($CDCl_3$): δ 1.82 (s, 3 H), 2.28 (s, 3 H), 3.53 (s, 2 H), 4.76 (s, 1 H), 4.79 (s, 1 H), 7.11 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H).

1-[(4-Methylphenyl)sulfinyl]-2-methylpropene[33] was synthesized by singlet oxidation of **7**. ^1H ($CDCl_3$): δ 1.81 (s, 3 H), 2.41 (s, 3 H), 3.37 (d, J = 12 Hz, 1 H), 3.54 (d, J = 12 Hz, 1 H), 4.82 (s, 1 H), 5.02 (s, 1 H), 7.31 (d, J = 8 Hz, 2 H), 7.52 (d, J = 8 Hz, 2 H).

3-Methyl-2-butenyl 4-methylphenyl sulfide (8) was synthesized in 84% yield by the method utilized for its 4-phenyl analogue.[34] The product was purified by elution on a chromatotron with hexane followed by preparative gas chromatography (column temperature 180 °C, He flow rate 80 mL/min, retention time 17 min). ^1H NMR ($CDCl_3$): δ 1.55 (s, 3 H), 1.70 (s, 3 H) 2.31 (s, 3 H), 3.49 (d, J = 8 Hz, 2 H), 5.39 (d, J = 8 Hz, 1 H), 7.08 (d, J = 8 Hz, 2 H), 7.25 (d, J = 8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 17.6 (q, J = 125 Hz), 21.0 (q, J = 127 Hz), 25.6 (q, J = 127 Hz), 32.9 (t, J = 140 Hz), 119.5 (d, J = 159 Hz), 129.4 (d, J = 157 Hz), 130.5 (d, J = 162 Hz), 132.9 (s), 136.0 (s), 136.1 (s).

1-[(4-Methylphenyl)sulfinyl]-3-methyl-2-butene[35] was synthesized by addition of 5 mL of CH_2Cl_2 solution of 180 mg of 85% MCPBA to 10 mL of CH_2Cl_2 containing 160 mg of **8** at 0 °C and stirring for 20 min. This mixture was poured into 10 mL of 10% aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer extracted with three 5-mL portions of ether. The combined organic layer was washed with saturated NaCl and dried with $MgSO_4$. The solvent was removed under reduced pressure to give 120 mg (69% yield) of the sulfoxide, which was purified by hexane/ethyl acetate (9/1) elution on a chromatotron plate. ^1H NMR: δ 1.44 (s, 3 H), 1.70 (s, 3 H), 2.40 (s, 3 H), 3.51 (m, 2 H), 5.06 (m, 1 H), 7.30 (d, J = 8 Hz, 2 H), 7.49 (d, J = 8 Hz, 2 H). ^{13}C NMR: δ 18.0 (q, J = 125 Hz), 21.4 (q, J = 125 Hz), 25.8 (q, J = 127 Hz), 56.6 (t, J = 139 Hz), 111.1 (d, J = 159 Hz), 124.4 (d, J = 164 Hz), 129.5 (d, J = 160 Hz), 140.1 (s), 141.3 (s), 141.9 (s).

Rate Constant Determinations. The rate constants for the reactions of 2,3-dimethyl-2-butenyl aryl sulfides were obtained in oxygen-saturated acetone solutions containing 2.04×10^{-5} M Rose Bengal. The kinetic apparatus consisted of (a) a Spectra-Physics DCR11 Nd:YAG pulsed laser with second and third harmonic (532 and 355 nm) capability, which delivers 10-ns pulses at rates up to 10 pps, (b) a germanium (Judson 2- or 5-mm ϕ) diode detector/customized preamplifier, (c) various optic, the most important of which is a 10-nm narrow band-pass nonfluorescing filter centered at 1.27 μm placed just ahead of the detector, (d) a 100-MHz LeCroy transient digitizer/signal averager interfaced to a 80386 based PC/AT computer, and (e) energy meter. Since the experimental decay is a convolution of the detector response (fwhm of approximately 10 μs for the 5-mm ϕ-detector and 5 μs for the 2-mm ϕ-detector) and the sample decay, it was necessary to implement a numerical deconvolutional analysis in order to accurately extract measured lifetimes 2 μs $\leq \tau \leq$ 100 μs from the recorded data. With this treatment lifetimes as low as 2 μs for certain nondeuterated solvent–sensitizer–amine combinations were available. The numerical deconvolution analysis of Demas[36] for exponential decays that also corrects artifacts caused by scattered excitation light that may reach the detector was used. This analysis was

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implemented on our laboratory computer using a general scientific/engineering analysis/data acquisition program called ASYST. Signal averaging 100 experiments, each with laser pump energies ≤5 mJ gave 8192 point decay curves, each of which produced pseudo-first-order rate constants with correlation coefficients (square root) better than 0.99.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

Supplementary Material Available: The data used to generate Figures 1 and 2 and time evolution data and plots for the photooxidation of **1b** in acetone-d_6 at −29 °C, in $CDCl_3$ at −60 °C, and in CD_3OD at −60 °C (12 pages). Ordering information is given on any current masthead page.

Photochemistry and Photophysics of Purine Free Base and 6-Methylpurine

E. Quiñones and R. Arce*

Contribution from the Department of Chemistry, University of Puerto Rico, Río Piedras, Puerto Rico 00931. *Received June 23, 1988. Revised Manuscript Received June 20, 1989*

Abstract: A comprehensive study of the photochemistry and photophysics of purine free base and 6-methylpurine has been carried out. The presence of the purine triplet state was determined by using the energy-transfer technique for sensitizing the crocetin triplet. The purine triplet quenching rate coefficients have been determined to be 7.1×10^9, 3.4×10^9, and 2.0×10^8 M^{-1} s^{-1} for crocetin (C), O_2, and Mn^{2+}, respectively. The decay time of the triplet under deoxygenated conditions and the triplet–triplet (T–T) molar absorption coefficient at 390 nm are, respectively, 1.7 μs and $(2.0 \pm 0.5) \times 10^3$ M^{-1} cm^{-1}. The intersystem crossing rate constant obtained from picosecond laser experiments, 1.4×10^8 s^{-1}, allowed an estimate of the singlet excited state (S_1) decay time, 7 ns, in favorable agreement with the value of the fluorescence decay time, 5 ns, obtained from single photon counting experiments. Photoionization of the purines was observed at an excitation energy of 4.7 eV, which is lower than their gas-phase photoionization energy. The purine radical cation was produced by oxidation of the purine by radiolytically generated azide radical. Its absorption maximum appears at 290 nm. The purine anion radical, which was generated from the radiolytically produced carbon dioxide radical anion, had an absorption band maximum and decay time of 275 nm and 16 μs, respectively. An intermediate species resulting from a fast reaction of the radical anion is postulated to account for the formation of the band at 320 nm. The electron scavenging rate coefficient for purine is 2.9×10^{10} M^{-1} s^{-1}.

Excellent reports describing the physical properties of the electronic states of purine bases are readily available.[1-8] However, the reactivity and dynamics of the electronically excited purines, especially in aqueous solutions, have not been studied to the same extent. Perhaps the extremely low emission yields of purines at 300 K and the lack of structure in their ground-state absorption spectra observed in aqueous solutions have discouraged this type of study. Traditionally, purine bases have been regarded as photochemically inert.[9] Nonetheless, it has been established that they are photochemically reactive[10-14] in recent reports. In the case of purine free base, Connolly[15] and Arce et al.[16] have made qualitative assignments of the transient absorption bands. No kinetic or quantitative data on reaction rates or excited-state parameters were reported, nor were the identities of the transient species definitely established. Under low- and high-pH conditions, the photoionization of the purine was postulated[16] to proceed through a purine triplet excited state and the presence of the purine radical cation and radical anion was inferred from an increase in absorbance.

Low-temperature UV–visible absorption and electron paramagnetic resonance techniques have been used[17-19] to characterize and quantify the intermediates produced during the continuous UV irradiation of purine free base in acid, neutral, and basic aqueous glasses at 77 K. A biphotonic ionization of the base through a triplet intermediate was established as one of the principal photodestruction paths in basic and neutral glassy solutions.

From the photochemical standpoint, we found it interesting that the title purines have three singlet excited-state components that are almost isoenergetic and oriented perpendicularly to each other: namely, two (π, π^*) and the (n, π^*)[5] states. Furthermore, theoretical works predict the participation of the (π, π^*) and Rydberg states,[1] as well as vibronic–electronic coupling that assists intersystem crossing processes[20] in this family of compounds. Mixing of these electronic states could lead to different photophysical processes as manifested by this work.

In this paper we report a study on the identification of the purine free base and 6-methylpurine intermediate species produced in aqueous media by 266-nm laser flash photolysis. A goal of our research is to provide kinetic data leading to the description of photophysical processes such as intersystem crossing, triplet and singlet state decay times, energy-transfer processes, and photoionization. Some of the reactive intermediate species have been

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