Ithaco Model 391A lock-in amplifier. A plot of the ac current as a function of the potential gave a voltammogram of the photogenerated free radical. All measurements were made at 53-Hz modulation with quadrature detection of the signal. The measured potentials are reported with respect to the saturated calomel electrode (SCE).

Kinetics. The triorganotin perchlorate was made by mixing the appropriate triorganotin chloride with an equivalent amount of silver perchlorate in THF. The silver chloride was removed by filtration and a fresh solution of cation perchlorate was used for the kinetic runs. An aliquot of solutions of R_3Sn^+ (5×10^{-3} M or 10^{-3} M) and DMFe (5×10^{-3} M) or TMPD (5×10^{-3} M) was transferred by syringe to the two compartments of a stop-flow apparatus (Hi-Tech Scientific Limited).

As a general procedure the decrease in the concentration of DMFe or TMPD was monitored by observing the appearance of $DMFe^{\bullet+}$ ($\epsilon = 21$) or $TMPD^{\bullet+}$ ($\epsilon = 425$) at 570 or 700 nm, respectively. The extinction coefficient of each radical-cation was determined by measuring the absorbance of a solution of the reaction mixture resultant from the reaction of DMFe or TMPD with a 97 mol % solution of $AgClO_4$. The metallic silver formed from the reaction was separated by centrifugation. The UV spectrometer used was a Unicam SP 1800.

Several control experiments were carried out in order to ensure that the generation of the ferrocenium ions was not due to residual levels of Ag^+ or of R_3SnCl. It was found that the tin chlorides did not react with TMPD or DMFe. However, the possibility remained that a detectable amount of Ag^+, due to the finite solubility of AgCl in THF, was responsible for the formation of the ferrocenium ions. This concern was eliminated by addition of ferrocene (0.001 M), which does *not* react with R_3Sn^+ but reacts readily with Ag^+. Aliquots of this "silver-free" solution of the tin cation were used to observe the oxidation reaction with TMPD, DMP, and DMFe.

Laser Flash Photolysis. The laser flash photolysis technique has been described in detail elsewhere.[23] Briefly, samples were irradiated with pulses from a nitrogen laser (337.1 nm, 8 ns duration, up to 10 mJ power) and the transients thus generated were monitored on a detection system consisting of a low powered xenon lamp and a monochromator fitted with a photomultiplier tube detector. Signals from the photomultiplier were digitized (Tektronix 7912) and were then transferred to a PDP 11/23 computer for storage and analysis.

In a typical experiment, a solution of Bu_3SnH (0.3 M) in a mixture of benzene/di-*tert*-butyl peroxide (4:1) were deoxygenated by nitrogen purging for 5 min. The decay of the $Bu_3Sn^{\bullet}$ radical was monitored (400 nm) as a function of the concentration of a nitro compound. A plot of k_{obs} versus concentration gave a straight line with the slope being the absolute rate constant.

(23) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

The Mechanism of Oxygen Transfer from an Oxaziridine to a Sulfide and a Sulfoxide: A Theoretical Study

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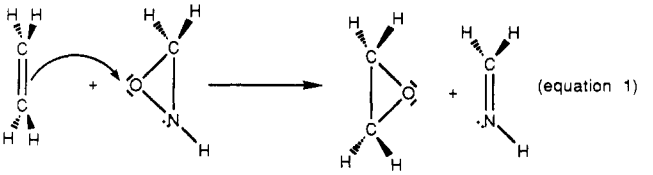
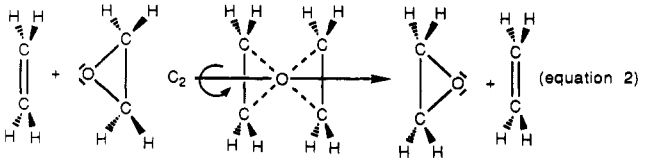
Chiral oxaziridines provide synthetically useful reagents for the asymmetric transfer of an oxygen atom to a variety of substrates. One of the fundamental questions pertaining to the approach of the reactants is whether either of the lone pairs on the electrophilic oxygen exerts a significant electronic influence on the transition structure. Employing a model reaction system, we have found that oxygen atom transfer from an oxaziridine to a sulfoxide is essentially invarient to the torsional orientation of the two fragments in the transition state. The planar and spiro transition structures differ in energy by only 0.4 kcal/mol at the MP4SDTQ/4-31G(d) level of calculation. These data are consistent with experimental observations and with the earlier ab initio calculations on this type of oxygen atom transfer.

Introduction

Oxygen transfer to a nucleophilic addend typically involves the cleavage of a relatively weak oxygen–oxygen or metal–oxygen σ-bond.[1] However, it has recently been shown[2] that a properly substituted oxaziridine functional group is a unique oxidizing agent in that a nucleophilic S_N2 type attack on the oxaziridine oxygen results in the displacement of an imine with transfer of its oxygen atom (eq 1). For example, in an alkene expoxidation reaction oxygen transfer to the nucleophilic carbon–carbon double bond is facilitated by the relatively weak oxygen–nitrogen bond and by the enthalpy of carbon–nitrogen π-bond





(1) (a) Sharpless, K. B. *Aldrichimica Acta* **1979**, *12*, 63. (b) Behrens, C. H., Sharpless, K. B. *Ibid.* **1983**, *16*, 67. (c) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 8, pp 247–301. (d) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (e) Bruice, T. C. *Aldrichimica Acta* **1988**, *21*, 87.

(2) (a) For a review of the chemistry of *N*-sulfonyloxaziridines, see: Davis, F. A.; Sheppard, A. C. *Tetrahedron* In press. (b) For a review on chiral *N*-sulfonyloxaziridines, see: Davis, F. A.; Jenkins, R. H., Jr. In *Asymmetric Synthesis*; Morrison, J. D., Ed., Academic Press: New York, 1984; Vol. 4, pp 313–353. (c) Davis, F. A.; Chattopadhyay, S. *Tetrahedron Lett.* **1986**, 5079. (d) Davis, F. A.; Towson, J. C. Weismiller, M. C.; Lal, S.; Carroll, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 8477 and references therein. (e) Davis, F. A.; Billmers, J. M., Gosiniak, D. J.; Towson, J. C.; Bach, R. D. *J. Org. Chem.* **1986**, *51*, 4240. (f) Davis, F. A.; ThimmaReddy, R.; Weismiller, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 5964. (g) Zhao, S. H.; Kagan, H. B. *Tetrahedron* **1987**, *43*, 5153. (h) Davis, F. A.; McCaulye, J. P.; Chattopadhyay, S.; Harakal, M. E.; Towson, J. C.; Watson, W. H.; Tavanaiepour, I. J. *J. Am. Chem. Soc.* **1987**, *109*, 3370. (i) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703.

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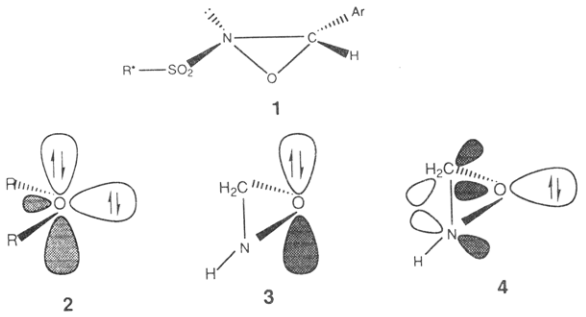


Figure 1.

formation in the transition state. The use of chiral oxaziridines such as **1** has provided a synthetically useful method for asymmetry-induced oxygen transfer to a wide variety of nucleophilic substrates including alkenes, sulfides, sulfoxides, and enolate anions.[2] A detailed understanding of the overall reaction pathway and the orientation of the reactants at the transition state is essential if reliable predictions are to be made concerning the expected absolute stereochemistry of the products of oxidation. One of the fundamental questions pertaining to the approach of the reactants is whether either of the lone pairs on the "electrophilic" oxaziridine oxygen exerts a significant electronic influence on the transition structure.

It is now well recognized that an ether type oxygen has two orthogonal lone pairs of electrons (σ and π) that typically differ in energy by ~1.35 eV (31.1 kcal/mol) as depicted in **2**,[3,4] (Figure 1). In a similar fashion the HOMO of an oxaziridine is partially comprised of the higher energy π-type (π_n, Ψ_{12}, Figure 7) lone pair on oxygen that is perpendicular to the plane of the three-membered ring as in **3**.[5] The second oxygen lone pair (σ_n, Ψ_{11}, Figure 7) lies in the plane of the ring and is part of the highest lying Walsh type orbital as qualitatively described in **4**. A plot of this molecular orbital (Ψ_{11}) is shown in Figure 2a.

Our first effort to study this type of oxygen-transfer process took advantage of the higher symmetry involved in the identity reaction between ethylene oxide and ethylene since the transition structure for such a process has a C_2 symmetry axis (eq 2).[4] In order to ascertain the energetic consequences of the relative orientation of the reactants at the transition state, a planar and a spiro transition structure was calculated. In the former all five heavy atoms occupy a common plane and in the latter the two C–C bonds are at right angles. The relative importance of these two types of transition structures has been a subject of controversy for some time and has assumed a special relevance in the debate on the origin of the high enantioselectivity in the Sharpless epoxidation.[1c,6] Both transition states exhibit prohibitively high activation barriers for this degenerate oxygen exchange process, and they are essentially identical in energy. The calculated (HF/6-31G*) energy difference between reactants and transition structures for the planar and spiro geometries are 87.8 and 87.7 kcal/mol, respectively (Table I).[7]

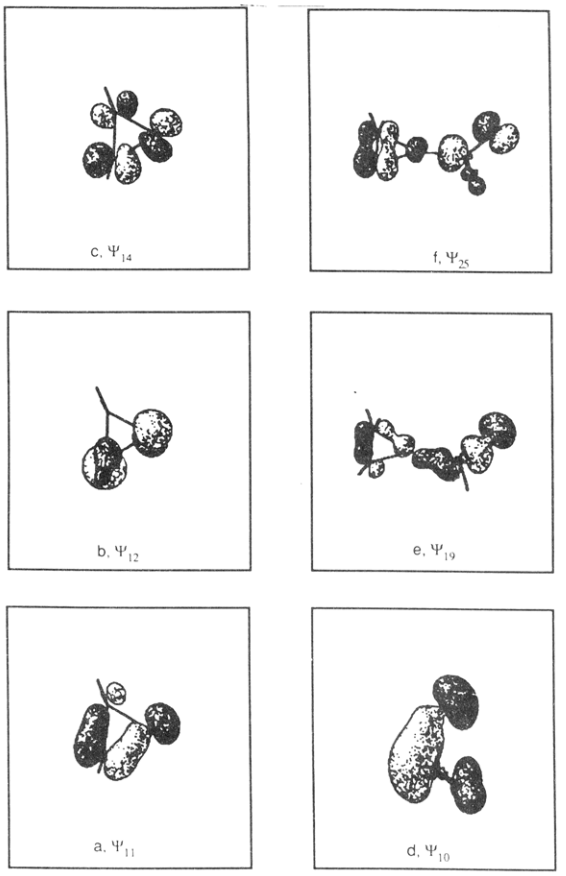


Figure 2. Molecular orbital plots (STO-3G) for oxaziridine (a–c), sulfoxide (d), and the transition state (e, f) for oxygen atom transfer.

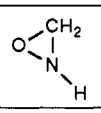
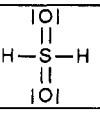
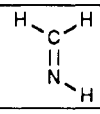
Table I. Summary of Activation Energies (kcal/mol) for Oxygen Atom Transfer

oxidizing agent	transition-state orientation	HF/STO-3G	HF/4-31G	HF/6-31G*
		Nucleophile = Ethylene		
ethylene oxide	planar	101.9	55.0	87.8
	spiro	100.1	55.0	87.7
oxaziridine	planar	85.3	29.1	57.6
	spiro	83.4	29.1	57.6
		Nucleophile = H_2SO		
		HF/STO-3G(d)	HF/4-31G(d)	MP4SDTQ 4-31(d)
oxaziridine	planar	73.2	25.8	31.1
	spiro	73.9	26.1	31.5
		Nucleophile = H_2S		
			HF/4-31G(d)	HF/6-31G*
oxaziridine			28.1	58.1

As anticipated, the energetics for oxygen transfer from an oxaziridine to ethylene (eq 1) are considerably more favorable. The bond dissociation energy of an N–O bond is lower than that of a C–O bond, and epoxide formation is also favored enthalpically. In an earlier study at the HF/4-31G//HF/STO-3G level, activation barriers of 34.0 and 37.4 kcal/mol for planar **5** and spiro **6** transition structures (Figure 3) were calculated. However, as anticipated on the basis of the fact that there is essentially no difference in the activation energies for the identity reaction (eq 2) noted above, this relatively small difference in $\Delta E^{\ddagger}$ is reduced to nearly zero with geometry optimization with the 4-31G basis. Activation energies of 29.1

(3) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599.
(4) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1410.
(5) Only the oxygen lone pair is shown in **2** in the interest of simplicity. The HOMO of this simplest of oxaziridines is actually comprised of the antibonding combination of the lone pair of oxygen with the adjacent lone pair on nitrogen. For an exact description see the molecular orbital plot of Ψ_{12} in Figure 2b.
(6) (a) Bach, R. D.; Willis, C. L.; Domagala, J. M. In *Applications of Molecular Orbital Theory in Organic Chemistry*; Csizmadia, I. E., Ed.; Elsevier: Amesterdam, 1977; pp 221–224. (b) Lang, T. J.; Wolber, E. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275. (c) Jorgensen, K. A.; Wheeler, R. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 3240.
(7) At a lower level of theory (4-31G//STO-3G) the barrier for the planar structure was 3.5 kcal/mol lower in energy than the spiro transition state.

Table II. Total Energies (au) for the Reactants, Transition Structures, and Products of Oxygen Transfer

basis set	$H_2S{-}\bar{O}\vert$		transition structure			ΔH, kcal/mol	$\Delta E^{\ddagger}$, kcal/mol
HF/STO-3G(d)	-468.16013	-166.64619	spiro -634.68861	-542.0094	-92.82304	-11.08	73.86
			planar -634.68968				73.19
HF/4-31G(d)	-472.92253	-168.53489	spiro -641.41584	-547.65731	-93.88256	-51.74	26.09
			planar -641.41630				25.80
MP4SDTQ/4-31G(d)	-473.19678	-168.89530	spiro -642.04185	-548.06323	-94.10711	-49.11	31.52
			planar -642.04248				31.12

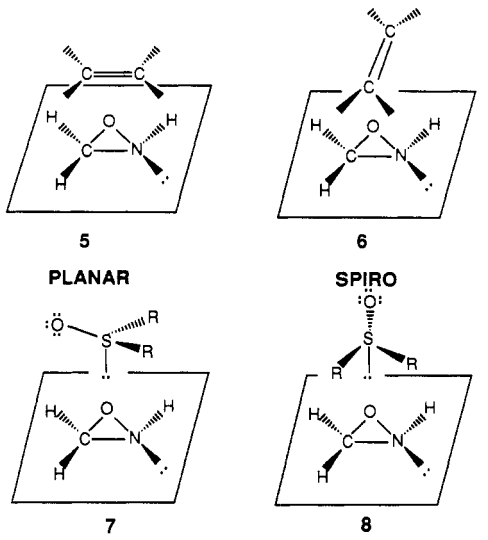


Figure 3. Transition state for oxygen transfer from an oxaziridine to an alkene and a sulfoxide.

kcal/mol were calculated for both transition structures (Table I). A single imaginary frequency was found for the spiro transition structure while the planar structure was a second order saddle point with a very low second imaginary frequency (13.95*i* cm^{-1}) corresponding to the rotation of the double bond toward the spiro structure. No attempts were made to further refine this structure since the rotational surface was extremely flat and changes in total energy were inconsequential. Although these barriers are still relatively high for this model system, it should be recalled that oxaziridine 1 is activated by a sulfone substituent on nitrogen that can facilitate O–N bond cleavage and stabilize the transition state for oxygen transfer. The experimental data for this reaction suggests that a planar orientation would be necessitated in order to afford the observed stereochemistry of the resultant chiral epoxide.[2] Since we have detected no discernable electronic effects for alkene epoxidation, we suggest that the observed product stereochemistry derives from steric interactions in the transition state. We now extend these studies to include the mechanism of the oxidation of a sulfide and a sulfoxide by an oxaziridine. In this study, our two primary objectives are to determine the preferred structure of the transition state for oxygen atom transfer and to examine closely the frontier orbital interactions involved in the oxygen-transfer step. This subject is of current interest because of the synthetic utility of the asymmetric oxidation of sulfides to sulfoxides.[2f,g] In a prior study, empirically based upon structure reactivity trends, a planar transition geometry was proposed for sulfoxide formation using a chiral *N*-sulfamyloxaziridine.[2h]

Results and Discussion

Molecular orbital calculations have been carried out at the HF/4-31G level of approximation using the GAUSSIAN 86 program system[8a] utilizing gradient geometry optimization.[8b] A preliminary transition structure geometry optimization utilized the STO-3G basis. In both cases a set of d orbitals were included on the sulfur atom with exponents of 0.75 and 0.54. These basis sets are denoted as 4-31G(d) and STO-3G(d), respectively.

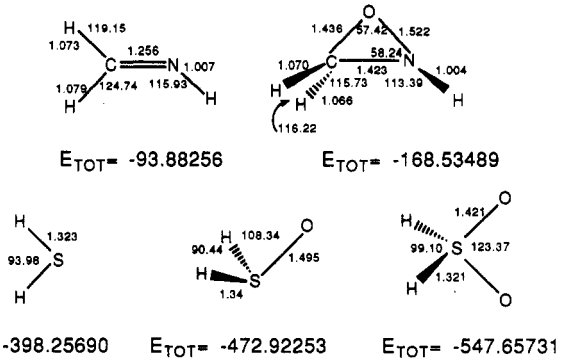


Figure 4. Geometries of reactants 4-31G(d).

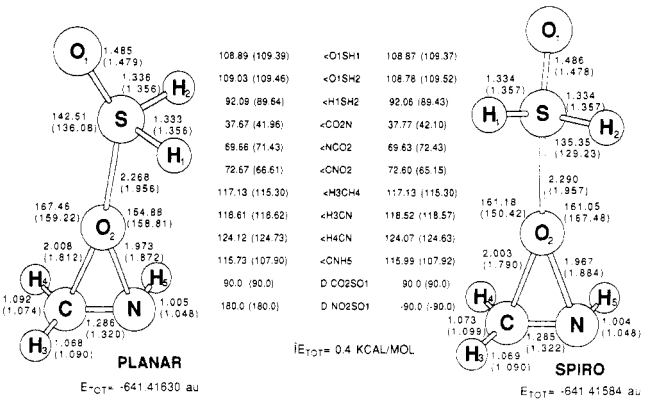


Figure 5. Transition structures for planar 7 and spiro 8 orientations for oxygen transfer from oxaziridine to ethylene (HF/4-31G(d)). Values in parentheses are HF/STO-3G(d).

The total energies for the reactants, transition structures and products are given in Figure 4 and Table II. A full set of vibrational frequencies was calculated by using analytical second derivatives for all structures at the 4-31G(d) level. Only one imaginary frequency was found for each transition structure. Interestingly, both the planar 7 and spiro 8 transition structures (Figure 5) are first-order saddle points, and they are therefore real transition states. A decrease in total energy of only 0.075 kcal/mol was noted for a single-point calculation when the $S{-}O_2$ bond axis of spiro structure 8 was rotated through 45°.

As previously noted,[4] the magnitude of the activation barriers is very basis set dependent. However, at both levels of theory the difference in $\Delta E^{\ddagger}$ for the planar versus the spiro orientation for oxygen transfer is less than 1

(8) (a) Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Whiteside, R. A.; Fox, D. J.; Martin, R. L.; Fluder, E. M.; Pople, J. A. *GAUSSIAN 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984. (b) Schlegel, H. B. *J. Comp. Chem.* **1982**, *3*, 214.

kcal/mol (Table I). It is also noteworthy that these activation barriers increase when electron correlation is calculated to full fourth-order perturbation theory (MP4SDTQ/4-31G(d), frozen core). At this level of theory the planar transition structure **7** is only 0.4 kcal/mol lower in energy than **8**. We therefore conclude that stereoelectronic effects associated with the energy differences in the lone pairs of electrons on the "electrophilic" oxygen atom of the oxaziridine plays only a minor role if any in the overall stereochemistry of sulfoxide formation. The nucleophilic properties of these electrons obviously contribute to the activation barrier as described below. The enantiomeric excess noted experimentally[2] most likely arises from steric interactions in the transition state. Despite the apparent agreement between theory and experiment, we felt that these calculations on a model compound that is essentially void of steric interactions did not provide a mandate for a special electronic interaction. The differences in energy between the two transition structures are simply too small to be meaningful. A summary of the calculated activation barriers for this type of oxidizing agent is given in Table I.

The geometries of the transition structures are given in Figure 5. The reaction trajectory of the approach of the sulfoxide to the oxaziridine approximates the geometry of the resultant sulfone product. Thus, the lone pair on the sulfoxide (Ψ_{13}) is directed at the in-plane lone pair on oxygen (Ψ_{11}) at an angle that is only 15–20° larger than the final O_1–S–O_2 experimental bond angle (~120°)[9] in dimethyl sulfone. The developing sulfur oxygen bonds (S–O_2) are 2.27–2.29 Å, which suggests a relatively early transition state with minimal S–O_2 bond formation. Based upon relative overlap populations of the S–O_2 bond in **7** and that in a sulfone, an S–O_2 bond order of ~2% is predicted for these model transition structures. In contrast, the geometry of the oxaziridine has been extensively altered with the O–N and O–C bonds elongated by 30 and 40%, respectively, relative to their calculated ground-state structures (Figure 4). In consonance with these data dissection of planar transition structure **7** into its two fragments shows that the H_2SO fragment at its transition state geometry has increased in energy by only 0.2 kcal/mol while the oxaziridine moiety ($CNOH_3$) has been destabilized by 29.9 kcal/mol. The bonding interaction in the transition state relative to the combined energies of the two isolated fragments was only 4.3 kcal/mol. The C–N bond has been contracted by ~10% at the transition state consistent with extensive carbon–nitrogen double-bond formation. The geometry of the spiro transition structure optimized with an STO-3G basis set is also given. Particularly noteworthy are the much shorter bond distances describing the principal reaction vector. The S–O_2 bond is ~0.33 Å shorter with the minimal basis while C–O and N–O bond distances are ~0.1 Å shorter. In general, we have found that the extended split valence basis containing polarization functions results in a much looser transition state reflecting the difference in the orbitals. For the sake of comparison, the transition structures for oxygen transfer to ethylene at the 4-31G basis are included (Figure 6). In both cases it is apparent that the geometry of ethylene and sulfoxide fragments have experienced little change while the oxaziridine moiety in both instances has been significantly perturbed.

A surprisingly high amount of negative charge (0.54 electrons based on Mulliken population analysis) has been transferred from the nucleophilic sulfoxide fragment

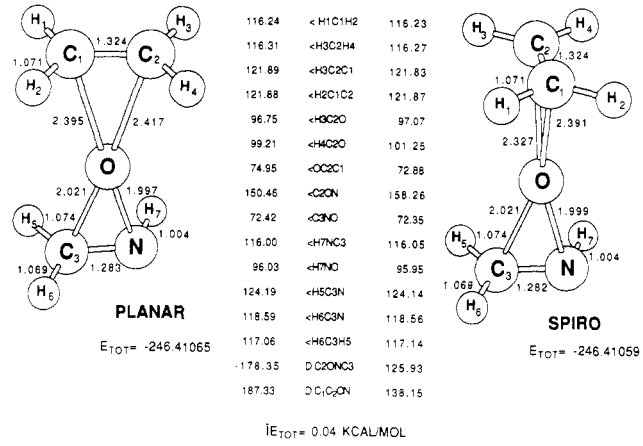


Figure 6. Transition structures for planar and spiro orientations for oxygen transfer from oxaziridine to ethylene (HF/4-31G).

(H_2SO) to the electrophilic oxaziridine moiety at the transition state. An increase in charge at nitrogen and carbon of 0.12 and 0.14 electrons is consistent with extensive displacement of the developing imine ($H_2C{=}NH$) fragment. Based upon Hammett substituent effects, a modest degree of stabilization of developing negative charge occurs at both carbon and nitrogen in a diaryl-substituted oxaziridine such as **1**.[2] Most significantly, however, the *increase* in electron density at the so-called "electrophilic" oxygen undergoing displacement is 0.24 electrons. Perhaps this is not too surprising since the product sulfone has a full octet around the oxygen, and this is being reflected in the transition state. However, as noted below the increase in charge at the "electrophilic" oxygen does not necessarily impede oxygen transfer because the orbital splitting attending closed shell repulsion serves to elevate the energy of the effective HOMO Ψ_B (Figure 2e).

Our second objective in this study is to provide a qualitative discussion of the frontier orbital interactions involved in the transfer of oxygen from this novel oxidizing reagent. When the oxaziridine and the oxygen acceptor both contain electron pairs that are directly involved in the rate-limiting oxygen-transfer step, a clear distinction between the electrophilic and nucleophilic nature of the reactants becomes less obvious. Although it is not essential to adhere to such classical descriptions, in the present case we prefer to classify the sulfoxide as the nucleophile. The sulfoxide has a lone pair on the sulfur and the oxygen that lies in the same plane combining to form filled bonding and antibonding orbitals with π-type symmetry. As shown in Figure 7, the occupied antibonding orbital Ψ_{13} is 0.226 au (151.8 kcal/mol) higher in energy than the corresponding bonding orbital Ψ_{10}. In the latter MO, the nucleophilic "lone pair" is spread out over the entire space comprising the S–O bond as shown in the three dimensional molecular orbital plot (Figure 2d, Ψ_{10}). The nucleophilic character of the higher lying π MO, Ψ_{13}, would be restricted to the sulfur atom in most instances because of symmetry considerations. Thus, the nucleophilic character of a sulfoxide may be attributed to the interaction of both MO's with an electrophilic center. The contribution that each orbital makes will be determined by their relative energies and by overlap considerations.

The origin of the electrophilic properties of an oxaziridine is more difficult to comprehend. As noted above, the two oxygen lone pairs on the oxaziridine are at 90° to one another and differ in energy (4-31G(d)) by 0.062 au (1.69 eV). The higher lying pure p lone pair depicted in **3** is orthogonal to the "π-system" comprising the nucleophilic

(9) Boyd, R. J.; Szabo, J. P. *Can. J. Chem.* **1982**, *60*, 730.

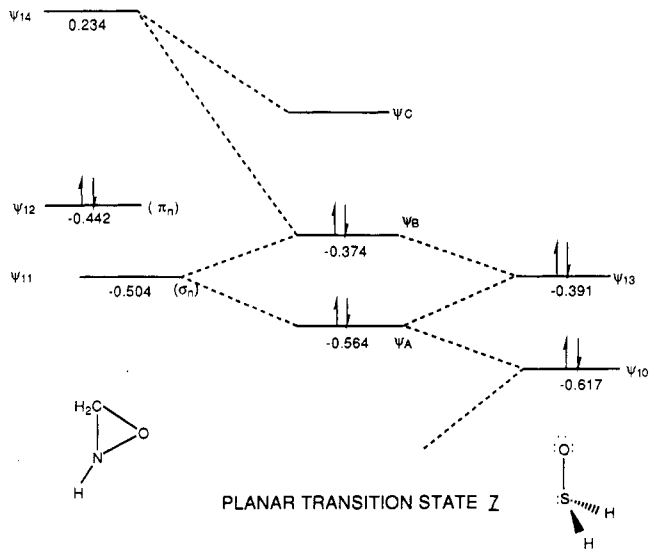


Figure 7. Three molecular orbital four-electron interaction involved in the transfer of oxygen from an oxaziridine to a sulfoxide (4-31G(d), au).

lone pairs on the sulfoxide in planar orientation **7** but can interact with the π^* antibonding combination in the spiro transition structure **8**. However, the angle of approach and the distance between the two oxygens in **8** suggests that this interaction or overlap would be small. In actuality, this MO (Ψ_{12}) is the antibonding combination of the oxygen lone pair with the one on the adjacent nitrogen as shown in the plot (Figure 2b). Since the O–N bond is significantly elongated at the transition state, Ψ_{12} decreases in energy to –0.513 au in **7** as a result of the diminution in the closed shell repulsion in this occupied O–N π^* orbital. Although this lone pair is not directly involved in the transfer step, this orbital stabilization makes a contribution to a lowering of the activation barrier.

Since the orbital interactions involving Ψ_{12} (Figure 2b) of the oxaziridine and Ψ_{10} (Figure 2d) of the sulfoxide are of secondary importance, the remaining relevant FMO interaction involves filled basis orbitals Ψ_{13} and Ψ_{12} and the virtual orbital Ψ_{14} that afford the three frontier MO's of the transition state Ψ_A, Ψ_B, and Ψ_C (Figure 7). Examination of the relative orbital energy levels in Figure 7 make it immediately obvious that the principal orbital mixing early along the reaction coordinate is the four-electron interaction between the higher lying filled sulfoxide orbital Ψ_{13} and the lower energy oxygen lone pair in Ψ_{11}. The resulting closed shell repulsion affording bonding (Ψ_A) and antibonding (Ψ_B) combinations are shown graphically in the molecular orbital plots (Figure 2, parts e and f). The antibonding (π^*) nature of the lone pairs on sulfur and oxygen are quite evident in Ψ_B (Figure 2f). Consistent with extended FMO theory,[4,10] the HOMO at the transition state consists of the antibonding combination of the S–O bond (Ψ_{13}) with the Walsh type oxaziridine orbital Ψ_{11} (Ψ_B, Figure 2e). The reduced electron density in the p orbital of the electrophilic oxygen in that orbital is due to orbital cancellation resulting from the mandatory mixing of developing Ψ_B with Ψ_{14} of the oxaziridine. It is a general phenomenon for all reactions involving atom transfer that the HOMO of the transition state is derived from the HOMO of the nucleophile interacting with a linear combination formed by interaction with both the HOMO and LUMO of the substrate or electrophilic species involved ($\Psi_{11} - \Psi_{13} + \Psi_{14}$). Thus, the antibonding nature of Ψ_B that exists prior to the transition state is able to undergo a change in orbital phasing at or near the transition state so that the newly formed S–O bond can become bonding on the product side of the potential energy barrier.[4,10] The major role of the HOMO–HOMO interaction in this process is to provide the net stabilization attending the decrease in energy of Ψ_A and to insure electron transfer from the developing Ψ_B to the "electrophilic" virtual orbital of the oxaziridine (Ψ_{14}). This is obviously facilitated by the orbital splitting resulting from the close-shell repulsion and the resultant decrease in energy of empty (LUMO) orbital Ψ_{14} (Figure 2c), resulting from perturbation and elongation of the σ bonds involved in the displacement.

The pertinent HOMO–HOMO interactions involving Ψ_{11} and Ψ_{13} afford Ψ_A at the transition state that is decreased in energy by 37.7 kcal/mol while Ψ_B is elevated by only 10.7 kcal/mol. Thus, *the three molecular orbital four electron interaction is net stabilizing by 27.0 kcal/mol.* As a result of the accompanying two-electron interaction of the developing effective HOMO Ψ_B with the empty Walsh type orbital (Ψ_{14}) on the oxaziridine, one might anticipate an increase in the energy of the third empty orbital Ψ_C. In principle, the resultant energy level of this orbital may be increased by mixing with orbitals below it or pushed down in energy by orbitals above it. However, as discussed above the significant 30–40% bond stretching of both the O–N and O–C bonds of the oxaziridine at the transition state resulted in a substantial decrease in the energy of the σ^* or antibonding counterpart Ψ_{14}. Although this observation is definitely not in consonance with the basic tenets of FMO theory, the net result of these two opposing forces resulted in a decrease in the energy of Ψ_C at the transition state. Although the LUMO does not contribute to the total energy of the system, we have identified two virtual orbitals with the proper symmetry, and both of these are lower in energy than the LUMO or Ψ_{14} of ground-state oxaziridine.

The electrophilic nature of oxaziridines and peroxides in general may be attributed to the fact that such compounds possess a relatively weak σ bond,[4] whose σ^* component can readily decrease in energy very early along the reaction coordinate. Although traditionally such reagents have been endowed with a partial positive charge on the electrophilic oxygen, we prefer to adhere to the position that nucleophilic attack on an oxygen atom that possesses two lone pairs of electrons is actually fostered by the presence of a low lying empty σ^* orbital. Indeed, oxygen transfer can actually be accompanied by an *increase* in charge at the "electrophilic" oxygen at the transition state. As noted above, in the present case 50% of the net charge transferred to the oxaziridine fragment resided on oxygen in the transition structure.

Finally, we wish to discuss the transition structure for oxygen transfer to a model sulfide, (H_2S). The barrier for this oxidation process is only slightly higher than that for the conversion of a sulfoxide to a sulfone (Table I). The geometry of the transition structure (Figure 8), which is a first-order saddle point, is interesting in that the S–O bond is quite long and the H–S–O bond angle is slightly less than 90° while the comparable angle in H_2SO is 108.3° (Figure 4). This presumably is a manifestation of the fact that the nucleophile is only slightly perturbed and consequently the essentially pure p higher lone pair orbital on sulfur is weakly interacting with the oxaziridine.

In summary, the basic mechanistic conclusions that may be drawn for oxygen transfer from an oxaziridine to a sulfoxide or a sulfide do not differ substantially from those

(10) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1401.

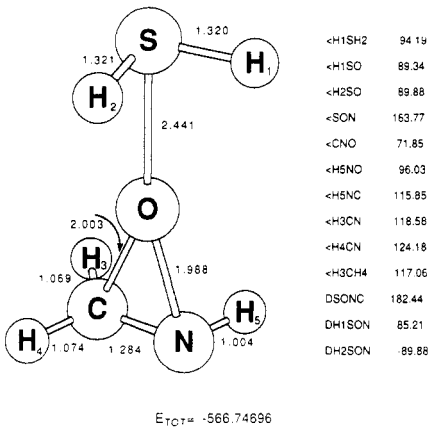


Figure 8. Transition structure for oxygen transfer from oxaziridine to hydrogen sulfide (HF/4-31G(d).

for epoxidation of ethylene. In all cases, the magnitude of the barrier is largely due to geometric distortions of the oxaziridine attending the bond breaking step or displacement of the imine from the oxaziridine. This is dramatically demonstrated by the relatively small difference in activation barriers with no apparent trend reflecting the nucleophilicity of the oxidant (Tables I and II). Very little enthalpic contribution from S–O bond formation was in evidence. The close-shell repulsion between the lone pairs on oxygen and sulfur serves as a driving force to elevate the developing HOMO (Ψ_B) in energy, to transfer electron density to the virtual orbital of the oxaziridine fragment, and to lower the overall activation barrier through the net stabilization of the attending three molecular orbital four-electron interaction. The salient point to be gained from these studies is that there are no stereoelectronic factors that favor a planar or spiro transition state orientation for the oxidation of sulfides to sulfoxides or for the epoxidation of alkenes by *N*-sulfonyloxaziridines. Rather the transition state orientation is steric in origin, dictated by the substituents attached to the oxaziridine carbon and nitrogens. Experimentally this has been observed for the asymmetric oxidation of enolates to optically active α-hydroxy carbonyl compounds using (+)-(camphorylsulfonyl)oxaziridine where both orientations are necessary to explain the structure reactivity trends.[2d]

Registry No. $H_2C{=}NH$, 2053-29-4; H_2S, 7783-06-4; H_2SO, 25540-60-7; HSO_2H, 81824-08-0; oxaziridine, 6827-26-5; ethylene oxide, 75-21-8; ethene, 74-85-1.

Acidities of Carboxamides, Hydroxamic Acids, Carbohydrazides, Benzenesulfonamides, and Benzenesulfonohydrazides in DMSO Solution

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A comparison of acidities of six series of analogous oxygen, nitrogen, and carbon acids in dimethyl sulfoxide (DMSO) solution and the gas phase has shown that the element effect usually causes nitrogen acids to be more acidic than their carbon acid counterparts by an average of 17 ± 5 kcal/mol, and oxygen acids to be more acidic than their nitrogen counterparts by a like amount. A much smaller difference was observed between the NH acidities of carboxamides and the CH acidities of ketones (1–2 kcal/mol in DMSO and 7–8 kcal/mol in the gas phase). Equilibrium acidities in DMSO for a number of substituted benzamides, acetamides, *N*-phenylacetamides, acetohydroxamic acids, benzohydroxamic acids, carbohydrazides, and benzenesulfonamides are reported. Aceto- and benzohydroxamic acids were found to be 9.8 and 10.1 pK_{HA} units more acidic in DMSO, respectively, than acetamide and benzamide. In each instance the effect of N-alkylation decreased the acidity more than did O-alkylation, which indicates that the parents are NH, rather than OH, acids in DMSO. Conclusive supporting evidence for the NH acid assignment was provided by the observation that the *N*-alkylhydroxamic acids exhibited strong homo-H-bonding, whereas the parent acids and their *O*-alkyl derivatives did not. Oxidation potentials of hydroxamate anions in DMSO are close to those of *O*-alkylhydroxamate ions, confirming that their conjugate acids are NH acids, but in MeOH they are close to those of *N*-alkylhydroxamate ions showing that their conjugate acids can act as OH acids in hydroxylic solvents. The *N*-alkyl- and *O*-alkylhydroxamic acids exhibited much stronger chelating power toward K^+, Na^+, and Li^+ ions than did the parent acids.

It has been recognized for many years that oxygen acids are more acidic than nitrogen acids and that nitrogen acids are more acidic than analogous carbon acids, but quantitative data have been lacking. Recent gas-phase measurements[1] have shown, however, that oxygen acids, such as phenol or water, are more acidic than their nitrogen acid counterparts, aniline and ammonia, by 12 or more kcal/mol and that these nitrogen acids are, in turn, more acidic than their carbon acid counterparts, toluene and methane, by similar amounts. Measurements in dimethyl sulfoxide (DMSO) solution of acidities of phenol, water, and aniline, together with estimates of acidities for ammonia, toluene, and methane, suggest that like differences also prevail in solution. In fact, they appear to be exaggerated therein.[2] Carboxamides exhibit anomalous behavior, relative to

(1) See the gas-phase acidity scale of Prof. J. E. Bartmess (available by request in care of the Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600).

(2) (a) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463–469. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

0022-3263/90/1955-3330$02.50/0