J. Org. Chem. 1992, 57, 6478–6487

NMR Spectra. Purified chloroform was added in appropriate amounts as such, or containing TBAB and/or Br$_2$, to acetonitrile-d_3 solvent (Aldrich, 99.5 atom % D). Spectra were run on a Bruker AC 200 instrument, the reproducibility of chloroform chemical shift being ±0.022 Hz.

Kinetic Measurements. Solutions of Br$_2$ and *cis-* or *trans-*stilbene in chloroform were prepared shortly before use, protected from the light, and mixed in appropriate amounts. The bromine disappearance was followed at 380, 410, and 480 nm on a Cary 2200 spectrophotometer. The absorbance/time data were fitted to the third-order or pseudo-second-order rate equation.

Bromination Procedure and Product Analyses. Chloroform solutions of *cis-* and *trans-*stilbenes **1** and **2** were mixed with bromine solutions in various ratios, the reagent concentrations after mixing being reported in Table II. The reaction mixtures were allowed to react in the dark at 25 °C for times ranging between 1 h and 2 days. The solutions were directly analyzed by HPLC (Waters 600 E, equipped with diode array detector), the yields being calculated by addition of *erythro*-1,2-dibromo-1-phenylpropane as standard[21] using a 25-cm Hypersil 70 C18 column, with methanol/water 72:28 v/v as the eluent at a flow rate of 1.2 mL/min. For each run reported in Table II *trans*-1,2-dichloroethylene was added at concentrations equal to that of **1**. No isomerization to the cis isomer was ever observed by HPLC analysis. The stability of dibromides **3** and **4** in CHCl$_3$ in the presence of Br$_2$ was also checked by exposing chloroform solutions of each dibromide to bromine concentrations varying in the range reported in Table II. Both pure dibromides were quantitatively recovered even after several days. The dibromide distributions reported in Table II are the averages of at least triplicate runs and were reproducible to ±3%, whereas the **2**:(**3** + **4**) ratios were reproducible to ±15% of the quoted values.

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Registry No. **1**, 645-49-8; **2**, 103-30-0; Bu$_4$N$^+$Br$^-$, 1643-19-2; Bu$_4$N$^+$Br$_3^-$, 38932-80-8; Bu$_4$N$^+$Br$_5^-$, 117040-00-3.

Supplementary Material Available: Tables containing the Br$_2$ and TBAB concentrations of the chloroform solutions used in the spectrophotometric measurements (Table A), all the measured data (wavelength, concentrations, absorbances, optical path) used in the determination of the equilibrium constants and spectral parameters relative to species involved in eqs 1 and 2 (Table B), and the calculated extinction parameters of TBAT and TBAP in chloroform in the 250–420-nm range (Table C) (10 pages). This material is contained in many 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.

Reaction of Organic Sulfides with Singlet Oxygen. A Theoretical Study Including Electron Correlation

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The reaction of H$_2$S and (CH$_3$)$_2$S with ^{1}O$_2$ has been reinvestigated with ab initio methods including electron correlation. While only a peroxy sulfoxide is an intermediate at the Hartree–Fock level of theory, a second intermediate, a thiadioxirane, is found at the MP2 level. The computational results suggest that these two intermediates are almost isoenergetic in the gas phase, but the peroxy sulfoxide may be slightly favored in solution. MP2/6-31G* vibrational frequencies are calculated for both species, and it is possible that a previously observed intermediate may be the thiadioxirane. The transition structures for the formation of the peroxy sulfoxide and for interconversion between the two intermediates have also been located. The peroxy sulfoxide formation is calculated to be entropy controlled, in agreement with experimental data. Interconversion between the two intermediates is calculated to have an activation energy close to 20 kcal/mol, inconsistent with the previously accepted reaction mechanism.

Introduction

The photooxidation of organic sulfides is probably one of the mechanistically most complex reactions of singlet oxygen studied so far.[1,2] The overall reaction is oxidation of the sulfide to sulfoxide and sulfone, and the former is usually the major product. The limiting quantum yield is two; i.e., each molecule of singlet oxygen results in 2 mol of sulfoxide.[3,4] Early studies showed that a reactive intermediate could act as an oxidizing species toward trapping agents such as diphenyl sulfide and diphenyl sulfoxide.[3-6] A peroxy sulfoxide structure ("persulfoxide") was tenatively assigned to this intermediate. Later it was found by competitive trapping studies that different kinetic schemes were observed in protic and aprotic solvents. In protic solvents a single intermediate is sufficient for explaining the kinetic data, while a scheme involving two different intermediates were suggested for aprotic solvents.[4,6] Trapping studies indicate that an oxygen-transfer agent acts as an electrophile toward phenyl sulfides,[7,8] while the intermediate that can be intercepted by phenyl sulfoxides is nucleophilic.[5] The structures of the inter-

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(1) (a) Schench, G. O.; Krausch, C. H. *Angew. Chem.* **1962**, *74*, 510. (b) Ando, W. In *Singlet Oxygen*; CRC Press: Boca Raton, 1984; Vol III, Part 2, p 1.

(2) For other related work see: (a) Miyke, A.; Tomoeda, M. *J. Chem. Soc., Chem. Commun.* **1970**, 240. (b) Adam, W.; Liu, J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 73. (c) Corey, E. J.; Quannes, C. *Tetrahedron Lett.* **1976**, 4263. (d) Burgess, E. M.; Zoller, U.; Burger, R. L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1128. (e) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478. (f) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 494. (g) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787.

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(5) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947.

(6) (a) Clennan, E. L.; Wang, D.-X.; Yang, K.; Hodgson, D. J.; Oki, A. R. *J. Am. Chem. Soc.* **1992**, *114*, 3021. (b) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, *114*, 3015.

(7) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677.

(8) (a) Kasher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765. (b) Monroa, B. M. *Photochem. Photobiol.* **1979**, *29*, 761. (c) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191.

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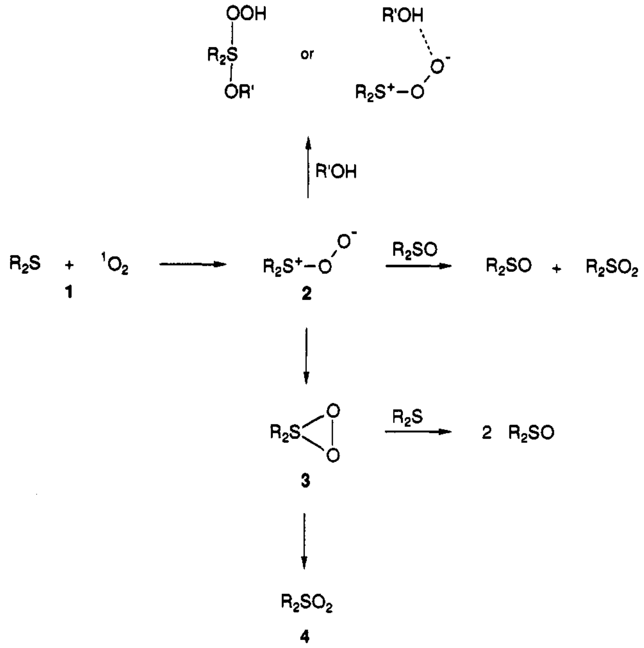
Scheme I



mediates in aprotic solvents are often assigned to be a peroxy sulfoxide (2) and a thiadioxirane (3). The reaction scheme suggested by Foote and co-workers involves an initial peroxy sulfoxide formation, which, depending on the conditions, can either rearrange to the thiadioxirane or transfer an oxygen atom to a suitable trapping agent.[4] The thiadioxirane can also act as an oxidizing species or it can rearrange unimolecularly to the sulfone as shown in Scheme I. Isotopic tracer studies involving ^{18}O have shown that the oxygen transfer to dimethylsulfoxide occurs via a linear oxygen configuration, consistent with a peroxy sulfoxide geometry.[9] In protic solvents the peroxy sulfoxide may be stabilized by hydrogen bonding or by actual solvent addition to form a sulfurane. Experimental results from photooxygenation of hydroxy sulfides showed that the hydroxy oxygen atom can be transferred to the sulfone group, strongly suggesting formation of a sulfurane, at least in this particular system.[10]

Additional experiments have shown that product formation is very efficient in protic solvents (i.e., almost all the generated $^1O_2$ results in products in CH_3OH) while physical quenching dominates in aprotic solvents (product formation accounts for only a few percent of $^1O_2$).[3,11,12] The physical quenching in aprotic solvents is reduced by lowering the temperature[3,6a,11] (i.e., the product-forming reaction has an apparent negative activation energy[7,13] and is entropy controlled). The ratio of sulfone to sulfoxide product increases with decreasing sulfide concentration, and by running the reaction in aprotic solvents.[3,6a,10] These facts are consistent with the reaction sequence in Scheme I if a (small) positive activation energy is assumed for the conversion of the peroxy sulfoxide to the thiadioxirane. Protic solvents stabilize the peroxy sulfoxide energetically, effectively preventing the back-dissociation to sulfide and ground-state oxygen (physical quenching), and disfavor the rearrangement pathway leading ultimately to the sulfone product. Lowering the temperature stabilizes the peroxy sulfoxide entropically relative to the reactants, and if trapping is inefficient (low concentration), unimolecular rearrangement to the sulfone (via the thiadioxirane) may become competitive.

Although the sulfone usually is a minor product in the reaction it provides important mechanistic information. Watanabe, Kuriki, Ishiguro, and Sawaki (WKIS) have recently shown that if a sulfide is photooxidated in a mixture of $^{36}O_2$ and $^{32}O_2$, the majority of the sulfone product contains either two or no ^{18}O atoms.[7] Even at 65% conversion almost all (96%) of the sulfone is doubly labeled when the sulfide is phenyl methyl sulfide, results which suggest that most of the sulfone is formed by a unimolecular pathway.[14] The high percentage of doubly labeled sulfone is surprising since sulfoxides have been shown to be efficient traps for an intermediate, producing sulfones as the product.[3-5,6a,9,12] With the employed conditions (0.01 M phenyl methyl sulfide in benzene, 65% conversion) the sulfoxide concentration should become high enough that sulfone formation via trapping of the intermediate, and thus isotope scrambling, should occur.[12] It is difficult to reconcile this result with other sulfoxide trapping experiments.[3-5,6a,9,12]

If the sulfone mainly is formed unimolecularly, rearrangement of a thiadioxirane would be an attractive pathway; however, it was also shown[7] that the yield of sulfone is independent of the addition of diphenyl sulfoxide,[15] which traps the peroxy sulfoxide. This is inconsistent with a sequential formation of the thiadioxirane from the peroxy sulfoxide and suggests that the two intermediates are formed directly from the reactants by independent pathways. Furthermore, addition of coordinating solvents like DMSO, DMF, or HMPA, or the use of acetonitrile as a solvent instead of benzene, increases the rate of chemical conversion for the sulfoxide product but has no effect on the sulfone formation. This is again indicative of two separate mechanisms for product formation, with the sulfone-generating intermediate being the less polar.[16] Another observation which appears incompatible with Scheme I is that the sulfone/sulfoxide ratio decreases with increasing conversion in the early stages of the reaction (conversion up to a few percent).[7,17] Finally the sulfone/sulfoxide ratio at low conversion was found to be *independent* of initial sulfide concentration,[7] in contrast to results by Foote and Peters.[3] This indicates that the dialkyl sulfide does not trap a sulfone-generating intermediate and does not increase the yield of sulfoxide either! *Addition of diphenyl sulfoxide, however, increases* the sulfoxide formation by intercepting an intermediate.

There is conflicting evidence regarding the temperature dependence of the sulfone/sulfoxide ratio. Foote and Peters originally found that the ratio changes from 1:1 at −78 °C to 1:50 at 25 °C (0.02 M diethyl sulfide in ether),[3] findings that have been substantiated recently by Clennan

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[9] Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203.

[10] (a) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044. (b) Clennan, E. L.; Yang, K.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5251. (c) Clennan, E. L.; Yang, K. *J. Org. Chem.*, in press.

[11] Gu, C.-L.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 6060.

[12] Cauzzo, G.; Gennari, G.; Re, F. D.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541.

[13] Clennan, E. L.; Oolman, K. A.; Yang, K.; Wang, D.-X. *J. Org. Chem.* **1991**, *56*, 4286.

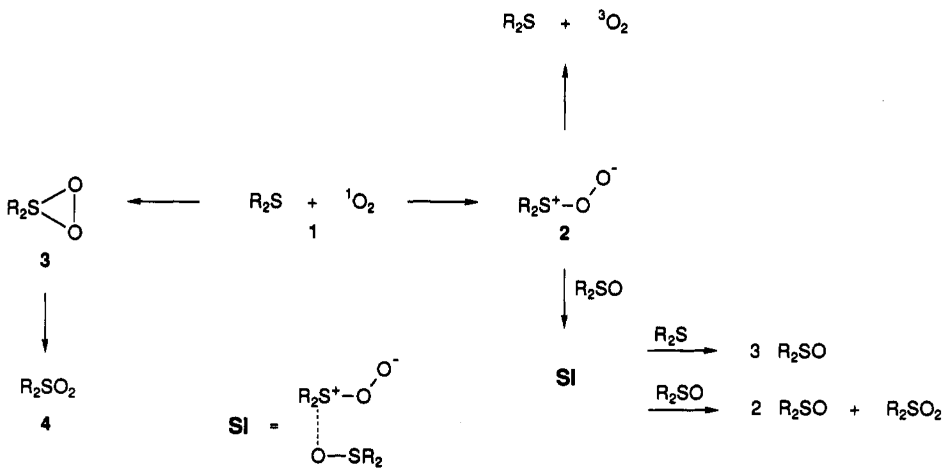
[14] The sulfone can also be formed by sulfoxide trapping of the peroxysulfoxide, which is a bimolecular process.

[15] Addition of diphenyl sulfoxide increases the chemical yield of sulfoxide; thus, it competes with physical quenching for a common intermediate.

[16] The only experimental evidence that suggests an intermediate in the formation of the sulfone product is the observation by Foote and Peters (ref 3) that low sulfide concentration increases the yield of sulfone. This has been challenged by WKIS (ref 7); i.e., it is a possibility that the sulfone is formed directly from the reactants, although this would stride against common chemical intuition.

[17] At higher conversions (>10%) the sulfone/sulfoxide ratio increases with increasing conversion, since sulfone production by trapping with sulfoxide then becomes significant; see ref 12.

Scheme II



et al.[6a] In the report by WKIS the relative yield of sulfone *increases* upon going from 0 to 60 °C, the ratio changes from 1:10 to 10:1 over the temperature range (octyl methyl sulfide in benzene).[7] The latter experiments gave apparent activation energies of −9.9 and +3.6 kcal/mol for the formation of sulfoxide and sulfone, respectively.

In order to explain these results WKIS proposed Scheme II for aprotic solvents.[18]

The important changes from the scheme proposed by Foote and co-workers are as follow: (1) The sulfone product is mainly formed by a separate reaction pathway. The sulfone-forming reaction is insensitive to addition of trapping agents, indicating that the conversion from thiadioxirane to sulfone is facile.[16] (2) The peroxy sulfoxide can dissociate to sulfide and ground-state oxygen (quenching) or undergo reactions with sulfoxides, but trapping with formation of sulfone product is assumed *not* to be a major pathway (this would give isotope scrambling when $^{36}O_2/^{32}O_2$ is used). (3) The secondary intermediate (**SI**) in aprotic solvents is formed by coordination of a sulfoxide or other coordinating species.[19] This secondary intermediate can then oxidize the sulfide substrate to produce sulfoxides. This feature explains that the sulfoxide/sulfone ratio increases as the reaction proceeds, since the sulfoxide-forming reaction is self-catalyzed. One may then ask how any sulfoxide is formed at all, since the formation of sulfoxides requires the presence of a sulfoxide! In order to remedy this it has to be assumed that either the peroxy sulfoxide can to a small extent oxidize the sulfide directly or the sulfone product can act as the coordinating species for the peroxy sulfoxide. The first alternative, interception by the starting material, cannot be a major pathway since sulfides do not compete with physical quenching. The latter alternative could be accessed experimentally by observing the effect of adding a sulfone to the reaction; this should increase the yield of sulfoxide and reduce the amount of physical quenching.

The scheme also includes the behavior in protic solvents as a limiting case, i.e., if the solvent can coordinate or add to the peroxy sulfoxide, then the secondary intermediate is formed very fast and quenching is inhibited; i.e., in protic solvents only the secondary intermediate is chemically active, capable of oxidizing both sulfides and sulfoxides. While a peroxy sulfoxide coordinated by sulfoxide or sulfone is a reasonable structure for the secondary intermediate in aprotic solvents, a sulfurane where actual solvent addition has taken place becomes an attractive structure in protic solvents.[10]

In contrast to these experimental data, a theoretical investigation of the reaction of H_2S and $(CH_3)_2S$ with $^1O_2$ by Foote and the present author gave the unexpected conclusion that only a peroxy sulfoxide appeared to be a stable intermediate on the potential energy surface (PES).[20] The theoretical level employed in this study consisted of geometry optimizations at the HF/3-21G(*) level and single-point calculations including electron correlation via the Møller–Plesset perturbation expansion using basis sets up to 6-311G(2d). Despite an extensive search no thiadioxirane structure could be located at that time, and we were thus somewhat puzzled by calculations reported in the paper by WKIS.[7] Here a thiadioxirane was shown to be a stable intermediate at the HF/3-21G* level with an energy that was 3.3 kcal/mol lower than that of the peroxy sulfoxide. Both this theoretical inconsistency and the new experimental data[7] suggested that a more detailed examination of the reaction at a higher level of theory would be appropriate.

In the present paper we show that the structure of the thiadioxirane obtained by WKIS is an artifact of the use of a small unbalanced basis set; however, when methods including electron correlation are used a thiadioxirane is indeed a stable structure. We have calculated harmonic vibrational frequencies at the MP2/6-31G* level for both the peroxy sulfoxide and the thiadioxirane and located the transition structures for the interconversion between some of the minima on the PES.

Computational Methods

Calculations have been performed with the Gaussian-90[21] and the Gamess[22] program packages. Standard notations and procedures according to ref 23 have been employed. MP2 optimi-

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[18] Scheme II is basicly Scheme III + eqs 7a–c of WKIS (ref 7), but differs slightly in the peroxy sulfoxide reactivity. They propose that it can be trapped by sulfides and sulfoxides, the latter giving either sulfone or a secondary intermediate which then subsequently can oxidize sulfides. However, sulfide trapping of the peroxy sulfoxide cannot be a major pathway, as discussed in the text, and trapping by sulfoxides must also be inefficient in order to be consistent with the isotope labeling experiments.

[19] Addition of a sulfoxide to the peroxy sulfoxide to form a cyclic peroxo intermediate is ruled out by the tracer experiments reported in ref 9.

[20] Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 2368.

[21] Frisch, M. J.; Head-Gordon, M.; Tucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian-90*; Gaussian, Inc., Pittsburgh PA, 1990.

[22] GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. *QCPE Bull.* **1990**, *10*, 52.

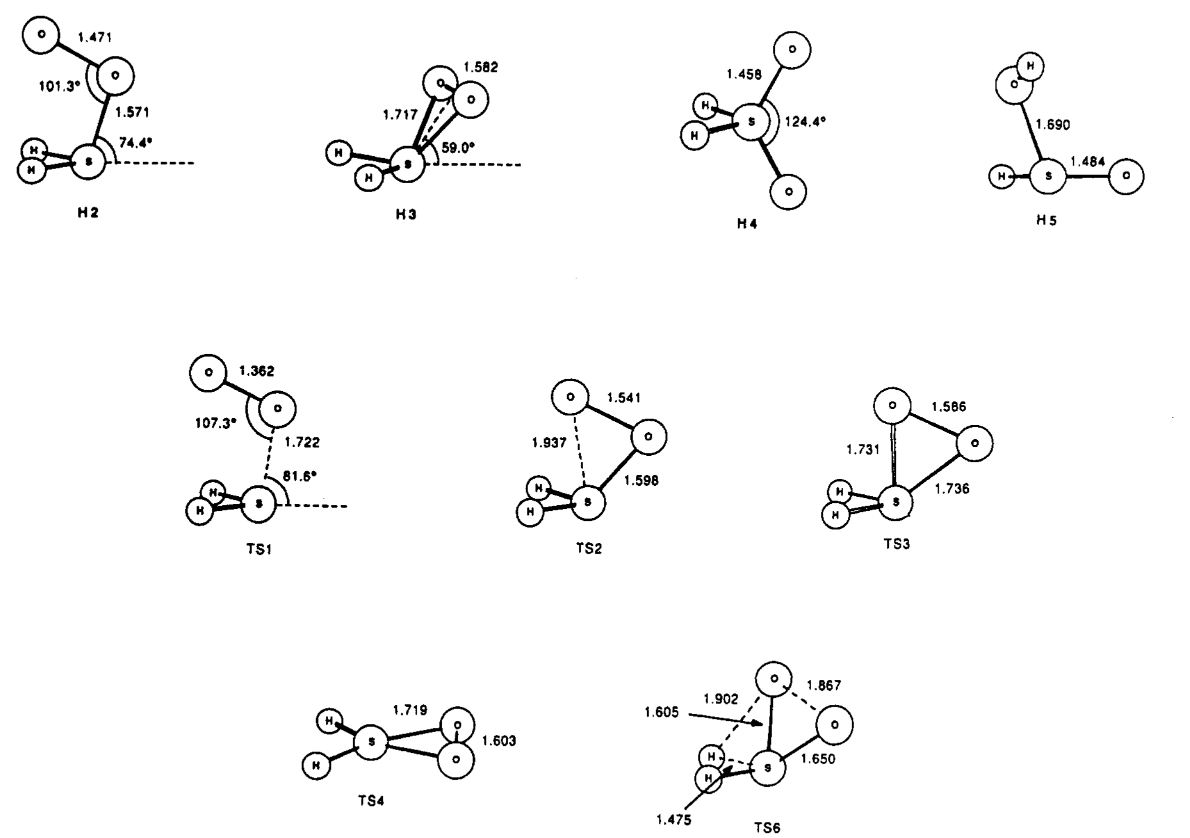


Figure 1. Optimized geometries for the H_2S + $^1O_2$ system. Distances in Å, angles in deg.

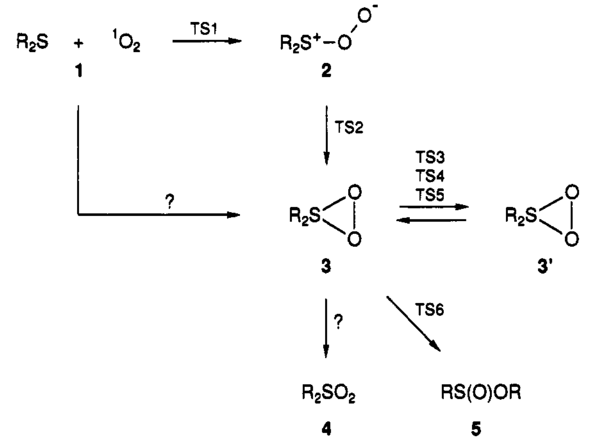
zations were done correlating all electrons while single-point calculations used the frozen core approximation. Stationary points have been characterized by frequency calculations, and the nature of the transition structures has been established by following the intrinsic reaction coordinate[24] to both sides. Energies for $^1O_2$ were obtained as previously[20] by adding the experimental singlet–triplet energy difference[25] to $^3O_2$.

Results and Discussion

We have used H_2S and $(CH_3)_2S$ as model sulfides in the reaction with $^1O_2$, and minima on the PES are labeled by **H** or **Me**, respectively, and a number corresponding to the structures shown in Schemes I and II. A sulfinic acid/ester product, RS(O)OR, was also found in the process; this is denoted **5**. Connecting transitions structures (TS) are numbered as shown in Scheme III. As the PES is qualitatively different at the HF and MP2 levels of theory (see below), we concentrate on the results obtained at the MP2 level. Drawings of the optimized geometries are shown in Figures 1 (H_2S) and 2 ($(CH_3)_2S$).

Structural Results. H_2S + $^1O_2$. In the previous investigation geometry optimizations were performed at the HF level using the 3-21G(*) basis set.[20] The (*) notation denotes the use of a single d-function on atoms Na–Ar but only the unpolarized 3-21G basis for atoms H–Ne. The 3-21G(*) basis is not a polarized basis set; rather, the use of a single d-function on, in this case, sulfur should be considered as the minimum extension of the 3-21G basis necessary for obtaining reasonable geometries for hypervalent compounds like sulfoxides and sulfones.[23] At the HF/3-21G(*) level a peroxy sulfoxide **H2** with C_s symmetry was shown to be a minimum on the PES. A second structure with C_1 symmetry and a geometry almost exactly like **H2**, except for a 120° rotation around the S–O bond was also found, denoted **H2′**. The energy of this species was 1.2 kcal/mol higher and at the time dismissed as an uninteresting rotational isomer of **H2**, and only **H2** was reoptimized at the correlated MP2/6-31G* level. Although the S–O bond length increased slightly and the O–O distance decreased, no qualitative changes occurred upon reoptimization (e.g., the distance from S to the outer O decreased from 2.47 to 2.35 Å). No other reaction intermediates were found in the previous study.

Scheme III



WKIS reported that a thiadioxirane **H3** could be optimized at the HF level with a 3-21G* basis set; the structure had no symmetry and S–O bond lengths of 1.894 and 1.541 Å and an O–O distance of 1.498 Å.[7] In this work, the 3-21G basis was supplemented with a d-function both on sulfur and oxygens, and **H3** is the equivalent of **H2′** with this basis set. When we tried to reoptimize WKIS's **H3** structure with the better 6-31G* basis set, which differs

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(23) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital* theory; Wiley: New York, 1986.

(24) (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(25) Krupenie, P. *J. Phys. Chem. Ref. Data* **1972**, *1*, 423.

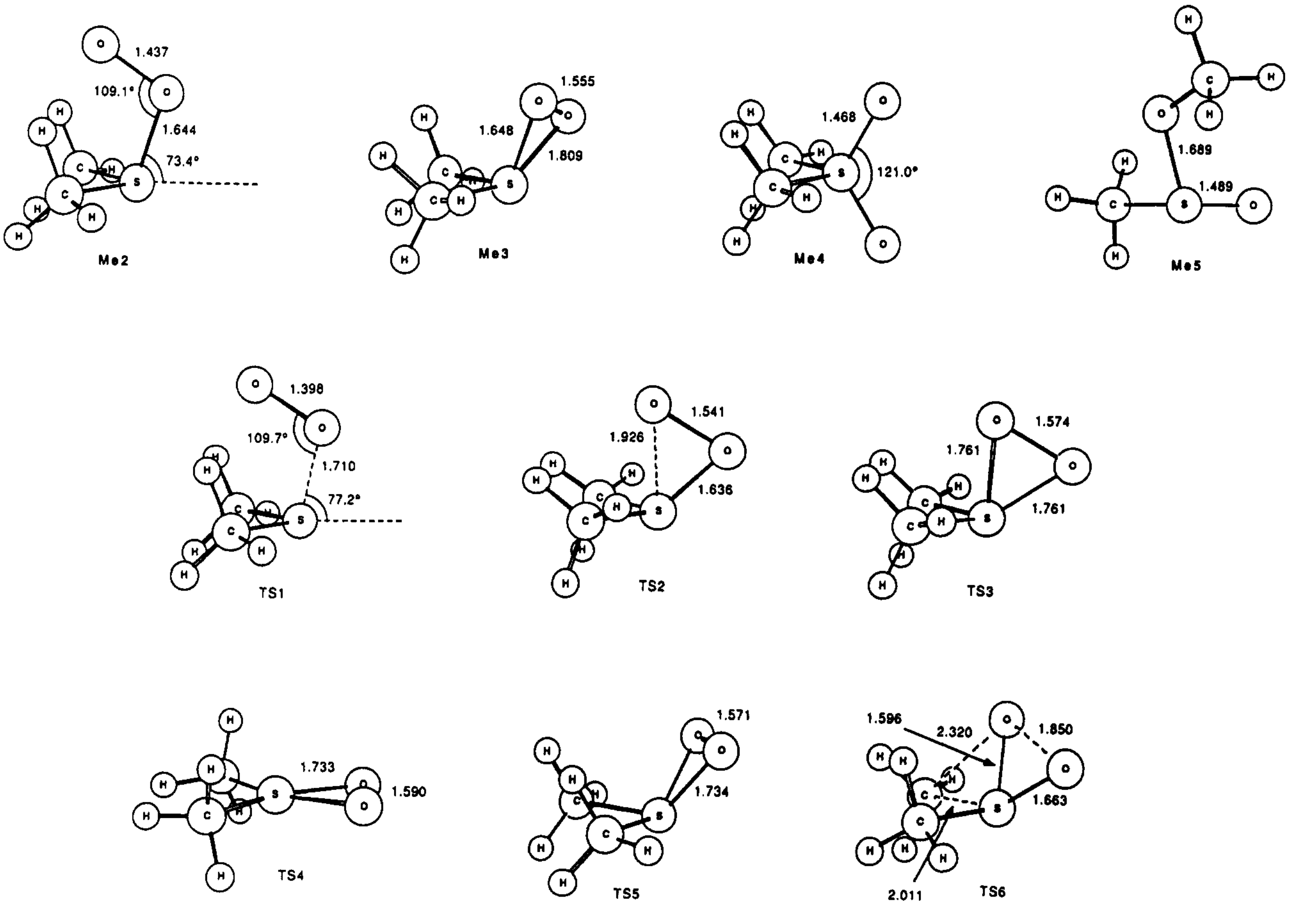

Figure 2. Optimized geometries for the $(CH_3)_2S + {}^1O_2$ system. Distances in Å, angles in deg.

from the 3-21G* only in a better description of the sp-functions, the geometry returned to an open peroxy sulfoxide structure like **H2′** (e.g., the distance from sulfur to the outer oxygen is 2.17 Å). Also with the larger 6-311G-(2d) basis does **H3** return to the open peroxy sulfoxide geometry **H2′** (S–O distance is 2.15 Å). It is thus clear that WKIS's results are due to the use of a basis set with too many polarization functions relative to the sp-basis; i.e., during the geometry optimization the outer oxygen is moved close to the sulfur so that the oxygen d-function may help compensate for the inadequate sulfur sp-basis.

WKIS's findings, however, prompted us to search for a thiadioxirane structure at a better theoretical level, and upon attempts of optimizing **H2′** at the MP2/6-31G* level it collapsed to a C_s symmetric thiadioxirane **H3**.[26] The structure has S–O distances of 1.72 Å and an O–O distance of 1.58 Å and is shown in Figure 1. On the HF PES there are thus two intermediates which essentially are rotational isomers of a peroxy sulfoxide, while the MP2 PES has two distinctly different stable species. Whether this should be considered an example of a qualitative different PES at the HF and MP2 levels of theory or that the structure **H2′**/**H3** is very sensitive to the level of theory is a matter of taste. In the present search on the MP2 PES we have been unable to find any stable intermediates other than **H2** and **H3**.

The geometry of TS1 has been reported previously; it has C_s symmetry and a forming S–O distance of 1.72 Å.[20] TS2 which connects the intermediates **H2** and **H3** has also C_s symmetry with the plane of symmetry defined by the sulfur and oxygen atoms. That this TS indeed connects **H2** and **H3** was proven by following the intrinsic reaction coordinate (IRC)[24] to both sides. As **H3** has the oxygen atoms on each side of the plane of symmetry, while both **H2** and TS2 have them in the plane, a bifurcation[27] must occur along the reaction coordinates after TS2.

As there are several equivalent **H3** structures on the PES there must be pathways connecting these. Two such TS's were found, one corresponding to a rotation of the O–O moiety relative to H_2S and the other corresponding to an inversion at the sulfur. The first has C_s symmetry (TS3) while the second belongs to the C_{2v} point group (TS4); both were characterized by frequency calculations and IRC following. Note that TS3 is quite close in structure to TS2 (Figure 1); in fact, TS3 can be obtained by following the IRC downhill from TS2 under the constraints of C_s symmetry. The imaginary frequency in TS2 is of a' symmetry, while the transition vector for TS3 belongs to the a'' irreducible representation; thus, the above-mentioned bifurcation must occur between these two TS's. No attempt was made to further refine the location of this point.

It has been suggested that **3** can rearrange unimolecularly to **4**, and in principle one can also envision a pathway leading directly from **2** to **4**. A direct formation of **3** from the reactants should also be a possibility, but all attempts of finding any of these transitions structures failed. As **2** and **4** have a common plane of symmetry it would at first glance appear likely that a connecting TS should also have this mirror plane. However, both TS2 and TS3 have geometries that suggest that a possible C_s pathway from **2** to **4** would pass through one or both of these TS's, indicating that there probably does not exist a direct C_s connecting TS. In the process of searching for a TS con-

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(26) Lowest vibrational frequency is of a'' symmetry and has a value of only 63 cm^{-1}.

(27) Baker, J.; Gill, P. M. W. *J. Comput. Chem.* **1988**, *9*, 465.

Table I. Calculated (MP2/6-31G*) Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Peroxy Sulfoxide Me2 and Thiadioxirane Me3

Me2		Me3	
freq	int	freq	int
154	6.4	156	3.4
237	15.6	235	0.1
253	7.1	270	0.9
299	0.7	326	5.5
305	9.5	359	6.8
350	7.6	366	6.5
400	6.9	450	66.4
660	10.3	649	54.8
735	1.6	740	30.5
767	1.3	807	56.9
887	47.5	945	8.2
992	8.0	963	9.2
1003	7.4	966	34.2
1045	32.3	1045	25.5
1121	8.2	1083	39.0
1362	18.1	1389	9.3
1395	25.1	1422	8.1
1494	0.0	1509	7.8
1519	10.6	1517	2.0
1537	9.1	1526	2.4
1556	17.0	1536	19.5
3055	9.4	3107	2.4
3062	81.9	3123	3.7
3206	0.8	3217	4.4
3209	16.4	3226	3.0
3255	0.3	3229	3.1
3259	0.1	3258	0.8

Table II. Calculated (MP2/6-31G*) Isotopic Shifts (cm^{-1}) of Selected Vibrations of Peroxy Sulfoxide Me2

SOO	$S^{18}OO$	$SO^{18}O$	$S^{18}O^{18}O$	^{34}SOO
253	0	−4	−4	0
350	−11	0	−11	−1
400	−5	−10	−15	−2
660	−25	−8	−32	−1
735	0	−1	−1	−6
767	0	0	0	−8
887	−22	−23	−46	−2

Table III. Calculated (MP2/6-31G*) Isotopic Shifts (cm^{-1}) of Selected Vibrations of Thiadioxirane Me3

SOO	$S^{18}OO$	$SO^{18}O$	$S^{18}O^{18}O$	^{34}SOO
156	−4	−2	−6	0
326	−3	−2	−5	−1
359	−3	−3	−6	−3
366	−1	−3	−4	−1
450	−7	−15	−21	−1
649	−2	0	−2	−5
740	−6	−2	−8	−7
807	−15	−4	−18	−8
945	−4	−8	−28	−1
963	−14	−17	−18	−4
966	−3	−4	−4	−1
1045	−2	−1	−3	−4

necting 3 and 4,[28] however, we found TS6 connecting **H3** with the sulfinic acid structure, **H5**.[29] TS6 is "early" as expected from the large reaction energy (see below), and a drawing is shown in Figure 1.

$(CH_3)_2S$ + $^1O_2$. In our previous paper,[20] it was shown that relative energies of some stationary points on the PES were significantly different for H_2S and for $(CH_3)_2S$ and also that structural features changed significantly by substituting CH_3 for H. The stationary points on the PES found for the H_2S system were thus reoptimized for $(CH_3)_2S$, also at the MP2/6-31G* level; **Me2** has previously been optimized at the HF/3-21G(*) level.[20] The most interesting geometrical features can be seen in Figure 2; full details are available from the author upon request. Structures 2 and 3 both have C_s symmetry for the H_2S system, and the corresponding dimethyl species were initially also optimized within C_s symmetry. Frequency calculations, however, showed that C_s symmetric **Me3** had one imaginary frequency (88i cm^{-1}); thus, it is a transition structure. Reoptimization without any symmetry constraints gave a structure 1 kcal/mol lower in energy with S–O bond distances of 1.65 and 1.81 Å. The C_s structure is thus the TS for interconversion of two such equivalent C_1 minima, denoted TS5 in the following. The large difference in S–O bond lengths in **Me3** and the small barrier for achieving TS5 indicate that the PES in this region is shallow. On the dimethyl sulfide PES there are thus several equivalent structures corresponding to **Me3**, and three transition states connecting these: TS3, TS4, and TS5. TS3 and TS4 are analogous to those for hydrogen sulfide; a minor difference is that TS4 corresponding to sulfur inversion only has a C_s symmetry in the methyl system. The substitution of methyl groups for hydrogens causes the S–O bond in **Me2** to become longer, and the steric bulk of the methyl groups also increases the SOO angle. The net result is that **Me2** structurally is very close to TS1; e.g., the S–O distance in TS1 is only 0.07 Å longer than in **Me2**.

As both **Me2** and **Me3** are stable intermediates it should in principle be possible to observe them experimentally. The MP2/6-31G* vibrational frequencies and associated IR intensities are shown in Table I. The predicted isotopic shifts in frequency upon oxygen or sulfur substitution for bands changing more than 2 cm^{-1} are shown in Table II and III.

Akasaka et al. have reported that UV irradiation of Ph_2S and PhSMe in oxygen matrices at low temperature produces a reactive intermediate with an IR absorption at 997 cm^{-1}, which is shifted to 978 cm^{-1} when $^{36}O_2$ is used and split into two bands if $^{34}O_2$ is employed.[30] They assign a peroxy sulfoxide structure to this intermediate based on comparison with the S–O band in phenyl methyl sulfoxide and rule out a thiadioxirane structure since it, with the assumed C_s symmetric geometry, should not show a band splitting in an $^{34}O_2$ matrix. However, if the thiadioxirane has nonequivalent oxygens, as indicated by the present calculations for $(CH_3)_2S$, the structural assignment should be reevaluated.

The experimentally observed band at 997 cm^{-1} is likely to be one of the more intense bands in the spectrum, and the isotopic shifts of 19 cm^{-1} in $^{36}O_2$, and 2 and 17 cm^{-1} in $^{34}O_2$ can be compared with the calculated data in Tables I–III. Although several calculated bands in each of the two species may be assigned to the experimental 997 cm^{-1} band based on intensity (Table I), the observed isotope shifts of 2, 17, and 19 cm^{-1} are really only compatible with those calculated for the 807 cm^{-1} thiadioxirane band, 4, 15, and

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(28) Several methods were used to generate trial geometries for a TS connecting 3 and 4. Constrained optimization using the O–O–S–C angle as reaction coordinate produced TS3. Using the energy maximum along the linear synchonous transit between **H3** and **H4** (or **Me3** and **Me4**) as a start guess gave TS6. As the imaginary frequency for TS3 is of *a″* symmetry, TS3 is a mininum within the C_s point group. We located the "transition structure" between TS3 and **H4** within C_s symmetry; it has two imaginary frequencies, one of *a′* and one of *a″* symmetry. Starting from this geometry and relaxing the symmetry constraints also resulted in TS6. Following hessian eigenvectors (Baker, J. *J. Comput. Chem.* **1986**, *7*, 385) starting either from **H3** or **H4** were also unsuccessful.

(29) A TS connecting **H4** and **H5** was also found with an energy of 53 kcal/mol above **H4** at the MP2/6-31G* level.

(30) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085.

Table IV. Relative Energies for the H_2S + $^1O_2$ System (kcal/mol)[a]

	MP2			MP3			MP4		
	A	B	C	A	B	C	A	B	C
H1	−36.6	−31.4	−20.3	−44.7	−41.8	−32.6	−37.1	−32.3	−22.2
H2	13.0	9.9	9.0	1.8	−1.8	−2.5	9.6	7.3	6.4
H3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H4	−84.0	−96.7	−98.1	−85.3	−97.6	−99.7	−79.3	−90.8	−92.0
H5	−99.6	−104.7	−105.4	−104.4	−109.7	−110.5	−96.9	−101.2	−101.6
TS1	16.8	15.8	15.6	6.6	5.2	5.4	12.3	12.0	12.0
TS2	25.7	22.7	21.9	21.0	18.0	17.0	22.8	20.3	19.5
TS3	17.0	14.9	15.3	19.4	17.3	17.8	15.7	13.7	14.2
TS4	31.9	31.3	29.8	31.0	30.7	29.9	31.8	30.9	29.6
TS6	17.4	13.2	13.4	23.5	20.3	20.8	15.6	11.1	11.3

[a] Basis set A is 6-31G*, B is 6-311G(2d), and C is 6-311 +G(2df).

Table V. Relative Energies (kcal/mol), Zero Point Energy Differences, and Dipole Moments (D) for the Me_2S + $^1O_2$ System[a]

	MP2			MP3		MP4		ΔZPE	μ(HF)
	A	B	C	A	B	A	B	A	B
Me1	−19.3	−13.4	−2.7	−25.1	−21.1	−18.4	−13.2	−2.4	1.7
Me2	3.0	2.7	4.2	−4.3	−5.0	0.7	0.8	−0.4	6.6
Me3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.9
Me4	−94.5	−104.2	−105.9	−93.8	−103.2	−89.3	−98.5	1.8	5.2
Me5	−88.2	−90.3	−91.9	−90.5	−92.6	−85.6	−87.2	1.1	3.0
TS1	3.1	3.2	7.2	−3.2	−3.2	0.6	1.1	−0.9	6.6
TS2	22.0	21.2	21.4	21.6	21.0	20.5	19.7	−0.7	5.1
TS3	17.4	17.5	18.3	23.1	23.4	17.4	17.2	−0.6	5.1
TS4	39.4	39.1	38.9	41.3	41.8	40.1	39.2	−0.6	5.5
TS5	0.9	1.9	2.4	4.2	5.3	1.8	2.7	−0.1	4.9
TS6	20.9	17.5	17.7	30.8	28.4	20.2	16.2	−1.0	3.4

[a] Basis set A is 6-31G*, B is 6-311G(2d), and C is 6-311+G(2df).

18 cm^{-1} (Table III). If the intermediate observed by Akasaka et al. has the thiadioxirane structure, this implies that the MP2/6-31G* frequency is in error by ~190 cm^{-1}. Such a deviation is larger than is normally found at this level, even considering the difference between the experimental phenyl methyl sulfide and the dimethyl sulfide used in the calculation. It is possible that structures **2** and **3** may belong to the class of theoretical "difficult" molecules, often found in connection with polar O–O bonds.[31] Further clarification of the observed intermediate will have to await higher level calculations and/or experimental investigation of a larger part of the spectrum than just the 960–1000 cm^{-1} region.

Energetic Results. In order to obtain improved estimates of relative energies of stationary points on the PES we have performed calculations with the 6-31G*, 6-311(2d) and 6-311+(2df) basis sets and included electron correlation up to MP4, all at the MP2/6-31G* optimized geometries. As the energy difference between the reactants and the other species is very sensitive to the quality of the basis set (see below), we have chosen to report energies relative to **3**, and they are shown in Tables IV and V. Since the calculations increase both in terms of electron correlation (MP2, MP3 and MP4) and quality of basis sets, an estimate of the "theoretically converged" value can be made.[32] This estimate is used for discussion in the text, Tables IV and V can be consulted for specific values.

The energy difference between **H2** and **H3** depends mainly on electron correlation, i.e. at the MP2 and MP4 levels is **H3** the most stable isomer while **H2** is lowest in energy at the MP3 level. From the data in Table IV it would appear that **H3** probably is slightly more stable than **H2** if better basis sets and additional electron correlation were included. The formation of **H3** (and **H2**) from the reactants **H1** is at all levels calculated to be *endothermic*, but the value is very sensitive to the quality of the basis set, especially the addition of polarization functions is critical. Since the energy difference change by 10–11 kcal/mol upon going from the 6-311G(2d) to the 6-311+G(2df) basis set, we have performed additional calculations in order to estimate the basis set "converged" value (see Appendix). The best basis sets used in an MP2 calculation are 6-311+G(3d3f) and 6-311+G(3d2f1g) where values of 14.9 and 14.0 kcal/mol are obtained, and it is estimated that additional basis set extensions would lower this value to ~10 kcal/mol. Inclusion of electron correlation beyond MP4 would probably increase the value; thus, our estimate would place **H3** ~15 kcal/mol above **H1**.[33]

The transition state for formation of the peroxy sulfoxide, TS1, is much less basis set dependent, and the theoretically converged value relative to **H3** is ~10 kcal/mol. The calculated energy of the transition structure connecting **H2** and **H3** (TS2) is at all levels higher than that of TS1. This might indicate that a lower energy pathway exists directly from the reactants to **H3**, but as stated above, we were unable to find such a TS at the MP2 level. The activation energies of the two TS's connecting the two equivalent **H3** structures, TS3 (rotation) and TS4 (sulfur inversion), are ~15 and ~30 kcal/mol, respectively.

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(31) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442.

(32) We have estimated the electron correlation converged value to be between the MP3 and MP4 result and closest to the MP4 value. Calculations with the QCISD(T) method supports this estimate, e.g., energies relative to **H3** with the 6-311+G(2df) basis for **H1**, **H2**, TS1, TS2 and TS6 are −25.3, 1.8, 5.7, 16.5, and 12.0 kcal/mol, respectively. Similar calculations with the 6-31G* basis give values for **Me1**, **Me2**, TS1, TS2, and TS6 (relative to **Me3**) of −19.4, −2.7, −3.3, 19.7, and 21.0 kcal/mol, respectively.

(33) The effects of basis set extension and electron correlation are almost independent; e.g., increasing the basis set from B to C changes ΔE(**H1**–**H3**) by 11.1 at the MP2 level and 10.1 at the MP4 level (Table IV). Considering the data in the Appendix the ΔE(**H1**–**H3**) basis set limiting MP4 value can thus be estimated to ~−12 kcal/mol. Based on the values at the MP2, MP3, MP4, and QCISD(T) levels (−20.3, −32.6, −22.2, and −25.3 kcal/mol with basis set C), it is likely that inclusion of more electron correlation will lower this value to ~−15 kcal/mol. Assuming similar effects for the dimethyl system gives an estimated ΔE(**Me1**–**Me3**) value of +3 kcal/mol.

The global minimum on the H_2SO surface is the sulfinic acid structure **H5**[29] which is calculated to be 10 kcal/mol below the sulfone, in agreement with calculations by Laakso and Marshall.[34]

The data in Table V indicate that **2** and **3** are essentially isoenergetic in the dimethyl sulfide system, at least in the gas phase. In solution, however, **Me2** may be slightly favored since it is the more polar of the two (e.g., the calculated dipole moment for **Me2** is 6.6 D compared to 4.9 D for **Me3**). A significant difference between the hydrogen and methyl systems is the destabilization of the reactant by the methyl groups. Relative to **3**, **1** is almost 20 kcal/mol higher in energy with dimethyl sulfide than with hydrogen sulfide. Combined with the estimated change by extending the basis set beyond 6-311+G(2df) from the hydrogen system, it is clear that the formation of **Me2**/**Me3** from $(CH_3)_2S$ and $^1O_2$ will be exothermic; the calculations suggest a value ~3 kcal/mol.[33] Solvation will further increase the exothermicity as the two intermediates are significantly more polar than dimethyl sulfide. An estimate of this effect was provided by calculations with the reaction field SCF method[35] where the solvent is modeled by a continuum. For a solvent dielectric constant of 3 (similar to, e.g., benzene and diethyl ether), the calculated solvation energies for **Me1** and **Me2** relative to **Me3** are +2.1 and −1.9 kcal/mol, respectively. With a dielectric constant of 40 (similar to, e.g., acetonitrile) corresponding values of +3.7 and −3.4 kcal/mol are obtained.

As indicated by the structural similarity of TS1 and **Me2** they are very close in energy. At the MP2/6-31G* level, at which the geometry is optimized, TS1 is only 0.1 kcal/mol higher in energy than **Me2**. Nevertheless, TS1 is still a genuine transition structure as indicated by a frequency calculation (imaginary frequency is 356i cm^{-1}). Addition of zero point energy places TS1 0.8 kcal/mol *below* **Me2**, but increasing the basis set again restores the energy ordering. With the PES in this region being this flat the exact location of TS1 will be dependent on the level of theory, but changing the geometry is unlikely to alter the conclusion that TS1 is (at most) a few kcal/mol above **Me2**. Solvent contributions to this energy difference are likely to be very minor.

The above considerations suggest that the initial formation of **Me2** from $(CH_3)_2S$ and $^1O_2$ via TS1 in solution probably will be slightly exothermic enthalpic.[36] This means that TS1 may be lower in energy than the reactants; i.e., at a sufficiently high level of theory it is likely that **Me2** is formed essentially without an enthalpic barrier. On the free energy surface, however, the decrease in entropy by forming a single molecule from two reactants probably causes a small barrier to exist, i.e., the reaction is entropy controlled.[37] The calculated entropy change upon going from **Me1** to TS1 is −38 esu, corresponding to a 11 kcal/mol contribution to the free energy at 298 K. The value at 195 K (−78 °C) is 7 kcal/mol. Experimentally, Clennan et al.[13] have determined $\Delta H^{\ddagger} = -4.1 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -46 \pm 1$ esu for the total product formation (sulfoxide and sulfone), while WKIS[7] report an activation energy of −9.9 kcal/mol for sulfoxide formation alone. These data are consistent with our theoretical estimates. A very flat energy surface for formation of **Me2** from the reactants also serves to explain why physical quenching is the dominant process in aprotic solvents. In the reactant the singlet state is 22.6 kcal/mol above the ground triplet state,[25] while at the TS1 geometry the triplet state is calculated to be 46 kcal/mol higher than the singlet.[38] Along the reaction coordinate there must thus be a range where the two states are close in energy, favoring intersystem crossing. The energy cost for achieving such conformations, either from the reactant or peroxy sulfoxide side, is very small due to the flatness of the free energy surface. The use of polar or protic solvents, or lowering the temperature, stabilizes preferentially **Me2** and thus disfavors geometries where intersystem crossing is facile, i.e., quenching is reduced.

The calculated barrier for interconversion between **Me2** and **Me3** is quite high, 20 kcal/mol, and solvent effects are unlikely to change this value significantly. This value is incompatible with Scheme I which requires a rapid interconversion even at low temperature. The data in Tables IV and V makes it unlikely that higher level calculations will reduce the activation energy significantly, and the barrier is also insensitive to the substitution of hydrogen by methyl, which should resemble the experimental diethyl sulfide system closely anyway.

If **Me3** is formed, however, it can interconvert with an equivalent structure **Me3′** via the C_s symmetric TS5 quite easily (activation energy 3–4 kcal/mol), but both the rotational TS3 and the inversion TS4 pathways appear to have too high of activation energies (~19 and ~39 kcal/mol, respectively) to play important roles.

In the dimethyl system the sulfone product **Me4** is lower in energy than the sulfinic ester **Me5** by ~10 kcal/mol, as expected. The formation of **Me5** from **Me3** (via TS6) is calculated to have an activation energy of ~20 kcal/mol, a value similar to that of TS2. As the sulfinic ester product is not observed experimentally this lends support to the conclusion that unimolecular interconversion of intermediates **2** and **3** is unimportant under the experimental conditions used so far. Note also that TS6 is quite high in energy despite the overall reaction energy of 90 kcal/mol; this may reflect the large bond reorganization occuring during the reaction.

Summary

The reaction of H_2S and $(CH_3)_2S$ with $^1O_2$ has been investigated by ab initio calculations employing optimizations at the MP2/6-31G* level followed by higher level calculations to obtain improved estimates of energy differences. Contrary to previous results at the HF level two distinct intermediates are found, a peroxy sulfoxide and a thiadioxirane. Calculated IR spectra for both intermediates suggest that a previously observed transient species is best explained to have a thiadioxirane structure based on isotopic changes in frequency.

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(34) Laakso, D.; Marshall, P. *J. Phys. Chem.* **1992**, *96*, 2471.

(35) Mikkelsen, K. V.; Ågren, H.; Jensen, H. J. Aa.; Helgaker, T. *J. Chem. Phys.* **1988**, *89*, 3086. The calculations were performed with the 6-31+G* basis set and a cavity radius of 4.0 Å. This corresponds to the Van der Waal radius of the molecules +0.5 Å.

(36) It has been argued that singlet oxygen reactions often proceed via an exciplex. We have not found any evidence of an exciplex in our computational study, but this may be due to inadequacies in the theoretical procedure. A proper description of the $^1\Delta_g$ state of molecular oxygen requires that the molecular orbitals are allowed to be complex, but it is unclear if a complex MP2 wave function is sufficiently accurate for locating a loosely bound exciplex.

(37) This argument has also been used in the reaction of carbenes; see: (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (b) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293. (c) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555. (d) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919.

(38) The singlet–triplet energy difference for the dimethyl sulfide system at the TS1 geometry is 50, 45, and 47 kcal/mol at the MP2, MP3, and MP4/6-31G* levels, respectively. The corresponding MP2 value for O_2 is 22.9 kcal/mol, compared to the experimental value of 22.6 kcal/mol.

Table VI

entry	basis	ΔE[a]
1	6-311G(d)	45.5
2	6-311G(2d)	31.4
3	6-311G(2d,p)	32.2
4	6-311+G(2d)	27.9
5	6-311+G(2d) + diffuse sp-functions[b]	27.8
6	6-311+G(3d)	24.7
7	6-311+G(3d) + tight d-function[c]	24.1
8	6-311+G(3d) + diffuse d-function[d]	23.7
9	6-311+G(4d)[e]	22.8
10	6-311+G(3df)	19.1
11	6-311+G(3d2f)[f]	15.5
12	6-311+G(3d2f)[f,g]	15.0
13	6-311+G(3d3f)[f]	14.9
14	6-311+G(3d2f1g)[g,h]	14.0

[a] $\Delta E = E(\mathbf{H3}) - E(\mathbf{H1})$ (in kcal/mol). [b] Additional diffuse sp-functions on S and O (exponents 0.0135 and 0.0282). [c] Additional d-functions on S and O (exponents 6.50 and 12.92). [d] Additional d-functions on S and O (exponents 0.065 and 0.1292). [e] Four d-functions covering the d-exponent space of the 6-311+G(3d) basis (split ratio of 2.5). [f] f-Exponents determined by splitting 1f-exponents (0.55 and 1.40) by ratio of 4.0. [g] All cartesian components of d-, f- and g-functions were used. [h] Exponents for g-functions were 0.65 (S) and 1.50 (O).

Although the present work represents a quite extensive investigation of the PES, there are still some troublesome disagreements between theory and different suggested reaction mechanisms. We have been unable to find a TS for direct formation of the thiadioxirane from the reactants; however, it is possible that a multiconfigurational wave function may be required to describe this process.[39] Of more concern is the inability to find a pathway for formation of the sulfone. In the reaction schemes suggested so far, the conversion from thiadioxirane to sulfone is assumed to occur with a low activation energy (a few kcal/mol). The employed MP2 wave function should be flexible enough to describe this process; at least there is no trouble calculating the conversion of thiadioxirane to sulfinic ester which also involves substantial bond reorganization. It would be puzzling if optimization algorithms which successfully locate high energy transition structures like conversion from thiadioxirane to peroxy sulfoxide and sulfinic ester, are unable to locate a low energy TS for formation of sulfone.

All experimental and theoretical results are consistent with an initial formation of a peroxy sulfoxide by an entropy-controlled TS, while the reverse process leads to physical quenching. In protic solvents this intermediate is rapidly transformed into the chemically active species by solvent coordination or addition, capable of oxidizing sulfides and sulfoxides. This mechanism rationalizes why quenching is reduced by polar and protic solvents, and by lowering the temperature. It is also clear that at least one more intermediate is required in aprotic solvent; this is the species responsible for oxidizing sulfides. The structure of this intermediate has been suggested to be either a thiadioxirane or a coordinated peroxy sulfoxide. Direct formation of a thiadioxirane by rearrangement of a peroxy sulfoxide seems to be ruled out by the present calculations.

Conflicting, and mutually inconsistent, results have been reported for formation of the sulfone product. WKIS results indicate that the sulfone is produced almost exclusively by a unimolecular pathway, favored by high temperature and independent on sulfide concentration and additives.[6] Foote and Clennan, on the other hand, report that low temperature and low sulfide concentration increase the yield of sulfone.[3,6a,11] Several groups have confirmed a bimolecular pathway for sulfone formation by sulfoxide trapping of a peroxy sulfoxide intermediate, although the fraction of product produced this way has not been quantified. A direct unimolecular rearrangement of a thiadioxirane appears unlikely given the current computational results.

In discussing possible reaction mechanisms one should be aware that only unimolecular pathways have been investigated in the present work. Experimental results suggest that the peroxy sulfoxide can be stabilized by coordination, and one may speculate whether a coordinated peroxy sulfoxide might have a lower barrier for rearrangement to the thiadioxirane than the free peroxy sulfoxide. Also the proposed conversion of the thiadioxirane to sulfone may feasible if the reaction occurs via a coordinated thiadioxirane.[6a,10] A theoretical investigation of such complexes would require significantly larger basis sets than employed in the present work or an explicit consideration of basis set superposition errors.

Several candidates are possible as coordinating species, WKIS have suggested that the sulfoxide product may stabilize the peroxy sulfoxide,[5,7] while the different reactivities of 1,5-dithiacyclooctane and 1,4-dithiane suggest that even sulfides may coordinate, at least if this can be accomplished intramolecularly.[6] Protic solvents or intramolecular hydroxy groups may be an extreme case of coordination where actual addition has taken place.[6a,10] Determination of a Hammett ρ value for the sulfoxide oxidizing species in CH_3OH, and comparing this value to those obtained for oxidation of phenyl sulfides[7,8] and for phenyl sulfoxides[5] in benzene, may help clarify this aspect.

When discussing solvent effects a distinction must be made whether the effect is due to a general polarity effect or to specific coordination. A particularly interesting pair of solvents to investigate would be acetonitrile and nitromethane; both have a similar dielectric constant but the nitro group may well be able to coordinate in a way similar to a sulfoxide. Addition of a sulfone to the reaction mixture, or the use of sulfolane as the solvent, may also be of interest. Finally, it would be desirable to verify the controversial results by WKIS that sulfone formation is almost exclusively unimolecularly and favored by high temperature.[7] It may well be that a more detailed understanding of the factors influencing sulfone formation may help refine the reaction mechanism.

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Appendix

As the energy difference between **H1** and **H3** clearly is not converged with the 6-311+G(2df) basis set, we have tried to estimate what the MP2 basis set limiting value is. From the data in Table VI, it is seen that polarization functions on hydrogen and addition of a second set of diffuse sp-functions have small effects (entries 2, 3 and 4, 5). Expansion of the 2d polarization space to 3d reduces the energy difference by 3.2 kcal/mol (entries 4, 6). Addition of a more tight d-function gives 0.6 kcal/mol (entries 6, 7), and a diffuse d-function gives 1.0 kcal/mol (entries 6, 8). Using 4 d-functions to cover the exponent space of the 3d basis further reduces the energy difference by 1.9 kcal/mol (entries 6, 9). Assuming additivity, the spd-basis

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(39) Attempts of locating a TS between **1** and **3** by following the appropriate hessian eigenvector from **3** within C_s symmetry resulted in symmetry-broken wave functions at S–O distances larger than ~2 Å. Symmetry-broken wave functions are often encountered when single determinant wave functions are used to describe systems which are multconfigural by nature; see, e.g.: Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

set limit is thus ~21 kcal/mol. The contribution from f-functions seems to converge when three f-functions are used, giving an energy reduction of 9.8 kcal/mol (entries 6, 10, 11, 13). Finally, the contribution from a single g-function is 1.0 kcal/mol (entries 12, 14). We thus estimate that the MP2 basis set limiting energy difference is close to 10 kcal/mol. This is 10 kcal/mol lower than the result with the 6-311+G(2df) basis.

Metal Arene Complexes in Organic Synthesis. Hydroxylation, Trimethylsilylation, and Carbethoxylation of Some Polycyclic Aromatic Hydrocarbons Utilizing η^6-Arene–Chromium Tricarbonyl Complexes

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The deprotonation of polycyclic aromatic hydrocarbon (PAH) chromium tricarbonyl complexes (PAH = naphthalene, anthracene, phenanthrene, pyrene, fluoranthene) using an in situ technique where the PAH complex, the base (LiTMP or LDA), and the electrophile (trialkyl borate, trimethylsilyl chloride, or ethyl chloroformate) were placed in solution simultaneously resulted in hydroxylation, trimethylsilylation, or carbethoxylation of the PAH after oxidative workup where the regiochemistry was controlled by steric factors. As a result, substitution at positions of the PAHs not readily available by electrophilic substitution were obtained in some cases. Conditions minimizing isomer mixtures and factors affecting the regiochemistry and the scope of the reaction sequence were examined.

Introduction

Direct regiospecific substitution of polycyclic aromatic hydrocarbons (PAHs) larger than naphthalene has generally been fraught with difficulty. Regiochemical control of electrophilic substitution of large PAHs can generally be attained for only a few of the possible isomers in many cases.[1] Monoelectrophilic substitution in these cases can frequently be controlled to give one predominant isomer.[1] Some isomers, however, are not available by electrophilic substitution. A number of ways around this latter problem have been explored. For example, 2- or 4-substituted pyrenes have been prepared by reduction of pyrene to 4,5,9,10-tetrahydropyrene[2–4] or 1,2,3,6,7,8-hexahydropyrene,[5–7] respectively, followed by electrophilic substitution of the resulting hydroaromatic, then rearomatization to pyrene. In general, methods of this type require more steps and more involved protocols[8,9] than a direct substitution method would with consequent decreases in overall yield.

Some of the above problems could be alleviated if the recent developments in the substitution chemistry of monocyclic benzenoids, naphthalene, phenanthrene, and acenaphthalene which utilize chromium tricarbonyl (CTC) complexes[10] were applied to other PAHs. Complexation of the CTC group to benzenes increases the acidity of the ring protons by 5–8 pK_a units.[11] In addition the strong CTC electron withdrawal (roughly comparable to a NO$_2$ group) facilitates nucleophilic attack on the ring and nucleophilic displacement of halogen.[10]

Deprotonation reactions have not been extensively examined with PAH complexes other than the naphthalene complex.[12,13] The position of attachment of the CTC group in these complexes is known for a number of common PAHs[14] (see Scheme I). [It can readily be predicted for those which have not been prepared. Normally the terminal ring or the most aromatic ring by valence bond criteria is the ring complexed. The aromatic sextet rational[1] summarizes a good deal of this information conveniently and provides either a rationale or a prediction of where complexation has or will take place.[14]] In PAH mono-CTC complexes the ring where deprotonation will take place can, thus, be predicted. Since the CTC group can be attached and removed under relatively mild conditions and is stable to a number of chemical conditions,[15,16]

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