

# Transition States of Epoxidations: Diradical Character, Spiro Geometries, Transition State Flexibility, and the Origins of Stereoselectivity

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**Abstract:** The transition structures for the epoxidations of ethylene by performic acid, dioxirane, oxaziridine, and peroxyntrous acid have been located with density functional theory methods using the Becke3LYP functional and 6-31G\* basis set. All of the epoxidations have spiro transition states; those with performic acid and dioxirane are early and involve synchronous oxygen transfer, while those with oxaziridine and peroxyntrous acid are later with asynchronous oxygen transfer. The results from Becke3LYP/6-31G\* theory are compared with MP2/6-31G\* literature values. Substitution on ethylene by methoxy, methyl, vinyl, and cyano groups changes the transition state geometries toward asynchronous spiro structures. The activation energies are lowered by all substituents except the cyano group in reactions of performic acid and dioxirane. Experimental stereoselectivities are rationalized by using transition structure models based upon these transition structures.

## Introduction

Asymmetric epoxidations of prochiral alkenes provide versatile intermediates for the synthesis of functionalized optically active organic substances. During the last decade, a number of new stereoselective epoxidation methods have been developed, including highly effective catalytic processes.<sup>1–4</sup> We wish to understand the source of chiral discrimination in these reactions, and to design even more effective catalysts, through a detailed mapping of the transition structures of these reactions.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, September 15, 1997.

(1) For a recent review on catalytic asymmetric epoxidation of unfunctionalized olefins, see: Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 4.2.

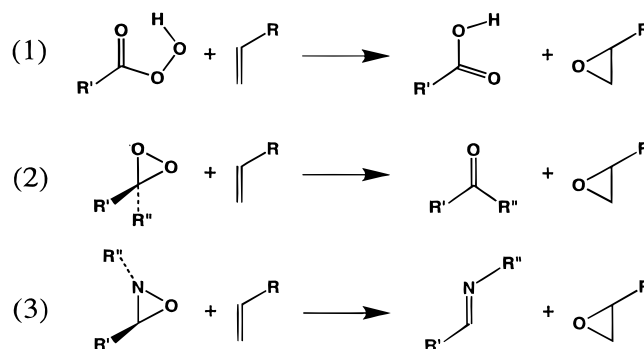
(2) For examples of stereoselective epoxidations by oxaziridine, see: (a) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703. (b) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123. (c) Davis, F. A.; Chattapadhyay, S. *Tetrahedron Lett.* **1986**, *27*, 5079.

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(4) For recent examples of stereoselective epoxidations by dioxiranes, see: (a) Curci, R.; Detomaso, A.; Prencipe, T.; Carpenter, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 8112. (b) Mello, R.; Ciminale, F.; Fiorentio, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 6097. (c) Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, J. M. *Tetrahedron Lett.* **1995**, *36*, 2437. (d) Lluch, A.-M.; Sanchez-Baeza, F.; Messegnier, A.; Fusco, C.; Curci, R. *Tetrahedron* **1993**, *49*, 6299. (e) Curci, R.; D'Accolti, L.; Fiorentino, M.; Rosa, A. *Tetrahedron Lett.* **1995**, *36*, 5831. (f) Brown, D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* **1995**, *51*, 3587. (g) Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *Tetrahedron Lett.* **1996**, *36*, 2437. (h) Yang, D.; Yip, Y.-C.; Tang, M.-W.; Wong, M.-K.; Zheng, J.-H.; Cheung, K.-K. *J. Am. Chem. Soc.* **1996**, *118*, 491. (i) Yang, D.; Wang, X. C.; Wong, M. K.; Yip, Y. C.; Tang, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 11311. (j) Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806. (k) Adam, W.; Smerz, A. K. *J. Org. Chem.* **1996**, *61*, 3506.

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## Scheme 1

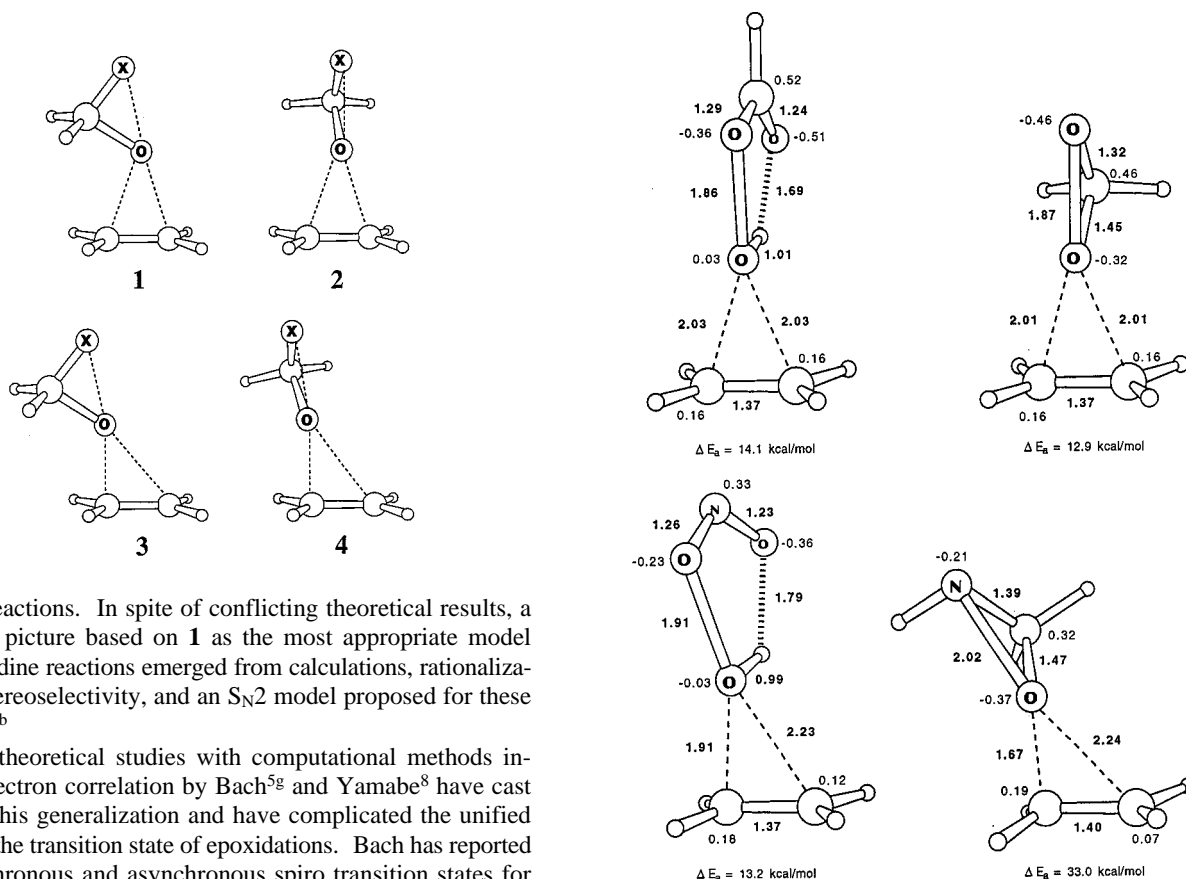


Pioneering theoretical calculations by Bach and co-workers<sup>5</sup> and others<sup>6</sup> have provided many insights into the nature of epoxidation transition states. Over the years, as increasingly accurate computational methods became available, models of epoxidation transition states have evolved. Discussions of performic acid (eq 1), dioxirane (eq 2), and oxaziridine (eq 3) epoxidations have all appeared. The baseline for all considerations was Bartlett's "butterfly mechanism",<sup>7</sup> a synchronous spiro transition state model for performic acid epoxidations. We use the terms "synchronous" and "asynchronous" to describe equal, and unequal, C–O bond formation, respectively, in the transition state. For the extensively discussed oxaziridine epoxidations, it was first proposed that the synchronous planar transition structure, **1**, explains the stereochemistry.<sup>2c,5b</sup> While the alternate transition structure with a synchronous spiro geometry, **2**, was found to be similar in energy, **1** was proposed nevertheless to account for the stereoselectivity of oxaziridine reactions. The experimental stereoselectivities could be explained on this basis.<sup>2c,5a,b</sup> Asynchronous spiro and planar transition structures, **3** and **4**, respectively,<sup>5c–e</sup> are also possible

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## Chart 1



for such reactions. In spite of conflicting theoretical results, a consensus picture based on **1** as the most appropriate model for oxaziridine reactions emerged from calculations, rationalizations of stereoselectivity, and an  $S_N2$  model proposed for these reactions.<sup>5b</sup>

Recent theoretical studies with computational methods including electron correlation by Bach<sup>5g</sup> and Yamabe<sup>8</sup> have cast doubt on this generalization and have complicated the unified picture of the transition state of epoxidations. Bach has reported both synchronous and asynchronous spiro transition states for epoxidations by performic acid and dioxirane.<sup>5f,g</sup> For performic acid epoxidations, Yamabe has reported a very unsymmetrical transition structure and even a diradical intermediate in the reaction formed from an asynchronous spiro process.<sup>8</sup> Recent evidence for a spiro transition state in epoxidations by dioxiranes has also been reported.<sup>4h,i</sup>

Calculations reported here have been performed by using density functional theory with the Becke3LYP/6-31G\* method. We also explored some systems at the MP2/6-31G\* theory level. Although there is qualitative agreement between these methods, the Becke3LYP hybrid density functional method appears to give a more accurate representation of the energetics of reactions involving performic acids and related compounds, and our conclusions are based on this method.<sup>9</sup> Since submission of this work, Professor R. D. Bach has informed us of extensive investigations of epoxidations of alkenes with performic acid and dioxirane using DFT and QCI methods. These results will appear in two papers in press.<sup>9a</sup> Their B3LYP results, with larger basis sets, and the QCISD optimizations are in accord with the spiro synchronous geometries described in this paper. In addition, we have recently reported a comparison of predicted and experimental kinetic isotope effects for peracid epoxidations<sup>9b</sup>

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(10) Gaussian 94 (Revision A.1), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oriz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

**Figure 1.** Transition structures (B3LYP/6-31G\*) for epoxidations of ethylene by performic acid, dioxirane, peroxyxynitrous acid, and oxaziridine.

which provide strong support for the computational methods described in this paper. Here we report quantum mechanical studies which establish detailed models for the shapes and flexibilities of transition states of asymmetric epoxidation reactions. This unified model is used to understand the origin of stereoselectivity in asymmetric epoxidations.

### Computational Methodology

Calculations reported here were conducted with the Gaussian94 program.<sup>10</sup> Full geometry optimizations were carried out by using density functional theory with the Becke3LYP functional and the 6-31G\* basis set. Both restricted and unrestricted Becke3LYP/6-31G\* were used for the transition structure searches for the parent systems with oxygen transfer from unsubstituted performic acid, dioxirane, peroxyxynitrous acid, and oxaziridine to ethylene. The restricted Becke3LYP/6-31G\* method is suitable for the closed-shell species while the unrestricted Becke3LYP/6-31G\* method is necessary to compute open-shell radical structures. Calculations with MP2/6-31G\* theory were repeated for the epoxidation of ethylene by oxaziridine and give results which are different from those in the literature.<sup>5c</sup> Frequency calculations have been carried out for all the transition structures to ensure the presence of only one imaginary frequency corresponding to C–O bond forming and O–X (X = O, N) bond breaking. The optimized reactants were also checked by frequency calculations to confirm that they are minima. Charges cited in the discussions are Mulliken charges.

### Results and Discussions

**Transition Structures for the Epoxidation of the Parent Systems.** Figure 1 shows the transition states for epoxidations of ethylene by performic acid, dioxirane, peroxyxynitrous acid,<sup>11</sup> and oxaziridine calculated by the Becke3LYP/6-31G\* method.

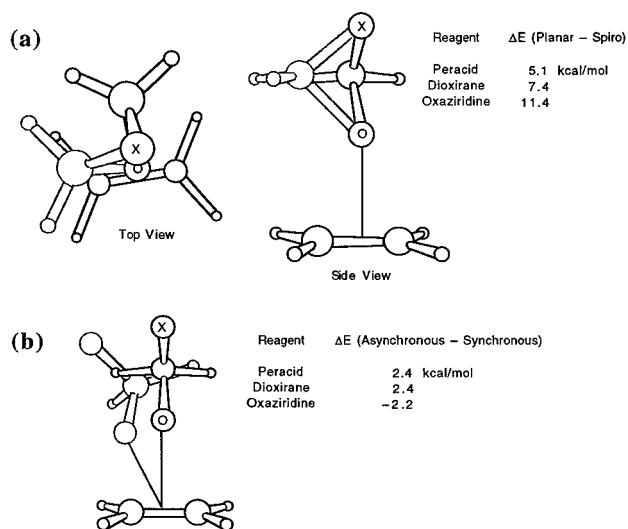
(11) Houk, K. N.; Condroski, K. R.; Pryor, W. A. *J. Am. Chem. Soc.* **1996**, *118*, 13002.

All of these transition structures have spiro, not planar, geometries. The timing of formation of the two C–O bonds varies from synchronous with performic acid to highly asynchronous with oxaziridine. The transition structures for the epoxidations by performic acid and by dioxirane are very similar: the breaking O–O bond lengths are 1.86 and 1.87 Å, respectively, and the two forming C–O bond lengths are 2.03 and 2.01 Å, respectively. Earlier calculations at the MP2/6-31G\* level by Yamabe and Bach gave very asynchronous transition structures for the epoxidations by performic acid<sup>8</sup> and dioxirane,<sup>5f</sup> with 0.5-Å differences in the two forming C–O lengths. The MP2/6-31G\* activation energies are 13.5 and 13.4 kcal/mol for performic acid and dioxirane epoxidations, respectively, which are quite close to our Becke3LYP/6-31G\* results of 14.1 and 12.9 kcal/mol, respectively. Because the calculated activation energy for the epoxidation by dioxirane with use of MP2/6-31G\* (13.4 kcal/mol) is much lower than the experimentally estimated O–O bond dissociation energy of ~36 kcal/mol,<sup>12</sup> Bach excluded the possibility of the radical character in the transition structure. When the transition structure was constrained to be synchronous, the energy of the secondary transition structure is 4.2 kcal/mol higher than those of the primary transition structures determined by MP2/6-31G\* methods. This synchronous transition structure was proposed to involve S<sub>N</sub>2 dominant character in the oxygen transfer from dioxirane to ethylene. The activation energies for the epoxidations by performic acid and dioxirane by both the Becke3LYP/6-31G\* and MP2/6-31G\* methods are in reasonable agreement with experimental results in solution, which are 15–18 kcal/mol for performic acid<sup>13</sup> and 14.1 kcal/mol for dioxirane.<sup>14</sup>

The epoxidation of ethylene by oxaziridine has been studied by different methods.<sup>5</sup> Previous calculations with MP2/6-31G\* yielded a synchronous transition structure,<sup>5e</sup> but we found that this transition structure is a secondary saddle point. The fully optimized transition structure for epoxidation of ethylene by oxaziridine with the MP2/6-31G\* level is a very asynchronous one, similar to the one found with Becke3LYP/6-31G\*. The activation energy of the fully optimized transition structure at MP2/6-31G\* is 26.8 kcal/mol, which is 10.8 kcal/mol lower than that for the synchronous transition structure reported earlier.<sup>5e</sup>

Peroxyntous acid is a very short-lived species which has not yet been observed to epoxidize alkenes.<sup>11</sup> The activation energy for the oxygen transfer from peroxyntous acid to ethylene is only 13.2 kcal/mol by Becke3LYP/6-31G\* theory. It has an asynchronous transition structure, in between the synchronous peracid and the asynchronous oxaziridine in character.

**Spiro and Planar Transition Structures.** The planar stationary points were also located by constraining the structures to be in one plane, but these are second-order saddle points, not transition structures. The difference in energy between the spiro and planar geometries was assessed computationally by using Becke3LYP/6-31G\*. Figure 2a shows a superimposition of spiro (heavy lines) and planar (faint lines) transition structures along with the energy difference between the planar and preferred spiro structure for each of the three epoxidizing reagents. The preference increases as the length of the most fully formed C–O bond decreases, from 5.1 kcal/mol with performic acid to 11.4 kcal/mol with oxaziridine. In all cases, there is a very large spiro preference. The large spiro preference is caused by the secondary orbital interaction between the



**Figure 2.** Summary of relative energies of (a) spiro and planar and (b) synchronous and asynchronous transition structures. The two types of transition structures are overlaid in the illustrations.

oxygen n orbital and the  $\pi^*$  orbital of the ethylene in the spiro transition structures described later in this paper.<sup>5b</sup>

**The Flexibility and Diradical Character of the Transition Structures.** The differences in energy between synchronous and asynchronous transition states for the parent systems are summarized in a similar way in Figure 2b. For performic acid and dioxirane, the actual transition structures are synchronous, and the energies of the asynchronous transition structure models are single point energy calculations at Becke3LYP/6-31G\* carried out on the MP2/6-31G\* optimized transition structure geometries. The synchronous transition structure for the epoxidation by oxaziridine is a second-order saddle point that was located by constraining the geometry to be synchronous in the optimization. The transition structures for the epoxidation by performic acid and dioxirane have relatively small activation energies and are early transition structures. There is a small preference for synchronicity in the early transition structures which occur with performic acid and dioxirane, but there is a strong preference for asynchronous bond formation in the late transition structure which occurs with the less-reactive oxaziridine. For performic acid and dioxirane, the distortion energy is only 2.4 kcal/mol, which means the synchronous transition structures are located in relatively shallow flat minima; unsymmetrical substitution may shift the transition states away from synchronicity. However, for oxaziridine, there is a small preference (2.2 kcal/mol) for the asynchronous transition structures.

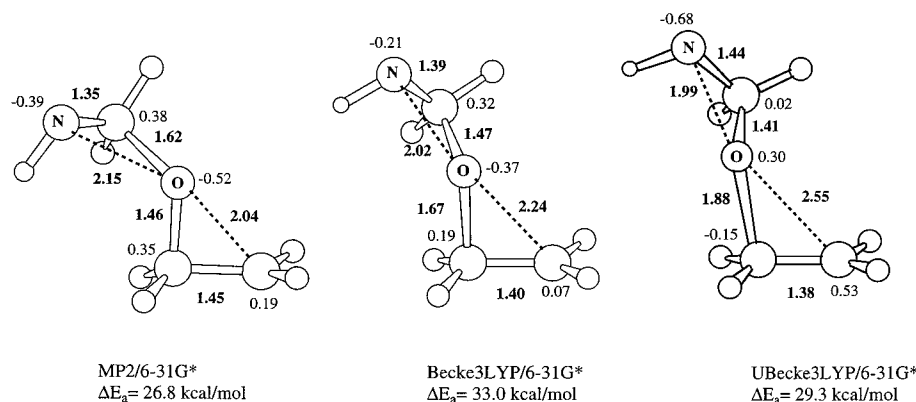
There is obvious diradical character in the asynchronous transition structures of epoxidation by oxaziridine. The partial radical centers are on the N-terminus of the oxaziridine and one C-terminus of ethylene. Because of the apparent diradical character, we also explored these reactions with unrestricted DFT theory (UBecke3LYP/6-31G\*) for the parent system. This allows separate orbitals for electrons with  $\alpha$  and  $\beta$  spin and is more suitable for representation of open-shell diradical systems. We have demonstrated the suitability of UB3LYP calculations for reactions involving diradicals and have discussed elsewhere the potential problems in radical calculations.<sup>15</sup> In the case of the oxaziridine transition state, the unrestricted solution is more stable than the restricted by 4.7 kcal/mol, and the spin densities are -0.68 and 0.53 at the N and C termini, respectively. Figure 3 shows the three transition structures for epoxidation of ethylene by oxaziridine with MP2/6-31G\*, as well as restricted

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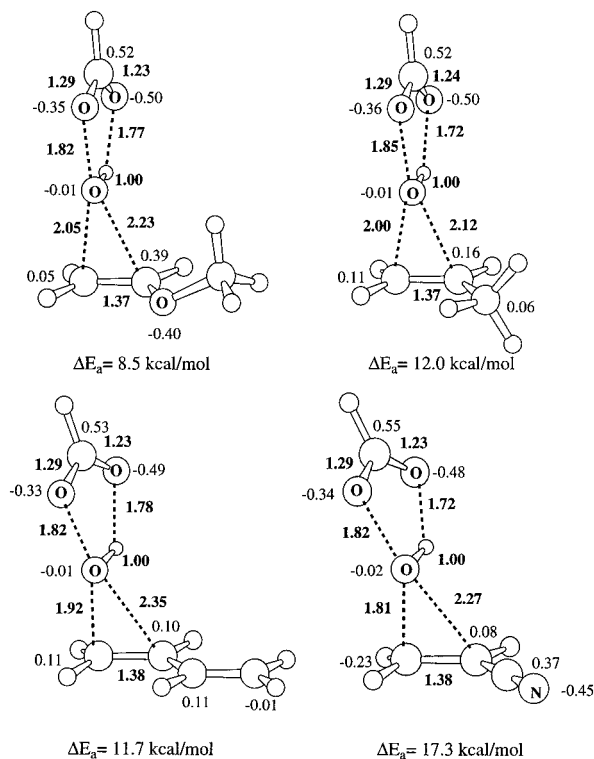


**Figure 3.** Transition structures for oxygen transfer from oxaziridine to ethylene by MP2/6-31G\*, restricted B3LYP/6-31G\*, and unrestricted B3LYP/6-31G\* methods. Charges are shown in the first two structures, and spin densities in the third.

and unrestricted Becke3LYP/6-31G\* methods. The Mulliken charges on heavy atoms are shown beside the atoms for transition structures obtained by the MP2 and restricted Becke3LYP methods, and the Mulliken spin densities for the heavy atoms are shown for the structure obtained by the unrestricted Becke3LYP method. MP2/6-31G\* predicts the latest and most asynchronous transition structure. The unrestricted Becke3LYP/6-31G\* method still predicts an asynchronous transition structure, but the difference between the extent of formation of the two C–O bonds is much smaller. The restricted Becke3LYP calculation gives the least asynchronous transition structures. It is likely that MP2 and UB3LYP exaggerate the diradical character of these transition states. The earlier transition states for the performic acid, dioxirane, and peroxyntous acid reactions are closed-shell. Although the transition structure for the peroxyntous acid is asynchronous, it appears to be more like an  $S_N2$  type reaction than a diradical type: the unrestricted Becke3LYP/6-31G\* predicts the same transition structures as the restricted Becke3LYP/6-31G\*, indicating that the restricted DFT solution is stable. The transition structure for the epoxidation by oxaziridine shows more diradical character than those by performic acid, dioxirane, and peroxyntous acid.

**Transition Structures for Epoxidations of Substituted Alkenes.** Transition structures for epoxidations of ethylene substituted by four different group—methoxy, methyl, vinyl, and cyano, ranging from electron-donating to electron-withdrawing—were located. For epoxidation reactions of these alkenes with performic acid, dioxirane, and oxaziridine, two transition structures can be found for each—*syn*, when the substituent is on the same side as the carbon of the epoxidizer, and *anti*, when the substituent is on the other side. The *anti* transition structures are usually about 0.5 kcal/mol lower in energy than the *syn* transition structures because of the steric hindrance in the *syn* transition structures.

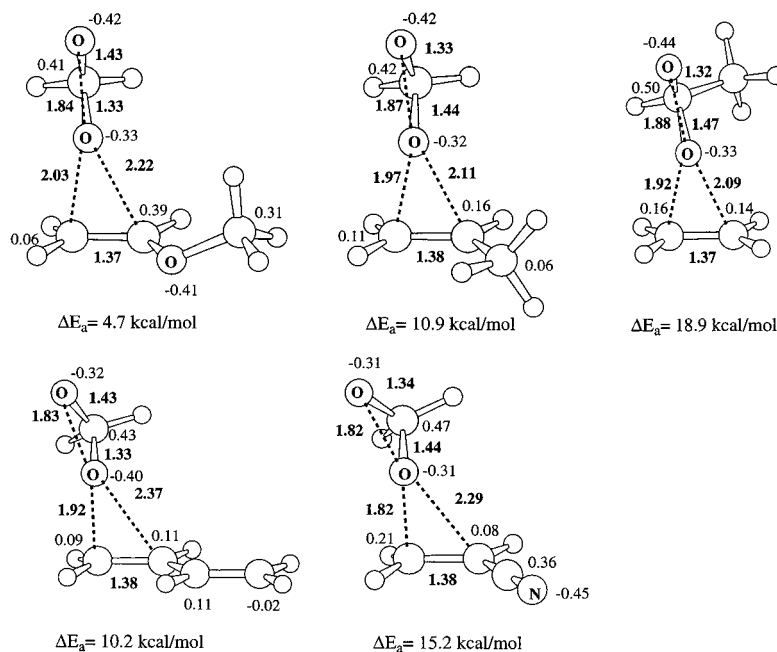
Figure 4 shows the four *anti* transition structures for the oxygen transfer from performic acid to the four substituted ethylenes. These are all asynchronous transition structures, contrary to the synchronous transition structure for the parent system. The asynchronicity is small with methyl and increases with greater electron-withdrawal or electron-donation by the substituent. The substituent stabilizes partial radical character on the C-terminus of ethylene in the asynchronous transition structures. If the substituents are placed on the carbons with the shorter forming C–O bond as initial structures, the transition structure searches finally end in the geometries in which the two forming C–O bonds have exchanged lengths such that the substituent is on the carbon with the longer C–O bond. By contrast, when the transition structure search was carried out with the MP2/6-31G\* method, four transition structures could



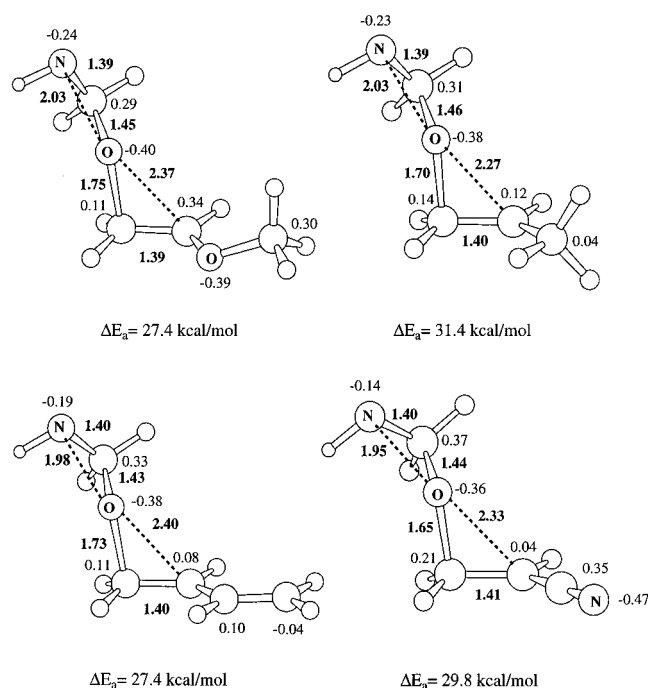
**Figure 4.** Transition structures (B3LYP/6-31G\*) for epoxidations of substituted ethylenes by performic acid.

be found, two *syn* and two *anti*; the substituents can connect to the carbon with the longer or shorter forming C–O bond. All of these transition structures are more asynchronous than those from the Becke3LYP/6-31G\* calculations. However, the experimental isotope effect on epoxidation of 1-pentene by MCPBA proves that the Becke3LYP/6-31G\* theory is a better method than MP2/6-31G\* theory for the calculation of isotopic effects which are very close to the experimental results.<sup>9b</sup> Compared to the parent system, the methoxy, methyl, and vinyl substituents decrease the activation energies, while the electron-withdrawing cyano increases the activation energy. This phenomena is consistent with an  $S_N2$ -type reaction. The asynchronicity of the transition structure for cyanoethylene by Becke3LYP/6-31G\* is similar to that of the transition structure for ethylene at the MP2/6-31G\* level, in which the two forming C–O bonds are 1.81 and 2.27 Å. Electron-withdrawing groups cause the epoxidation to involve a later transition structure which is very asynchronous.

For the oxygen transfer from dioxirane, substituents have the same effect that they have on the epoxidation by performic acid. All the transition structures are asynchronous, with the substi-



**Figure 5.** Transition structures (B3LYP/6-31G\*) for epoxidations of substituted ethylenes by dioxirane and ethylene by methyldioxirane.



**Figure 6.** Transition structures (B3LYP/6-31G\*) for epoxidations of substituted ethylenes by oxaziridine.

tuted groups on the carbon with the longer forming C–O bonds (Figure 5). One unsymmetric substituent such as methyl on the dioxirane can also cause the transition structure to become somewhat asynchronous. The methoxy, methyl, and vinyl groups all decrease the activation energies of the epoxidation reaction, and the electron-withdrawing cyano group increases the activation energy.

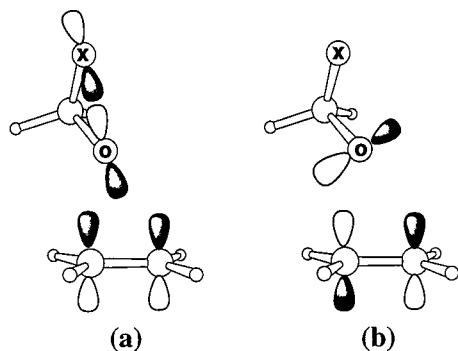
The transition structure for oxygen transfer from oxaziridine to ethylene is already very asynchronous for the parent system, and the four different substituents have little influence on the timing of the two forming C–O bonds (Figure 6). All four substituents decrease the activation energies as compared to the parent system, with the methoxy and vinyl groups stabilizing the transition structures the most. Instead of destabilizing the transition structures as in the performic acid and dioxirane system, the cyano group decreases the activation energy of

epoxidation by oxaziridine. This reflects the significant diradical character of the transition structure for the oxaziridine system.

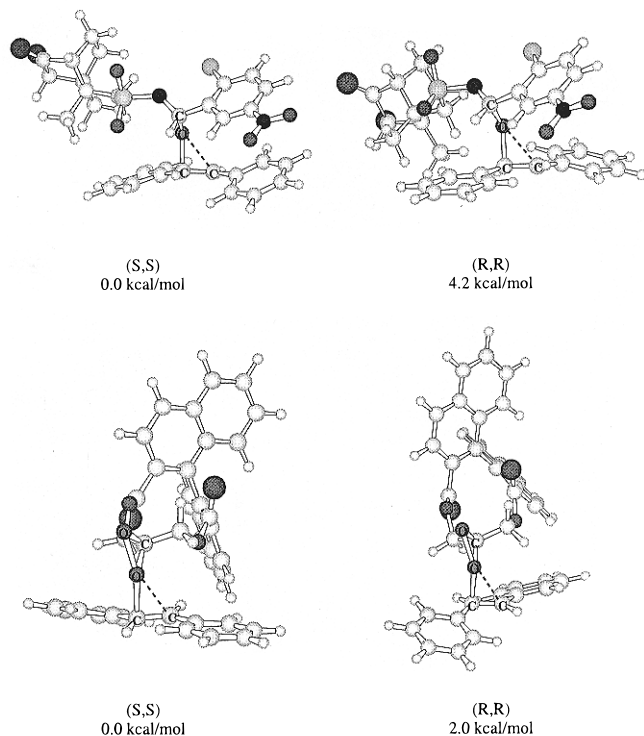
The partial charges are given next to the heavy atoms in Figure 1 for the parent system and in Figures 4, 5, and 6 for the epoxidation of substituted ethylene by performic acid, dioxirane, and oxaziridine. All the transition structures have no more than 0.35 charge transfer from alkene to the epoxidizing reagent, indicating diradical, rather than zwitterionic, character for the transition structures. The more asynchronous the transition structures are, the less the charge transfer, and the more diradical character. There is very little hydrogen transfer in the reaction of performic acid and peroxyxynitrous acid, and relatively little CO bond-breaking in the dioxirane and oxaziridine reactions.

The transition states for these reactions vary from nucleophilic ( $S_N2$ ) to homolytic ( $S_H2$ ) in character, depending upon the substituents. In the epoxidation of ethylene by performic acid and dioxirane, the transition states are  $S_N2$ -like for the parent system, and the electron-donating substituents on ethylene lower the activation energies while the electron-withdrawing cyano increases the activation energy. Substituents on ethylene make the transition structures asynchronous and more  $S_H2$ -like. In the epoxidation of ethylene by oxaziridine, the transition structure is very homolytic ( $S_H2$ ) in character. All substituents lower the activation energy. The vinyl group has the largest effect, indicating that there is more radical than cation character on the adjacent carbon. Figure 7 summarizes the principal frontier orbital interactions occurring in the transition states. Relatively early transition states involving  $S_N2$ -like interactions have been described in detail by Bach.<sup>5b</sup> The alkene HOMO interacts in a stabilizing fashion with the OO  $\sigma^*$  orbital, and a synchronous geometry is favored. When the leaving group is less able to stabilize a negative charge, the transition state becomes more advanced and  $S_H2$  in character, which favors an asynchronous geometry. This involves interaction of the O lone pair with the alkene  $\pi^*$  orbital, which is enhanced in an asynchronous geometry. Those two FMO interactions give a diradicaloid transition state when they are comparable in magnitude. The trajectory predicted by this model follows that trajectory that is well-known for carbene cycloadditions.<sup>16</sup> The

(16) (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (b) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.



**Figure 7.** FMO interactions in the transition states of epoxidations: (a) alkene HOMO-oxidant LUMO and (b) oxidant HOMO-alkene LUMO.

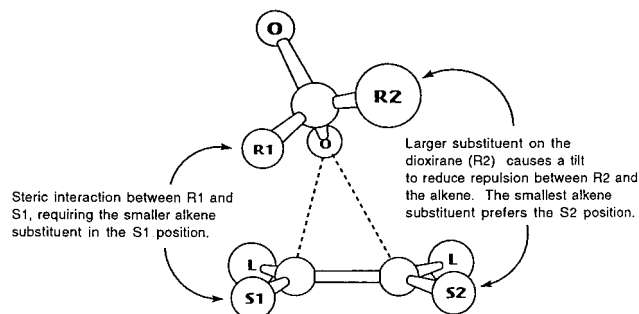
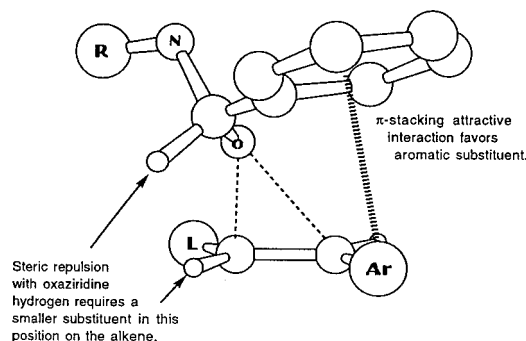


**Figure 8.** Force field models of asymmetric epoxidations with Davis's oxaziridine and Yang's chiral dioxirane.

spiro geometry is favored significantly, because the oxygen lone-pair HOMO interaction with the alkene LUMO is maximized in the spiro geometry but is eliminated in the planar transition state. The importance of this increases as the transition state becomes more advanced.

**The Origin of Stereoselectivity.** This transition state model provides a good qualitative explanation for stereoselectivities which have been observed. Figure 8 shows the transition states of epoxidation of *trans*-stilbene by one of the Davis chiral oxaziridine reagents<sup>2</sup> and the Yang chiral binaphthyl dioxirane.<sup>4h</sup> The transition states were built by constraining the five atoms involved in bonding changes to the transition state optimal geometry determined by DFT calculation and minimizing all the other parts by MM2\* using MacroModel 5.0.<sup>17</sup> The energy difference predicted between the transition states corresponding to experimentally favored and disfavored products is 4.2 kcal/mol for oxaziridine and 2.0 kcal/mol for dioxirane (Figure 8). This energy difference corresponds to a higher selectivity than that observed by experiment, but the models are nevertheless

(17) MacroModel V5.0: Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440. MM2\* is the MacroModel implementation of MM2.



**Figure 9.** Qualitative models to rationalize stereoselective epoxidations by oxaziridines and dioxiranes.

useful for the prediction of the sense of the observed selectivity.<sup>2,4h</sup> The factors which control the stereoselectivity are shown in Figure 9. In the oxaziridine, experimental results can be rationalized by the model shown: on the left carbon of the alkene, the larger substituent prefers to be back, away from the protruding H of the oxaziridine. At the other terminus,  $\pi$ -stacking causes aromatic substituents to prefer the forward position. Alkyl or bulky groups will prefer to be back. Radical stabilization causes the substituents to be favored at one terminus in an unsymmetrical case;  $\pi$ -stacking as shown in the sketch and steric hindrance, involving groups on the reagent and on the alkene, dictate the position of groups in the transition state.

The qualitative model shown for dioxirane epoxidation also rationalizes experimental data.<sup>4h</sup> Here the interaction of the larger dioxirane substituent with the alkene substituent dominates, and *trans*-alkenes place groups at S1 and L in spite of the fact that the large substituent on the left carbon would prefer to be back.

The application of this model to understand stereoselectivities of epoxidation by oxaziridine and dioxirane, and to design catalysts, will be reported in future publications.

## Conclusions

The transition states of the epoxidation by performic acid, dioxirane and oxaziridine are all concerted, but vary from  $S_N2$  to homolytic  $S_H2$  in character. Substituents on the alkene make the transition structures more asynchronous and diradicaloid in nature. The spiro geometry is highly favored in all cases. The transition state model can be used to rationalize the stereoselectivities of oxaziridine and dioxirane epoxidations.

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