hydroxide solution. Let us first consider the theoretical predictions for the various mechanisms for the equatorial system. The dco CD for the –COOH chromophore is positive. $-C_z^{00}xyz$ and $C_y^{00}x(1 - 5y^2)$ are negative ($C_x^{00} \approx 0$), and $K_{\text{mom}}^{\text{dip}}$ is positive, so the dipolar CD is negative. The sign of the charge mechanism is opposite from that of $K_{\text{mom}}^{\text{ch}}$. Thus if we are to account for the positive CD of the 4-equatorial system in both NaOH and water, and the fact that the observed CD in NaOH (more dissociation so more charge contribution) was larger than in water, $K_{\text{mom}}^{\text{ch}}$ must be negative.

A negative $K_{\text{mom}}^{\text{ch}}$, however, fails to account for the negative CD of the axial compound in both solvents, since the dco CD is positive, the dipolar axial CD is positive (as for the F case above), and a negative $K_{\text{mom}}^{\text{ch}}$ results in a positive charge contribution. The magnitude is also a problem since the *r* dependence should in fact make this CD larger, rather than smaller, than the corresponding equatorial one. Solvent effects once again present a resolution of the dilemma. The potential for contributions from the solvent in these systems is even larger than in the previous β-axial systems considered, since the solvents can readily hydrogen bond to $-COO^-$ and –COOH. This introduces a large number of complicating factors. It is probable that, in its most stable association, the OH^- would project into a different quadrant from the COO^- and would thus generate a CD contribution of opposite sign from the COO^-. Similarly, it is likely that a hydrogen-bonded water molecule would make a net negative contribution.

4. Conclusions

It has been shown that for a wide variety of ketones in which a C_{2v} chromophore can be identified, the observed CD can be understood in terms of a perturbative mechanistic approach. In general, the isotropic polarizability dynamic coupling (dc) mechanism is dominant, so the CD reflects an octant rule geometry dependence on the positions of the inducing chromophores. However, before assuming a dco rule dependence, a number of questions must be answered. (i) Have all net-inducing chromophores been considered and their relative polarizabilities correctly accounted for? (ii) Have all potentially significant conformations of the system been considered? (iii) Are the net inducers positioned so that the geometry term *xyz* is not approximately 0? (iv) Are there no strongly dipolar or charge-inducing chromophores in the system? (v) Is the solvent completely randomly oriented with respect to the carbonyl chromophore? If the answer to any one of these questions is "no", then dco behavior is not necessarily to be expected as there will be either additional dco contributions (i, ii, and v), or other significant mechanisms (iii, iv, and perhaps v). For such situations the CD may still have the dco sign, but its magnitude will be inconsistent with that mechanism.

The neglect of solvent molecules about the carbonyl chromophore has been implicit in any theoretical work on carbonyl CD to date. The analysis in this paper suggests that there may be instances where this assumption is invalid. The β-axial substituent in such compounds as adamantones may create a "solvent hole" from which solvent molecules are excluded, resulting in a net solvent contribution of opposite sign from that of the dco contributions of the β-axial substituent. This hypothesis could be further investigated in a number of ways, including gas-phase CD experiments, molecular mechanics calculations on the solvent/β-axial carbonyl interaction, and further temperature-dependent studies. Theoretical investigations of the solvent structure about a carbonyl chromophore are in progress.

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Reaction of Singlet Oxygen with Organic Sulfides. A Theoretical Study

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Abstract: The intermediates in the reactions of singlet oxygen with H_2S and Me_2S have been calculated at Hartree–Fock, Møller–Plesset, and multiconfiguration levels of theory. A peroxy sulfoxide structure, which has been proposed as an intermediate in the photooxidation of organic sulfides, was found to be a stable intermediate, but the barrier for dissociation to reactants is calculated to be only a few kilocalories per mole. The infrared frequencies and intensities of this intermediate were calculated for the purpose of possible spectroscopic identification. A cyclic thiadioxirane, which also has been suggested as a possible intermediate, was found not to be a minimum on the potential energy surface. Large-scale MCSCF calculation shows that the peroxy sulfoxide is best described by a zwitterionic, not a biradical, structure. Calculated activation energies and overall reaction energies are found to require a very large basis set in order to give reasonable agreement with experimental results.

The reactions of singlet oxygen with simple organic sulfides have been studied extensively by several groups.[1-3a,4] The overall reaction is usually an oxidation of 2 mol of the sulfide by 1 mol of singlet oxygen to give 2 mol of the sulfoxide, although sulfones can be obtained under some conditions.[2] Trapping experiments suggest that the reaction proceeds via at least one intermediate, for which a peroxy sulfoxide structure has been proposed. Kinetic studies showed that the peroxy sulfoxide can rearrange in aprotic solvents to a second intermediate, suggested to have a cyclic thiadioxirane structure.[3] Sulfones can arise from further oxidation of the sulfoxides, but kinetic studies indicate that they can also be formed by unimolecular rearrangement of an intermediate (the

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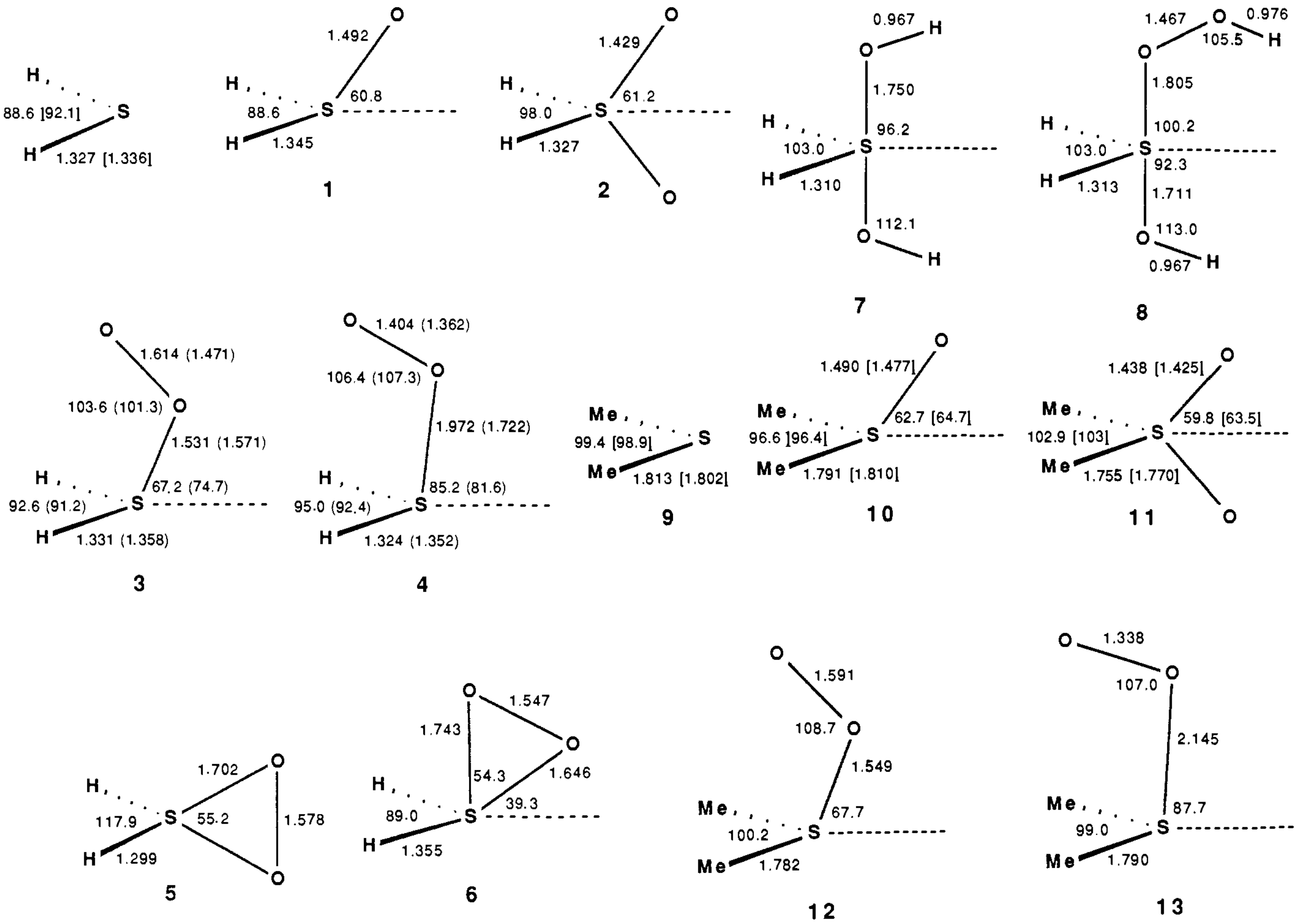

Figure 1. HF/3-21G(*)-optimized geometries in angstroms and degrees. Values from MP2/6-31G* optimizations are in parentheses; experimental values[29] are in brackets.

ratio of sulfone to sulfoxide product increases when the sulfide concentration decreases).[2a] In protic solvents such as methanol, the quantum yield for the formation of sulfoxides is much higher than in aprotic solvents, and it has been suggested that the peroxy sulfoxide intermediate is stabilized by hydrogen bonding or by formation of a solvent adduct, a sulfurane.[2,3a,4]

The reactions of thioketones,[5] thioketenes,[6] thiiranes,[7] and other organic sulfur compounds[1a,8] with singlet oxygen have also been reported. In many of these cases the observed products can be rationalized by assuming that a reactive intermediate is formed. With simple sulfides, these intermediates are usually suggested to be peroxy sulfoxides. No spectroscopic identification for any of the postulated intermediates has appeared. We have previously reported HF/3-21G(*) calculations for the reaction of singlet oxygen with thiirane.[7a] We now report ab initio calculations for the reaction of singlet oxygen with H_2S and Me_2S at the Hartree–Fock (HF), Møller–Plesset (MP), and multiconfiguration (MCSCF) levels of theory. The infrared frequencies and intensities of the peroxy sulfoxide structure have also been calculated to aid in possible spectroscopic identification.

Calculations

All calculations for singlet states were carried out with the restricted HF (RHF) procedure due to Roothaan and Hall.[9] For triplet states, the unrestricted (UHF) method of Pople and Nesbet was used.[10] Structures reported in this paper have been optimized at the HF/3-21G(*) level, except when noted otherwise. The 3-21G(*) basis has d orbitals on second-row elements only.[11] The effect of electron correlation was estimated by the perturbation theory of Møller and Plesset.[12] The MP single-point calculations used the frozen-core approximation,[13] except when noted otherwise, while optimizations at the MP2 level included all orbitals. The MP4 results include all excitations (SDTQ) relative to the reference HF wave function. For $^1O_2$ ($^1\Delta_g$), a wave function with complex orbitals is necessary for a correct description. Because of program limitations, we were only able to include electron correlation up to MP2 for $^1O_2$. At this level, the singlet–triplet gap is calculated to be 23.4 kcal/mol with the 6-31G* basis and 22.8 kcal/mol with the 6-31G(2d) basis. The experimental value is 22.6 kcal/mol,[14] and the total energies of $^1O_2$ at the MP3 and MP4 levels were estimated by adding the experimental singlet–triplet energy difference to the total energy of $^3O_2$. The frequency calculations were performed by using an analytical method at the HF level and by numerically differentiating the analytic gradients

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at the MP2 level. These calculations were done with the GAUSSIAN 82 program package.[15] The MCSCF calculations were done with the GAMESS program.[16]

Results and Discussion

H_2S was initially chosen as a model for an organic sulfide. The HF/3-21G(*)-optimized geometries of this compound, the model sulfoxide H_2SO (**1**), and sulfone H_2SO_2 (**2**) are shown in Figure 1. This basis set has been shown to give geometries in good agreement with experimental data and higher level calculations.[11]

The 3-21G(*) basis was used in the search for stable intermediates on the potential energy surface (PES). A structure corresponding to the proposed peroxy sulfoxide was found without any problems.[17] The most stable conformation has C_s symmetry, with the outer oxygen syn to the hydrogens, as shown in structure **3** in Figure 1. That this structure is indeed a minimum on the PES was proven by a frequency calculation. There are two additional (equivalent) structures corresponding to an approximately 120° rotation around the S–O bond (gauche), which are 1.2 kcal/mol higher in energy. A structure with C_s symmetry and the outer oxygen anti to the hydrogens was found to be a transition state between the two gauche structures and located 4.0 kcal/mol higher in energy than the gauche conformation.

The most characteristic feature in the peroxy sulfoxide structure **3** is the very long O–O bond (1.614 Å). For the carbon analogue, carbonyl oxide, the geometry has been shown to be very dependent on the level of theory used for the optimization.[18-20] For formaldehyde oxide, the O–O bond is 1.634 Å at the HF/3-21G level[21] and is reduced to 1.295 Å when optimized at the MP2/6-31G* level.[19] An essentially identical geometry has been obtained by a CASSCF wave function using a DZ + P basis set.[20] In the present case, the peroxy sulfoxide **3** was reoptimized at the MP2/6-31G* level, and the MP2 values are given in parentheses in Figure 1. At this level the O–O bond length is reduced to 1.471 Å while the S–O bond is elongated from 1.531 to 1.571 Å. This latter geometry is probably a more realistic structure. The dipole moment at the HF/6-31G* level using the MP2 optimized geometry is 6.54 D, which should be compared to calculated values of 4.12 D for H_2SO, 3.98 D for H_2SO_2, and 1.41 D for H_2S at the same level. The energetics for the reaction will be discussed below.

The transition structure (TS) for the addition of singlet oxygen to H_2S leading to the peroxy sulfoxide **3** was initially located at the HF3-21G(*) level. Transition structure **4** has C_s symmetry with an S–O bond length of 1.972 Å. That this structure is indeed a transition structure was confirmed by a frequency calculation. The geometry was reoptimized at the MP2/6-31G* level, and at this level the forming S–O bond length is reduced to 1.722 Å. Both geometries are shown in Figure 1. The dipole moment at the MP2 geometry is 6.73 D at the HF/6-31G* level.

The search for a cyclic intermediate having a thiadioxirane structure[3] proved much more difficult. Optimization under C_{2v} symmetry at the HF/3-21G(*) level using various starting geometries all converged to the sulfone structure **2**. A C_{2v} stationary point (zero force structure) could be located by holding both the O–O and S–O distances fixed at different values and optimizing the S–H distances and HSH angle. The structure of this stationary point **5** is shown in Figure 1; it has an S–O bond distance of 1.702 Å and an O–O distance of 1.578 Å. These bond lengths should be compared to those calculated for dioxirane, C–O = 1.428 Å and O–O = 1.522 Å at the same level,[21,22] and experimental values of 1.388 and 1.516 Å.[23] A frequency calculation on structure **5** revealed three imaginary frequencies; thus, it is not a minimum but a third-order maximum on the PES. Two of the imaginary frequencies correspond to symmetric and antisymmetric out-of-plane hydrogen bending (B_2 and A_2 symmetry, respectively), while the third (B_2 symmetry) is a distortion toward the *syn*-peroxy sulfoxide structure (**3**).

Since the C_{2v} thiadioxirane structure proved to be a maximum on the PES, a search for a lower symmetry thiadioxirane structure was carried out. Under the constraint of C_s symmetry, a stationary point **6** with the geometry shown in Figure 1 was found. The bond lengths are similar to those of the C_{2v} structure; the S–O bond lengths are 1.646 and 1.743 Å, and the O–O bond is 1.547 Å. A frequency calculation, however, showed that this structure is not a minimum on the PES either. At the HF/3-21G(*) level, structure **6** has two imaginary frequencies. The lowest is of A′ symmetry and corresponds to a distortion toward the *syn*-peroxy sulfoxide while the second imaginary frequency is of A″ symmetry and corresponds to a distortion toward the *gauche*-peroxy sulfoxide.

These cyclic thiadioxiranes should not have any significant amount of diradical character,[24] and the RHF procedure should give a reasonable description of the wave functions. It is therefore unlikely that structures corresponding to **5** and **6** would be stable intermediates at a higher level of theory (e.g. including electron correlation). We have been unable to find any further stationary points with a thiadioxirane structure within C_s symmetry. It is conceivable that a thiadioxirane could have only C_1 symmetry, but we find it very unlikely.

The above calculations lead to the somewhat surprising conclusion that a cyclic thiadioxirane is not an energy minimum. This is in contrast to the carbon analogue, where both a carbonyl oxide and a dioxirane are stable intermediates. Although the comparison between the carbon and sulfur case is tempting, it is important to realize that there are significant differences. The tetravalency of sulfur is due to "hyper" valency while carbon has a "natural" valency of 4. This feature is revealed, for example, in the different geometry around the central atom in carbonyl oxide and the peroxy sulfoxide. The carbonyl oxide has a planar arrangement around the carbon[18a,19-21] while the sulfur is approximately pyramidal. The difference is also reflected in the trigonal-bipyramidal structure of sulfuranes (see below), in contrast to the tetrahedral geometry of carbon diols (diethers).

The only evidence for more than one intermediate in the photooxidation of sulfides comes from kinetic data.[3a] It was shown that no simple reaction scheme with only one intermediate could explain the observed concentration dependence but that a scheme with two intermediates could. Kinetic data, however, are only useful in the context of a model reaction sequence, and it is likely that there are other schemes that also would show the observed concentration dependence.[25] Furthermore, kinetic data do not give any indication of the structure of an intermediate.

Rearrangement of the *gauche*-peroxy sulfoxide would be a possible mechanism for the formation of the sulfone product.[2]

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(25) For example, dimeric species analogous to those proposed by Sawaki and Ogata and by Akasaka and Ando: References 4a and 1h.

Table I. Total Energies (Hartress) for Structures in Figure 1

system	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*
$^3O_2(^3\Sigma_u)$	148.769 09	149.608 42 149.615 46^c 149.656 62^d	149.949 68 149.995 45^c 150.063 53^d	149.941 98 149.988 24^c	149.964 82
$^1O_2(^1\Delta_g)$	148.712 20	149.547 16 149.553 52^c	149.912 39 149.959 10^c 150.027 58^{b,d}	149.905 98^b 149.952 22^{b,c}	149.928 82^b
H_2O	75.585 96	76.009 76	76.196 48	76.202 38	76.206 94
H_2S	396.819 64	398.667 32 398.671 39^c 398.673 42^d	398.788 22 398.808 42^c 398.813 06^d	398.806 53 398.828 32^c	398.811 62
H_2SO (**1**)	471.173 62	473.437 64 473.485 64^d	473.746 36 473.848 78^d	473.756 57	473.775 19
H_2SO_2 (**2**)	545.610 72	548.279 54 548.307 39^c 548.368 84^d	548.773 70 548.858 90^c 548.955 79^d	548.772 51 548.856 43^c	548.802 46
c-H_2SOO (**3**)	545.497 01	548.142 76 548.141 07^c 548.156 50^{a,c} 548.207 63^{a,d}	548.613 92 548.622 77^c 548.695 64^{a,c} 548.781 38^{a,d}	548.628 75 548.635 83^c 548.707 36^{a,c}	548.660 31 548.665 82^a
TS (4)	545.466 51	548.111 97 548.124 71^a	548.620 53 548.617 48^a	548.626 53 548.628 92^a	548.672 78 548.662 66^a
$H_2S(O)_2$ (**5**)	545.319 98	547.971 60	548.524 96		
$H_2S(O)_2$ (**6**)	545.427 52	548.078 54	548.610 75		
$H_2S(OH)_2$ (**7**)	546.748 20	549.421 31	549.928 00	549.942 80	549.963 67
$H_2S(OOH)(OH)$ (**8**)	621.100 60	624.167 27	624.860 72		
Me_2S (**9**)	474.456 98	476.735 30	477.120 61		
Me_2SO (**10**)	548.846 67	551.537 04	552.111 15		
Me_2SO_2 (**11**)	623.303 62	626.391 15	627.150 43		
Me_2SOO (**12**)	623.180 04	626.246 48	626.990 20		
Me_2 TS (**13**)	623.136 36	626.216 46	627.018 04		

[a] MP2/6-31G*-optimized geometries. [b] Estimated by adding the experimental singlet-triplet energy difference[25] to the total energy for the triplet state. Calculated at HF/3-21G(*)-optimized geometries. [c] 6-31G(2d) basis. Calculated at HF/3-21G(*)-optimized geometries. [d] 6-311G(3d) basis. Calculated at HF/3-21G(*)-optimized geometries. [e] 1 Hartree = 327.51 kcal/mol, all energies listed are negative.

Table II. Relative Energies (kcal/mol)

reaction	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*
$2H_2S + {}^1O_2 \rightarrow 2H_2SO$ (**1**)	2.7	4.1	−2.4 −27.5^c	3.7	1.1
$H_2S + {}^1O_2 \rightarrow H_2SO_2$ (**2**)	−49.5	−40.8 −51.8^b	−45.9 −57.3^b −72.9^c	−37.7 −47.6^b	−38.9
$H_2S + {}^1O_2 \rightarrow H_2SOO$ (**3**)	21.9	45.0 46.1^a 42.9^{a,b}	54.4 48.9^a 45.7^{a,b} 37.2^{a,c}	52.6 48.1^a 45.9^{a,b}	50.3 46.8^a
$H_2S + {}^1O_2 \rightarrow$ TS (4)	41.0	64.3 56.3^a	50.3 52.2^a	54.0 52.5^a	42.5 48.8^a
$H_2S + {}^1O_2 \rightarrow H_2S(O)_2$ (**5**)	133.0	152.5	110.3		
$H_2S + {}^1O_2 \rightarrow H_2S(O)_2$ (**6**)	65.5	85.3	56.4		
$H_2SO + H_2O \rightarrow H_2S(OH)_2$ (**7**)	7.1	16.4	9.3	10.1	11.6
$H_2SOO + H_2O \rightarrow H_2S(OOH)(OH)$ (**8**)	−11.1	−9.3	−31.6		
$2Me_2S + {}^1O_2 \rightarrow 2Me_2SO$ (**10**)	−42.2	−35.3	−43.1		
$Me_2S + {}^1O_2 \rightarrow Me_2SO_2$ (**11**)	−84.4	−68.2	−73.7		
$Me_2S + {}^1O_2 \rightarrow Me_2SOO$ (**12**)	−6.8	22.6	26.9		
$Me_2S + {}^1O_2 \rightarrow Me_2$ TS (**13**)	20.6	41.4	9.4		

[a] At MP2/6-31G*-optimized geometry. [b] 6-31G(2d) basis. [c] 6-311G(3d) basis.

Despite an extensive search at both the HF/3-21G(*) and MP2/3-21G(*) levels of theory, we were unable to find the transition structure connecting these minima. The main difficulties were that severe convergence problems for the SCF procedure occurred and that the geometry optimization converged to one of the two transition structures connecting the peroxy sulfoxides (i.e. gauche to gauche and gauche to syn), instead of the desired peroxy sulfoxide to sulfone TS. It is possible that the PES near the TS cannot be properly described by a single determinant wave function, but geometry optimization at the MCSCF level is currently prohibitively expensive.

As mentioned in the introduction, it has been postulated that the peroxy sulfoxide can form a solvent adduct with protic solvents such as methanol. This adduct should have a sulfurane structure similar to those isolated by Martin et al.[26] and Schomburg et al.[26] The geometries of these sulfuranes are approximately trigonal bipyramids, with the most electronegative ligands occupying the

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(26) For a review of sulfurane chemistry, see: Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry*; Bernardi, F., Csizmadia, I. G., Mangini, A., Ed.; Elsevier: New York, 1985; p 408. (a) Hodges, K. C.; Schomburg, D.; Weiss, J.-V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096. (b) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1155. (c) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1972**, *94*, 5010. (d) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1971**, *93*, 6674. (e) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735. (f) Schomburg, D.; Mir, Q.-C.; Shreeve, J. *J. Am. Chem. Soc.* **1981**, *103*, 406. (g) Mir, Q.-C.; Laurence, K. A.; Shreeve, R. W.; Babb, D. P.; Shreeve, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 5949. (h) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001. (i) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127. (j) Kalman, A.; Sasvari, K.; Kapovits, I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 355.

Table III. Total and Relative Energies of H_2SO_2 (**2**) and H_2SOO (**3**) by Different Methods

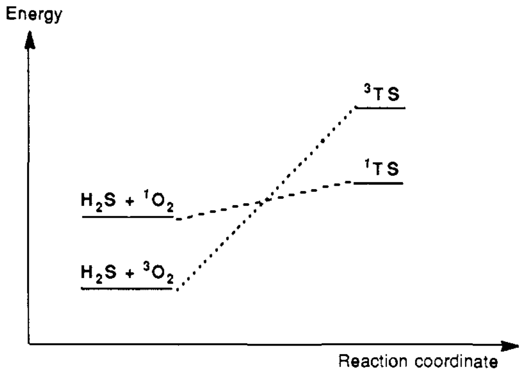
level[a]	$-E_{total}$ (H_2SO_2)	$-E_{total}$ (H_2SOO)	ΔE, kcal/mol
HF/3-21G(*)	545.610 72	545.486 90	77.7
MP2(val1)/3-21G(*)	545.647 27	545.528 07	74.8
MP3(val1)/3-21G(*)	545.649 35	545.537 52	70.2
MP4(val1)/3-21G(*)	545.655 89	545.543 38	70.6
MP2(val2)/3-21G(*)	545.853 98	545.711 37	89.5
MP3(val2)/3-21G(*)	545.850 02	545.722 01	80.3
MP4(val2)/3-21G(*)	545.872 06	545.738 23	84.0
MP2/3-21G(*)	545.985 19	545.836 67	93.2
MP3/3-21G(*)	545.976 26	545.847 47	80.8
MP4/3-21G(*)	546.012 59	545.875 62	86.0
HF/6-31G*	548.279 54	548.141 07	86.9
MP2/6-31G*	548.773 70	548.622 77	94.7
MP3/6-31G*	548.772 51	548.635 83	85.8
MP4/6-31G*	548.802 46	548.665 82	85.7
Full-Cl(val1)/3-21G(*)	545.656 79	545.547 04	68.9
MCSCF(val1)/3-21G(*)	545.741 41	545.613 25	80.4

[a] (Val1) indicates orbitals 11–21, while (val2) indicates orbitals 11–41. See text for discussion.

axial positions. The structures of sulfuranes corresponding to addition of H_2O to H_2SO and H_2SOO were calculated at the HF/3-21G(*) level. Here, H_2O serves as a model for MeOH. The dihydroxysulfurane, $H_2S(OH)_2$ (**7**), was optimized under both C_{2v} and C_1 symmetry. The C_1 structure was found to be only 0.04 kcal/mol lower in energy than the C_{2v} structure at the HF/3-21G(*) level, and consequently only the C_{2v} structure was used for single-point calculations. Similarly, only a C_s structure was used for the hydroxyhydroperoxysulfurane structure, $H_2S(OOH)(OH)$ (**8**). The optimized geometries of these species are shown in Figure 1. The S–O bond lengths for the sulfuranes (1.750 Å for the dihydroxy and 1.805 and 1.711 Å for the hydroxyhydroperoxy) are much longer than those found in sulfoxides or sulfones but are close to those found by X-ray crystallography in related compounds.[26]

The calculated total energies of the species studied here are given in Table I. Table II shows some calculated reaction energies at different levels of theory. At the HF/3-21G(*) level, peroxy sulfoxide formation is calculated to be endothermic by 22 kcal/mol and to have a barrier of 41 kcal/mol. The use of a better basis, 6-31G*, which includes polarization functions on all the heavy atoms, gives a substantially higher barrier. At the HF level, the activation energy is calculated to be 64 kcal/mol, and the peroxy sulfoxide is 45 kcal/mol higher in energy than H_2S and $^1O_2$. When electron correlation is included, the activation energy is lowered while the peroxy sulfoxide is raised in energy. Indeed, single-point calculations at the MP2 and MP4 levels of theory at the HF/3-21G(*)-optimized geometries place the transition structure **4** for the formation of peroxy sulfoxide **3** below the peroxy sulfoxide by 4 and 8 kcal/mol, respectively. When both structures are reoptimized at the MP2/6-31G* level, however, the transition structure is 3 kcal/mol higher in energy than the peroxy sulfoxide at the MP2 level and 2 kcal/mol higher at the MP4 level. It thus appears that the peroxy sulfoxide remains a stable, although not very strongly bound, intermediate at a level including electron correlation. A frequency calculation at the MP2/6-31G* level also shows that the peroxy sulfoxide is a minimum on the PES (see below). At the MP4/6-31G* level, the peroxy sulfoxide and the corresponding transition structure are calculated to be ~45 kcal/mol above the reactants, H_2S and $^1O_2$. Also in Table II are some calculated overall heats of reaction. The oxidation of 2 mol of H_2S by 1 mol of $^1O_2$ is calculated to be approximately thermoneutral, while the formation of the sulfone, H_2SO_2, is exothermic by ~40 kcal/mol.

Decomposition of the peroxy sulfoxide intermediate to ground-state oxygen may be the mechanism of nonreactive quenching of singlet oxygen by sulfides. For O_2, the ground state is a triplet while that of the peroxy sulfoxide is a singlet. There must therefore be a crossing of the singlet and triplet PES's along the reaction coordinate for the formation of **3**. The position of this point is important for understanding the physical quenching. At the optimized TS **4**, the triplet state is 24 kcal/mol higher in energy than the singlet at the MP2/6-31G* level.[27] Since the singlet–triplet gap for $^1O_2$ is well estimated at this level (see above), the singlet–triplet PES crossing must occur fairly early along the reaction coordinate. This indicates that the peroxy sulfoxide intermediate probably is not directly involved in the quenching of singlet oxygen.



The cyclic thiadioxirane structures **5** and **6** were found to be high in energy, as expected since they are maxima on the PES (Table II). At the HF/3-21G(*) level, **5** is located 133 kcal/mol higher in energy than H_2S and $^1O_2$, while **6** is 65 kcal/mol higher. Stability calculations on the wave functions[28] for these structures show that they are the lowest energy RHF wave functions (i.e. the SCF procedure has not accidentally converged to an excited state). Inclusion of a better basis and electron correlation does not significantly alter the relative energies of these structures. At the MP2/6-31G* level, they are still 110 and 56 kcal/mol, respectively, over the reactants.[24]

The HF/3-21G(*)-optimized geometries of Me_2S (**9**), Me_2SO (**10**), Me_2SO_2 (**11**), Me_2SOO (**12**), and the transition structure **13** for the formation of Me_2SOO are shown in Figure 1, and the total energies are given in Table I. The calculated geometries for Me_2S, Me_2SO, and Me_2SO_2 agree well with experimental results (experimental values in brackets).[28] Structures corresponding to the thiadioxirane structures **5** and **6** were not calculated for the Me_2S system since they are not stable intermediates with H_2S, and there is no reason to believe that substitution of Me for H would change these stationary points from maxima to minima.

The structure of the dimethyl peroxy sulfoxide (**12**) is very similar to that found for H_2SOO, the O–O bond being slightly shorter for the dimethyl case. The transition structure **13** leading to **12** is somewhat earlier than for H_2S; the S-O-forming bond is 2.15 Å, which is almost 0.2 Å longer than for H_2S. It is expected, however, that the S–O and O–O bonds for structures **12** and **13** would change if they were optimized at a better level of theory. For systems of this size (five heavy atoms), optimization at the MP2/6-31G* level is currently prohibitively expensive.

The formation of the dimethyl peroxy sulfoxide (**12**) is calculated to be endothermic by 27 kcal/mol at the MP2/6-31G*//HF/3-21G(*) level, which is 27 kcal/mol lower than for H_2SOO. A reoptimization at the MP2/6-31G* level and inclusion of electron correlation up to MP4 would probably lower the relative energy of Me_2SOO to ~17 kcal/mol over $Me_2S + {}^1O_2$, as judged

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[27] The triplet wave function has an $\langle S^2 \rangle$ value of 2.03, indicating negligible spin contamination. The total energies of the triplet state are −548.127 41 hartrees at the HF/6-31G* level and −548.584 76 hartrees at the MP2/6-31G* level.

[28] Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 3045.

[29] Experimental geometries. H_2S, Me_2SO: Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structural Data on Free Polyatomic Molecules*; Landolt-Bornstein Series II; Springer: Berlin, 1976; Vol. 7. Me_2S: Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479. Me_2SO_2: Oberhammer, H.; Zeil, W. *J. Mol. Struct.* **1970**, *6*, 399.

from the results at this level for H_2SOO. The transition structure **13** leading to the peroxy sulfoxide structure **12** is 41 kcal/mol higher in energy than the reactants at the HF/6-31G* level but only 9 kcal/mol at the MP2/6-31G* level. At the MP2/6-31G*//HF/3-21G(*) level, TS **13** is 17 kcal/mol lower in energy than the peroxy sulfoxide **12**. This is probably just an artifact of the inadequate level of optimization, as shown by the better calculations for H_2SOO. Experimentally, it is observed that alkyl sulfides react readily with singlet oxygen, even at low temperature.[2] This suggests that there is only a very small barrier (≤ 5 kcal/mol) for the reaction, which agrees with the reported near-zero activation energies for sulfides.[30] Assuming that the transition state leading to peroxy sulfoxide **12** is located a few kilocalories per mole higher in energy than **12**, the calculated activation energy is thus in error by ~15–20 kcal/mol at the MP2/6-31G* level. The overall heat of formation of dimethyl sulfone is calculated to be 74 kcal/mol at the same level (Table II), in poor agreement with the experimental value of 101 kcal/mol.[31] Similarly, the formation of 2 mol of dimethyl sulfoxide from dimethyl sulfide and singlet oxygen is calculated to be exothermic by 43 kcal/mol, compared to the experimental value of 75 kcal/mol.[31] The agreement with experimental data is surprisingly poor, since the MP2/6-31G* level usually gives much better results.[13]

The large stabilization (30–40 kcal/mol) of the sulfur–oxygen species on substitution of a methyl group for hydrogen is somewhat unusual. In quantum mechanical calculations, it is often assumed that hydrogen is a good model for an alkyl group. This may be a poor approximation when reactant(s) and product(s) have very different polarities, as in the present study. The stabilization by methyl groups can be rationalized by the increase in positive charge on sulfur upon formation of a S–O bond.[32]

The overestimation of the activation energy could arise because the PES near the peroxy sulfoxide and transition state is poorly represented by a single-determinant wave function, and inclusion of electron correlation based on a single determinant may be insufficient to repair this deficiency. To test this hypothesis, we carried out multiconfiguration (MCSCF) calculations on H_2SOO and H_2SO_2 with the 3-21G(*) basis. This basis set is somewhat less flexible than desirable but is currently the limit for these systems with the given program code. The MCSCF wave function was of the complete active space (CASSCF) type,[33] where the active space was chosen as the conceptual minimal basis valence orbitals, minus the three lowest lying orbitals (which approximately correspond to oxygen 2s and sulfur 3s orbitals). This active space thus includes 14 electrons in 11 orbitals and is labeled val1. For H_2SO_2 (C_{2v} symmetry), this results in a total of 8300 symmetry-adapted configurations, while the calculation on H_2SOO (C_s symmetry) included 16 430 configurations. For H_2SO_2 the HF/3-21G(*)-optimized geometry was used, while the MP2/6-31G* geometry was employed for H_2SOO.

The total and relative energies of H_2SO_2 and H_2SOO at different levels of theory are shown in Table III. The sulfone structure should be well represented by a single-determinant (HF) solution, and consequently an energy lowering of the peroxy sulfoxide relative to the sulfone by the MCSCF calculation would indicate that the peroxy sulfoxide is poorly represented by the HF wave function. It should be noted that orbitals 1–10 are constrained to be doubly occupied in the CI and MCSCF calculations, and only the first four virtual orbitals are included. The results from these calculations can therefore not be directly compared to MPn calculations, where all occupied valence orbitals and the full virtual space are used. Two types of limited MPn calculations were carried out for comparison. The first is labeled MPn(val1) and uses only orbitals 11–21 (i.e. same orbital space as for the CI calculation) for electron correlation. The second is labeled MPn(val2), which denotes that orbitals from 11 to 41 are used (i.e. all the virtual orbitals). The MCSCF procedure optimizes the orbital coefficients for the active orbitals, and although only the four lowest virtual orbitals are explicitly included in the MCSCF wave function, the remaining virtual orbital can mix into the wave function via this optimization. It is therefore proper to compare the MCSCF results with those obtained from MPn(val2) calculations.

The CI wave function for H_iSO_2 in the valence space defined above has a coefficient of 0.978 for the HF configuration, while the corresponding coefficient for the peroxy sulfoxide is 0.964. These coefficients are close to unity, which indicates that both structures are well described by a single determinant, and the peroxy sulfoxide therefore is best represented by a zwitterionic and not a biradical structure.[34] The RHF/6-31G* wave function is also stable[28] with respect to an UHF wave function, which further indicates very little biradical character.[35] The large coefficients for the HF configuration indicate that the MP perturbation series should be suitable for introducing electron correlation.[24] Indeed, the MP4(val1) energy difference is very close to that from the full CI(val1) calculation, as seen in Table III. At the MCSCF level, the energy difference between the peroxy sulfoxide and the sulfone is 80 kcal/mol, which is close to the MP4(val2) result of 84 kcal/mol. The energy difference is also close to that obtained (86 kcal/mol) when all the valence orbitals are used. The MCSCF result thus also indicates that the MP method should be well suited for calculating the effect of electron correlation. The use of the large 6-31G* basis gives relative energies virtually identical with those obtained with the 3-21G(*).

Having established that inclusion of electron correlation via a perturbation expansion is valid, the limited basis set is thus the most likely source of error. To test the effect of an improvement of the basis set, we carried out calculations at the MP3/6-31G(2d) and MP2/6-311G(3d) levels. There is currently no standard 6-311G basis for second-row elements, but a 6-311G(3d) type basis for sulfur was constructed from the 6-31G(3d) basis by addition of a set of s and p functions with an exponent of 0.035. The results from these calculations are shown in Tables I and II. At the MP2/6-311G(3d) level, the overall heat of reaction for formation of H_2SO_2 is increased to 72 kcal/mol, compared to the 6-31G* value of 46 kcal/mol. Assuming that the formation of Me_2SO_2 from Me_2S and $^1O_2$ would show a similar effect upon increasing the basis set, we can thus estimate that the heat of reaction for formation of Me_2SO_2 would be 100 kcal/mol, in good agreement with the experimental value of 101 kcal/mol.[31] Similarly, the formation of 2 mol of Me_2SO can be estimated to be exothermic by 69 kcal/mol, while the experimental value is 75 kcal/mol.[31] With the 6-311G(3d) basis set, H_2SOO is calculated to be 37 kcal/mol above the reactants at the MP2 level or 12 kcal/mol lower than with the 6-31G* basis (Table II). Again assuming a similar response for the dimethyl system, the dimethyl peroxy sulfoxide should be ~8 kcal/mol over the reactants. These values now agree reasonably well with experimental data.

Table II shows some calculated reaction energies for formation of sulfuranes **7** and **8**. The strong dependance of reaction energetics on basis sets makes it difficult to draw any conclusion as to whether the calculated energetics are reliable. Nevertheless, the formation of dihydroxysulfurane (**7**) from H_2SO and H_2O is calculated to be endothermic by ~10 kcal/mol, which agrees with the experimental facts that sulfoxides do not add H_2O (MeOH) and sulfuranes are very suceptible to loss of one of the

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[30] Koch, E. *Tetrahedron* **1968**, *24*, 6295.

[31] Wagner, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (supp. 2).

[32] The net charges on sulfur (Mulliken population analysis) at the HF/6-31G* level are the following: H_2S, −0.22; H_2SO, +0.66; H_2SO_2, +1.18; H_2SOO, +0.62; $H_2S(OH)_2$; +0.68; $H_2S(OH)(OOH)$, +0.68. See also: reference 7a.

[33] (a) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69* (Part 2), 399. (b) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (c) Siegbahn, P.; Heiberg, A.; Roos, B. *Phys. Scr.* **1980**, *21*, 323. (d) Roos, B. O. *Int. J. Quantum. Chem., Symp.* **1980**, *14*, 175.

[34] The next-largest expansion coefficient for the sulfone is 0.058 and corresponds to a double excitation. For the peroxy sulfoxide, the second largest coefficient is 0.092 for a configuration with a single electron promoted from the HOMO to the SLUMO, which gives the CI wave function ~1% diradical character from this configuration.

[35] Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871.

Table IV. Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for the Peroxy Sulfoxides **3** and **12**

H_2SOO (**3**)				Me_2SOO (**12**): HF/3-21G(*)			
freq	int	freq	int	freq	int	freq	int
261	3.1	308	4.8	188	0.4	1204	24.1
310	14.8	338	36.1	221	1.6	1512	14.8
714	105.2	764	1.1	233	1.4	1538	30.2
962	79.6	870	30.4	290	4.6	1603	5.4
1035	0.6	889	0.2	350	7.3	1624	9.1
1106	11.3	1023	18.5	353	17.7	1646	14.2
1443	16.3	1305	9.1	436	5.9	1666	32.4
2848	10.9	2608	2.6	732	10.6	3223	3.2
2860	9.5	2631	35.4	760	67.7	3226	13.3
				793	5.3	3306	0.4
				942	54.2	3309	2.8
				1063	11.0	3338	0.0
				1086	0.8	3341	17.2
				1153	65.1		

ligands.[25] The formation of hydroxyhydroperoxysulfurane (**8**) from peroxy sulfoxide **3** and H_2O is calculated to be exothermic by ~25 kcal/mol at the MP2/6-31G* level. The calculations for Me_2SOO suggest that substitution of Me for H stabilizes the peroxy sulfoxide, so that the formation of a sulfurane corresponding to **8** from Me_2SOO and H_2O is probably less exothermic. Even so, the present calculations suggest that the reaction may be at least thermoneutral. Hydrogen bonding by solvent may further stabilize a sulfurane.

The major approximation made in the above discussion is that the effects of including more electron correlation corrections and improving the basis set are the same for the hydrogen and methyl systems. When the reaction energies are as different as observed at the MP2/6-31G* level, it is of course of concern whether this approximation is valid. The justification rests mainly on the reasonable agreement with experimental data for the overall heat of reaction for formation of dimethyl sulfone and sulfoxide. It would be of interest to carry out calculations on the dimethyl system with a large basis set, but this is currently beyond our capabilities.[36] Finally, all of these calculations refer to gas-phase reactions. The polar species, such as the peroxy sulfoxide and the TS leading to it, should be stabilized more than the nonpolar reactants (sulfide and singlet oxygen) by solvation, and consequently their relative energies are overestimated by the present calculations. The magnitude of the solvent stabilization is difficult to estimate, but experimental activation energies for the reaction of singlet oxygen with alkenes in solution and in the gas phase suggest values of ~5 kcal/mol.[37]

Since the peroxy sulfoxide is probably a very shallow minimum on the PES, any spectroscopic identification will probably have to be carried out at low temperatures in an inert-gas matrix. The frequencies and intensities for the infrared spectrum of the peroxy sulfoxide were calculated in order to aid in the interpretation of future experimental data. The correlation between calculated and experimental infrared spectra has proven a valuable tool in other cases.[38] At the HF level, the calculated frequencies are usually overestimated by 10–15%, while the error at the MP2 level is somewhat smaller, typically ~5%.[39] The quality of calculated intensities has been shown to be much more dependent on the level of theory than the frequencies,[40] and consequently only a qualitative classification into strong, medium, and weak bands can be expected to correlate with experimental results. For the smaller system, H_2SOO, the IR spectrum was calculated at both the HF/3-21G(*) and MP2/6-31G* levels of theory. The more realistic system, Me_2SOO, was calculated only at the HF/3-21G(*) level due to economic limitations, and the results are given in Table IV.

Table V. Calculated Isotopic Shifts (cm^{-1}) of Selected Bands of the Peroxy Sulfoxides **3** and **12**

system	R_2SOO	$R_2S^{18}OO$	$R_2SO^{18}O$	$R_2S^{18}O^{18}O$
3, HF/3-21G(*)	714	−19	−20	−40
	962	−33	0	−33
	1106	−6	0	−7
3, MP2/6-31G*	764	−17	−6	−24
	870	−18	−19	−35
	1023	−24	−3	−27
12, HF/3-21G(*)	732	−9	−8	−25
	760	−14	−12	−19
	942	−35	0	−35

The two most characteristic bands for H_2SOO at the HF/3-21G(*) level are predicted to be at 714 and 962 cm^{-1}. These correspond approximately to O–O and S–O stretches, respectively. At the MP2/6-31G* level these absorptions are predicted to be at 870 and 1023 cm^{-1}. Both bands are predicted to be strong at both levels. For the larger Me_2SOO system, the normal modes (corresponding approximately to O–O and S–O stretches) are calculated to be at 760 and 942 cm^{-1}, although the band at 732 cm^{-1} also contains significant amounts of an O–O stretching motion. On the basis of the changes that occur upon replacing H with Me and going to the MP2/6-31G* level, we estimate that Me_2SOO should have two strong bands at ~910 and 1000 cm^{-1}. Due to anharmonicity in the experimental frequencies, observed frequencies may be slightly lower than these estimates. Experimentally, Me_2SO has an S–O stretch at 1050 cm^{-1},[41] while Me_2SO_2 has S–O stretches at 1125 and 1290 cm^{-1}, in addition to bending frequencies at 750 and 920 cm^{-1}.[41]

To aid further in the possible identification of the peroxy sulfoxide, the effect on the frequencies of substituting either one or both of the oxygens with ^{18}O was calculated. Table V shows the three bands that are most effected by isotopic substitution for the systems in Table IV. The effect on the bands not shown is small (less than 10 cm^{-1}), and these bands are less characteristic for structure identification. The frequency of the S–O stretch is predicted to be lowered by approximately 30 cm^{-1} when the oxygen bonded to sulfur is replaced with the heavier isotope, independent of the mass of the outer oxygen. The frequency lowering is insensitive to the level of theory and to the nature of the R group. The frequency of the O–O stretch is predicted to

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(36) On the basis of the results for the H_2S system, it appears that a basis set of at least triplet split-valence quality with several sets of polarization functions is necessary, and electron correlation correction should be included. For the dimethyl system these requirements make calculations very expensive. Furthermore, it is possible that higher angular momentum functions (i.e. f functions) may be important for a reasonable description of some of the species (e.g. the peroxy sulfoxide).

(37) (a) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604. (b) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6854.

(38) For a recent review of the use of calculated IR spectra in the identification of unusual molecules, see: Hess, B. A., Jr.; Schaad, L. J. *Chem. Rev.* **1986**, *86*, 709.

(39) (a) Reference 12, pp 226–260. (b) Pople, J. A.; Schlegel, H. B.; Krishan, R.; DeFrees, D. J.; Binkley, J. S.; Whiteside, R. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum. Chem., Symp.* **1981**, *15*, 269. (c) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(40) (a) Yamaguchi, A.; Frisch, M.; Gaw, J.; Schaefer, H. F.; Binkley, S. J. *J. Chem. Phys.* **1986**, *84*, 2262. (b) Jensen, F.; Miller, M. D.; Chapman, O. L.; Houk, K. N., submitted for publication.

(41) Sadtler Standard Infrared Spectra 536, 32415: Sadtler Research Laboratories, 3316 Spring Garden St., Philadelphia, PA.

be lowered by 20–40 cm^{-1}, depending on the level of theory used and the nature of the substituent. The effect of replacing only one oxygen with a heavy isotope is approximately half that of replacing both, as would be expected for an O–O stretch.

Conclusion

The reactions of singlet oxygen with H_2S and Me_2S have been calculated by ab initio methods. A peroxy sulfoxide structure is found to be a stable, but weakly bound, intermediate. This result supports the mechanism proposed for the photooxidation of organic sulfides. A second proposed intermediate, a cyclic thiadioxirane, is found to be a local maximum on the potential energy surface and is not a valid intermediate. Large-scale MCSCF results show that the peroxy sulfoxide is best described by a zwitterionic and not a biradical structure. Activation energies and overall heats of reaction are very sensitive to the quality of the basis set. When additivity of the effects of improving the basis set and inclusion of electron correlation are assumed, the activation energy for the formation of dimethyl peroxy sulfoxide at the MP2/6-311G(3d) level is estimated to be ~10 kcal/mol. This is 5–10 kcal/mol higher than experimentally observed and suggests that even higher level calculations are necessary. The formation of a solvent adduct in protic solvents from the peroxy sulfoxide (a sulfurane) is calculated to be approximately thermoneutral, although an accurate prediction is difficult from the present calculations. The infrared spectrum and isotopic shifts of the peroxy sulfoxide have been calculated for possible spectroscopic identification.

After this work was completed, Ando et al.[42] reported IR spectra of a reactive intermediate formed upon irradiation of a sulfide in an oxygen matrix at 13 K. The intermediate formed from diphenyl sulfide has an IR absorption at 997 cm^{-1}, which is shifted to 978 cm^{-1} when $^{18}O^{18}O$ is used and split into two bands at 993 and 984 cm^{-1} when $^{18}O^{16}O$ is used. These data agree reasonably well with the calculated values in this work. If the observed intermediate is indeed a peroxy sulfoxide, the calculations predict that there should be another strong IR band at ~910 cm^{-1} (only the region 960–1040 cm^{-1} was reported in ref 42), which should show a characteristic frequency shift upon isotopic substitution.

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Remarkable Stabilities of the Diatomic Multiply Charged Cations $SiHe^{\bullet 3+}$ and $SiHe^{4+}$

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Abstract: Ab initio molecular orbital theory using basis sets up to 6-311G(MC)(2d,2p) and with electron correlation incorporated at the fourth-order Møller–Plesset level has been used to study the series of diatomic ions $SiHe^{n+}$ (n = 1–4). The $SiHe^{\bullet +}$ monocation and $SiHe^{2+}$ dication are found to be weakly bound species with long silicon–helium bonds. On the other hand, the $SiHe^{\bullet 3+}$ trication and $SiHe^{4+}$ tetracation are characterized by considerably shorter Si–He bonds (1.670 and 1.550 Å, respectively). In spite of the availability of extremely exothermic fragmentation processes, $SiHe^{\bullet 3+}$ and $SiHe^{4+}$ are predicted to be potentially observable species in the gas phase. The trend of Si–He bond lengths in the series of $SiHe^{n+}$ ions can readily be understood in terms of the number of electrons occupying antibonding orbitals. $SiHe^{4+}$, with just two valence electrons, is the smallest stable polyatomic tetracation yet reported in the literature.

The chemistry of helium-containing cations[1] has attracted increasing recent interest. In spite of the chemical inertness of the helium atom, many helium-containing ions are predicted to be stable and to contain strong bonds to helium. Indeed, several such ions have recently been observed in mass spectrometry experiments.[2] Most studies of helium-containing ions to date have dealt mainly with singly charged or doubly charged species. In recent theoretical investigations, however, we have shown[3] that even highly charged ions, CHe_4^{4+}, $CHe_3^{\bullet 3+}$, and $HeCF^{3+}$, display remarkable stability despite extreme coulomb repulsion. In this paper, we present evidence for the stability of the *diatomic* tri- and tetracations, $SiHe^{\bullet 3+}$ and $SiHe^{4+}$. Results are reported for the series of diatomic ions $SiHe^{n+}$ (n = 1–4) and rationalized in terms of a simple orbital interaction model.[4]

Method and Results

Standard ab initio molecular orbital calculations were carried out with a modified version[5] of the Gaussian 82 system of programs.[6] Geometry optimizations for all systems were performed with the triple-split-valence plus dp-polarization 6-311G(MC)** basis set[7-9] and valence-electron correlation incorporated at the

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