Reassessment of the Level of Theory Required for the Epoxidation of Ethylene with Dioxiranes

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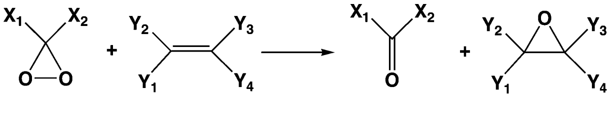
High level ab initio and CASSCF calculations on the epoxidation of ethylene with dioxirane (DO) and dimethydioxirane (DMDO) have been carried out to distinguish between a symmetrical versus an unsymmetrical *spiro* orientation of the dioxirane in the transition structure for oxygen atom transfer. The optimized C_1 DO/ethylene unsymmetrical *spiro* CASSCF(12,12)/6-31G(d) transition structure is a first-order saddle point that is 5.5 kcal/mol lower in energy than the corresponding constrained C_s symmetrical approach (a second-order saddle point) after correction for dynamic correlation [CASSCF(MP2)]. However, a single-point energy correction at the BD(T)/6-311+G(d,p) level on these CASSCF geometries suggests that the C_1 TS is only 0.6 kcal/mol lower in energy than an symmetrical *spiro* TS. Both the BD(T) correction to the CAS(8,8)/6-31+G-(d,p) and RSPT2 energy correction on CAS(8,8)/6-31G(d) DO/ethylene structures slightly favors the C_s structures. BD(T)/6-311+G(d,p) single point calculations on the C_1 and C_s transition structures optimized at the CCSD(T)/6-31G(d) level slightly favor the unsymmetrical TS. These combined data suggest that the potential energy surface for the approach of dioxirane to the C=C of ethylene is very soft with the C_1 transition structure being slightly favored. For DMDO epoxidation, we conclude that the approach of DMDO to a symmetrically substituted alkene should result in an essentially symmetrical transition structure.

Introduction

The transfer of an oxygen atom to a carbon−carbon double bond remains one of the more useful synthetic reactions in Organic Chemistry.[1,2] The use of chiral dioxiranes in the synthesis of optically active epoxides has also recently gained prominence.[1c] The mechanism of the dioxirane epoxidation of alkenes (eq 1) has been the subject of both experimental and theoretical study for many years. The basic characteristic of this epoxidation method has many things in common with peracid epoxidation. The generally accepted planar "butterfly" mechanism[3] for peracid epoxidation of alkenes involves the transfer of the proton of the peracid to the carbonyl oxygen with simultaneous transfer of the oxygen atom. The plane of the peracid moiety prefers to be perpendicular to the C=C bond axis in a "*spiro* transition state"[4] that describes the local tetrahedral environment about the attacking electrophilic oxygen atom. In an idealized *spiro* orientation, the H−O−C−C dihedral angle is 90.0°



(1)

Recent experimental[5a] and theoretical[5b] studies suggest that even sterically encumbered alkenes prefer a *spiro* TS over a planar one. A combined experimental kinetic isotope effect and theoretical (B3LYP) study has also recently appeared that provides convincing evidence that peracid epoxidations of simple alkenes proceed by a symmetrical transition structure.[5c] The preferred *spiro* approach is thought to be due to a relatively small back-bonding interaction of the distal oxygen lone-pair of electrons with the C=C π^* orbital.[4] This favorable electronic interaction is maximized with a tetrahedral array around the developing oxirane oxygen and is "turned off" in the planar transition structure. The preferred approach of dioxirane to the axis of the C=C double bond is also *spiro*-like in nature but the potential energy surface (PES) for approach seems to be quite soft.

There has also been a long-standing controversy over the symmetrical versus asymmetrical approach of peracids and dioxiranes to the C=C double bond. Although the MP2 method tends to give unsymmetrical transition structures,[6a] where the two developing C−O bonds are of unequal length, more highly correlated methods [QCISD, CCSD, and CCSD(T)] give very symmetrical *spiro* transition structures with synchronous formation of the developing C−O oxirane bonds for symmetrically substituted alkenes. Density functional calculations (DFT) also typically produce symmetrical *spiro* transition structures for both types of alkene epoxidation.

The *spiro* mechanism for peracid epoxidation has recently been questioned, and a planar TS was suggested where the peracid prefers to be parallel with the C=C bond axis ($\angle$H−O−C−C ≈ 0.0°).[6b] We have responded[7] to that proposal with additional evidence in support of the *spiro* orientation that is always of lower energy than a planar approach with simple unhindered alkenes. In the present study, we reexamine the approach of dioxirane (DO) and DMDO to ethylene at several levels of theory and suggest that the *spiro* orientation is the preferred approach for alkene epoxidation with dioxiranes.

Computational Methods

Molecular orbital calculations using density functional theory (DFT) methods,[8a] quadratic configuration interaction restricted and unrestricted procedures [QCISD and QCISD(T)],[8b] and Brueckner theory[8c−e] [BD(T)] were performed with the Gaussian 98 program.[9] The Becke three-parameter hybrid functional,[10,11]

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combined with the Lee, Yang, and Parr (LYP) correlation functional,[12] denoted B3LYP,[13] was employed in the calculations. Geometries were optimized[14] at the B3LYP and QCISD levels using the 6-31G(d), 6-31+G(d,p), and 6-311+G(3df,2p) basis sets (the latter was used only for the B3LYP optimizations). The CCSD(T) calculations have been performed using the ACES II program[15] that implements the coupled-cluster and many-body-perturbation-theory methods. The CASSCF theory[16a] that was employed utilized the GAMESS program.[16b] Multireference second-order perturbation theory corrections to the CASSCF wave function were also implemented mostly with the GAMESS[16b] program and in part (multireference RS perturbation theory, RSPT2) using the MOLPRO[17] suite of programs. The stationary points on the potential energy surfaces were characterized by calculations of vibrational frequencies at the level of theory used in the geometry optimization (if this option is available for the method). The classical barriers were estimated using total electronic energies without zero-point vibrational energy corrections.

Results and Discussion

The use of such single-reference methods as B3LYP for calculations concerning the epoxidation reaction has been questioned recently.[6b] We have reported a thorough systematic comparison of the B3LYP variant of density functional theory with higher computational methods including QCISD, CCSD, CCSD(T), and CASSCF methods for the optimization of transition structures for ethylene epoxidation with peroxyformic acid.[18a] Our more recent paper has confirmed these findings and has provided a detailed analysis of CASSCF calculations for such oxygen transfer reactions.[7] One of the intriguing observations that has pervaded our prior theoretical studies is the rather large influence that triple electron excitations have upon activation barriers for epoxidation. For example, the QCISD/6-31+G(d,p) peroxyformic/ethylene activation barrier is 23.4 kcal/mol, but when the triples contribution (QCISD(T)) is included with a single-point energy correction, the barrier is reduced to 16.4 kcal/mol.[18b] Despite this rather large effect, *optimization* of the peroxyformic acid/ethylene TS *with the triples* (CCSD(T)) had essentially no impact upon the TS geometry.

In the current study, we observe that the triples contribution has the same pronounced effect upon the magnitude of the activation barrier for ethylene epoxidation with dioxirane (Table 1). However, although the transition structure optimized at the CCSD/6-31G* level of theory has an essentially symmetrical *spiro* geometry, when the triples contribution was included (CCSD(T)/6-31G*), a highly unsymmetrical C_1 TS was obtained albeit with a *spiro* orientation ($\angle$C−C−O−C = −90.1°). The symmetrical structure optimized with a C_s symmetry constraint is 1.4 kcal/mol higher in energy (Figure 1). The angle $\angle$C−C−O−C = −101.3° is consistent with a *spiro* geometry.

TABLE 1: Activation Barriers ($\Delta E^‡$, kcal/mol) for the Epoxidation of Ethylene with Dioxirane (DO) Calculated at Different Levels of Theory for Unsymmetrical (C_1-TS) and Symmetrical (C_s)[a] Approaches

method	$\Delta E^‡$ C_1-TS	$\Delta E^‡$ C_s	$\Delta\Delta E^‡$ (C_s vs C_1)
B3LYP/6-31G(d)	12.94	12.95	0.01
B3LYP/6-311+G(3df,2p)	13.98	14.00	0.02
CCSD/6-31G*	25.37[a]		
CCSD(T)//CCSD/6-31G*	17.03[a]		
CCSD(T)/6-31G*	15.56	16.98	1.42
BD(T)//CCSD(T)/6-31G*	16.11	17.84	1.73
BD(TQ)//CCSD(T)/6-31G*	16.79	19.11	2.32
BD(T)/6-31+G(d,p)//CCSD(T)/6-31G*	13.38	13.90	0.52
BD(TQ)/6-31+G(d,p)//CCSD(T)/6-31G*			1.20
B3LYP/6-311+G(3df,2p)//CCSD(T)/6-31G*	15.14	12.58	−2.56
MP2−FC/6-31G(d)			2.91
BD(T)/6-311+G(d,p)//CAS(12,12)/6-31G(d)			0.60
BD(TQ)/6-311+G(d,p)//CAS(12,12)/6-31G(d)			1.37
BD(T)/6-311+G(d,p)//CAS(8,8)/6-311+G(d,p)			−0.29
CAS(8,8)/6-31G(d) + MP2[b]	15.41	17.51	2.10
CAS(10,10)/6-31G(d) + MP2[b]	14.69	20.07	5.38
CAS(12,12)/6-31G(d) + MP2[b]	13.88	19.42	5.53
BD(T)/6-311+G(d,p)//CAS(10,10)/6-311+G(d,p)	15.54		
RSPT2//CAS(8,8)/6-31G(d)			−0.11

[a] C_s structures are optimized with C_s symmetry constraint imposed by Z-matrix input; the C_1-TS optimized at the CCSD/6-31G* level of theory is essentially symmetrical. [b] Reactants energies are at the CAS(10,10)/6-31G(d)+MP2 level.

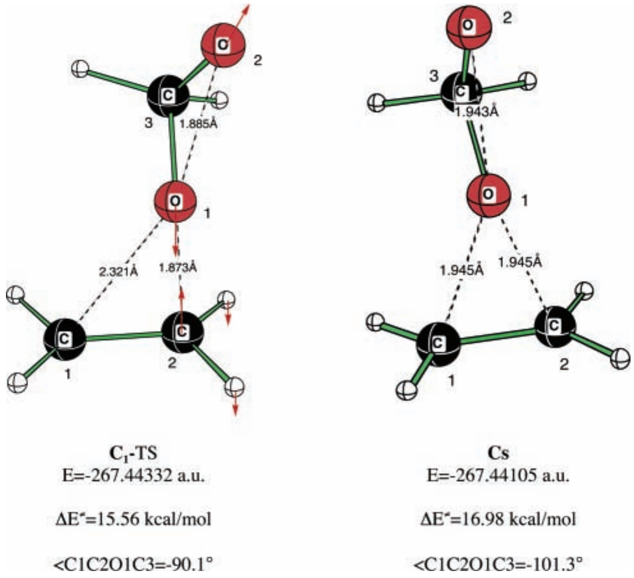


Figure 1. Unsymmetrical (C_1) transition structure and symmetrical (C_s) structure (constrained) for ethylene epoxidation with dioxirane optimized at the CCSD(T)/6-31G* level of theory. Red arrows are schematic reaction-coordinate vectors corresponding to the imaginary frequency.

Although a $\Delta\Delta E^‡$ of only 1.4 kcal/mol is not that significant, the differences in the two TS geometries (Table 1) rekindles the controversy over symmetrical versus unsymmetrical transition structures in peracid epoxidation.[7] Moreover, the reliability of such highly correlated, but single-reference, methods as QCISD and CCSD is brought into question. This observation takes on particular relevance since the B3LYP method, now in such common use for oxygen atom transfer chemistry, typically gives very symmetrical TSs regardless of the flexibility of the basis set used. Moreover, the same symmetrical TS was obtained after optimization of the initially unsymmetrical TS using UB3LYP with an unrestricted initial guess by mixing HOMO and LUMO (guess = mix)[9] to ensure, at least initially, an unrestricted wave function. These conflicting observations prompted a closer examination of the C_1 and C_s TSs comparing B3LYP and CCSD geometries, with what has become to be considered by many, the more reliable CASSCF method.

Optimization of the transition structure for ethylene epoxidation with dioxirane (DO) at the B3LYP/6-311+G(3df,2p) level typically results in an almost perfectly symmetrical transition structure (Table 1). The corresponding **Cs** constrained structure has a nearly identical geometry and classical activation barrier ($\Delta\Delta E^‡$ = 0.02 kcal/mol, Table 1). *Both structures* are

TABLE 2: CASSCF(e,o)/6-31G(d) Total Energies (E_{tot}, a.u.) and CASSCF(e,o) with MP2/6-31G(d) Dynamic Correlation Corrections (CAS(e,o)+MP2, a.u.) and Corresponding Relative Energies (E_{rel}, kcal/mol) of the C_s and C_1 Structures for Ethylene Epoxidation with Dioxirane Optimized by Using Two Active Spaces of Different Size[a]

(e,o)	structure	E_{tot}	E_{rel}	CAS(e,o)+MP2	E_{rel}
8,8[b]	C_s	−266.72201	14.7	−267.36006	2.1
8,8[c]	C_1	−266.74540	0.0	−267.36341	0.0
10,10	C_s	−266.74499	19.1	−267.35597	5.4
10,10	C_1	−266.77550	0.0	−267.36455	0.0
12,12	C_s	−266.78110	14.6	267.35702	5.5
12,12	C_1	−266.80442	0.0	−267.36584	0.0

[a] e is the number of electrons and "o" is the number of orbitals in the CASSCF active space. [b] CASSCF(8,8)/6-31G(d)-optimized C_s structure is a saddle point of second-order characterized by two imaginary frequencies, $\upsilon_i = 744.3i$ and $506.3i$ cm^{-1}. [c] CASSCF(8,8)/6-31G(d)-optimized C_1 structure is a transition structure characterized by a single imaginary frequency $\upsilon_i = 843.0i$ cm^{-1}.

TABLE 3: Key Distances (Å) in Symmetrical C_s and Unsymmetrical C_1 Structures Optimized at Different Levels of Theory

method	C−O	C−O	O−O
C_s			
B3LYP/6-31G(d)	2.0116	2.0116	1.8735
B3LYP/6-311+G(3df,2p)	2.0395	2.0395	1.8616
CCSD(T)/6-31G*	1.9453	1.9453	1.9434
CCSD(T)/aug-cc-pVDZ	2.0228	2.0228	1.9128
CAS(8,8)/6-31G(d)	1.9470	1.9470	2.0267
CAS(8,8)/6-31+G(d)	1.9622	1.9622	2.0400
CAS(8,8)/6-311+G(d,p)	1.9584	1.9584	2.0425
CAS(10,9)/6-31G(d)	1.9444	1.9444	1.9567
CAS(10,10)/6-31G(d)	2.0065	2.0065	1.9477
CAS(12,10)/6-31G(d)	1.9353	1.9353	2.0079
CAS(12,11)/6-31G(d)	1.9816	1.9816	1.9445
CAS(12,12)/6-31G(d)	1.9826	1.9826	1.9665
C_1-TS			
B3LYP/6-31G(d)	2.0115	2.0117	1.8732
B3LYP/6-311+G(3df,2p)	2.0389	2.0392	1.8620
CCSD/6-31G*	1.9071	1.9993	1.8996
CCSD(T)/6-31G*	1.8725	2.3213	1.8849
CAS(8,8)/6-31G(d)	1.9383	2.6363	1.9472
CAS(8,8)/6-311+G(d,p)	1.9562	2.6504	1.9561
CAS(10,9)/6-31G(d)	1.9218	2.6298	1.9297
CAS(10,10)/6-31G(d)	1.8991	2.5998	1.9323
CAS(12,12)/6-31G(d)	1.8747	2.5564	1.9106

first-order saddle points characterized by almost identical single imaginary frequencies [$\upsilon_i(C_s) = 463.6i$ cm^{-1} and $\upsilon_i(C_1) = 464.3i$ cm^{-1}, B3LYP/6-31G(d)] with geometries that did not differ significantly from those derived with the 6-31G(d) basis set.

As noted above, in contrast to the other single reference methods, geometry optimization of the dioxirane/ethylene TS (Figure 1) with the triples contribution [CCSD(T) method] gave a highly unsymmetrical transition structure (C−O = 1.87 and 2.32 Å). Single-point energy corrections on CCSD(T)/6-31G*-optimized C_1 and C_s structures (Table 1) calculated at different levels of theory [BD(T), BD(TQ), and B3LYP with different basis sets] gave relatively small energy differences of 0.5 to 2.3 kcal/mol in favor of the unconstrained **C_1-TS.** In particular, the Brueckner doubles (BD) model is closely related to the QCISD and CCSD wave functions but differs in that the contribution of the singles excitations is eliminated and the orbitals relax in the presence of the dynamic correlation (double excitations). The BD(T) single-point energy corrections on the CASSCF geometries should provide a reliable estimate of their energy differences. With BD(T) and BD(TQ)/6-311+G(d,p) single-point corrections to the CCSD(T) geometries, the energy difference is reduced to only 0.5 and 1.2 kcal/mol in favor of the C_1 TS. However, with a B3LYP energy correction, the symmetrical CCSD(T) TS is favored by 2.6 kcal/mol. This DFT variant does recover significant electron correlation and has proven useful in the treatment of dioxiranes and other multireference problems in which one configuration is dominant.[19] In all cases (using DFT), we see a definite preference for a highly symmetrical approach of the dioxirane to the C=C. On balance, with the BD(T)/CCSD(T) methods, we see a very soft approach of dioxirane to the alkene carbon−carbon double bond with a small bias toward an asymmetric transition structure.

If indeed some biradical character is associated with the dioxirane oxygen transfer reaction, then this should be discernible with a multireference method such as CASSCF. With the peracid/ethylene TS, we found[7] that the smallest active space that gave an acceptable description of the static electron interactions was eight electrons in eight orbitals (8,8). To get a better idea of the orbital nature and energetics of this reaction, CASSCF calculations of different size active space have been performed (Table 2). We typically start from an 8,8 active space [π orbitals of ethylene, σ orbitals of O1−O2 and O1−C3 and an oxygen lone pair [lp(O1)] perpendicular to the COO dioxirane plane plus their antibonding counterparts]. The initial orbitals were chosen by examination of molecular orbitals derived from either UHF or UB3LYP calculations. The CASSCF optimized C_1 TS (8,8)/6-31G(d) is a first-order saddle point ($\nu_i = 843.0i$ cm^{-1}, Table 2). We used the same active space for optimization of the C_s-constrained structure but obtained a second-order saddle point characterized by two imaginary frequencies (744.3i and 506.3i cm^{-1}) that was 14.6 kcal/mol higher in energy. When we correct for dynamic electron correlation with a single-point CASSCF(MP2) calculation (Table 1), we find the unsymmetrical C_1 TS to be only 2.1 kcal/mol lower in energy than the corresponding symmetrical C_s saddle point of second-order. To the contrary, with the smaller active space, RSPT2//CAS(8,8)/6-31G(d) calculations slightly favor the C_s approach (by 0.11 kcal/mol, Table 2). Single-point BD(T)/6-311+G(d,p) energy corrections for the C_1 and C_s structures optimized at the CAS(8,8)/6-311+G(d,p) level also indicate a slight preference (0.3 kcal/mol) for the C_s approach.

Interestingly, the third highest virtual orbital (LUMO+3) but least occupied, was initially comprised of an oxygen lone pair [lp*(O1)] perpendicular to the DO plane where it had the proper symmetry to enjoy an interaction with the C=C π* orbital. After geometry optimization, this orbital had rotated into the C−O−O plane where this interaction is "turned off". The C_1-TS was reoptimized with the more flexible 6-311+G(d,p) basis set. The choice of relevant active space, the value of the imaginary frequency ($\upsilon_i = 831.7i$ cm^{-1}) and the geometry (Table 3) were not affected significantly by the larger basis set.

To examine the potential role of the size of the active space we located both C_1 and C_s structures with a set of orbitals comprising a 10,10 and 12,12 CASSCF, and found the C_1 structures to be 19.1 and 14.6 kcal/mol lower in energy. CASSCF(MP2) correlation corrections with active spaces (10,10) and (12,12) suggest that the unsymmetrical C_1-TS is the lowest-energy transition structure, but the energy differences are vastly reduced to 5.4 and 5.5 kcal/mol (Table 2). Thus, all three CASSCF calculations with varying size active space (8,8 to 12,12) suggest an unsymmetrical transition structure for DO epoxidation. It is also worthy of note that the MP2 corrections are essential to reduce these very large energy differences (Table 2). A BD(T)/6-311+G(d,p) calculation on the (12,12) geometries suggested an energy difference of only 0.6 kcal/mol in favor of the C_1-TS. The BD(T) single point correction to the CAS(10,10)

C_1-TS differs from the CAS(MP2) barrier by less than a kcal/mol suggesting this as a possible complimentary method to correct the CAS total energy differences. From these data, we suggest that the unsymmetrical approach is slightly favored and that the PES for approach of dioxirane to the C═C is very soft. On balance, it would appear that the unsymmetrical C_1-TS is only slightly favored and that an approximately *spiro* orientation of the approach is maintained.

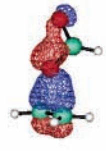
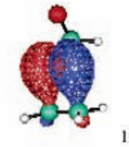
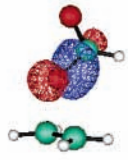
A comparison between the most active orbitals of the C_1-TS and C_s structures that we have found is also informative. We summarized the most active 4 occupied and 4 virtual orbitals selected from the active spaces of the two CAS (12,12)/6-31G-(d)-optimized structures (Table 4).

A comparison of the HOMOs (antibonding combination of $\pi_{C=C}$ and σ_{O1-O2}) suggests that it's occupation decreases with a decrease in symmetry. The next to the highest occupied molecular orbital, (HOMO-1), [the bonding combinations of $\pi_{C=C}$ and σ_{O1-O2}] also have a lower electron occupancy in the unsymmetrical case. The other two occupied orbitals (HOMO-2 and HOMO-3) have almost identical occupations (1.97) in both C_1 and C_s, but the symmetrical C_s structure has an lp(O1) orbital as HOMO-2, whereas in the C_1-TS, it is HOMO-5 (not shown in Table 4) and another orbital (σ_{C3-O2}) that represents HOMO-2. This situation is very similar to our recent observations[7] for the CASSCF(12,12) optimized transition structures for the epoxidation of ethylene with peroxyformic acid, where we found that in the higher energy unsymmetrical *spiro* TS lp(O1) (HOMO-3 in the symmetrical *spiro* TS) is replaced by the σ orbital of the C3−O2 bond. The lp(O1) molecular orbital and it's interaction with the $\pi^*_{C=C}$ orbital of ethylene is largely responsible for the symmetrical attack in both oxygen transfer reactions, epoxidation with dioxirane and peroxyformic acid.

The lowest virtual orbitals (LUMO) are all of similar character (antibonding combination of $\pi_{C=C}$ and σ^*_{O1-O2}). The C_1-TS LUMO orbital has a 2-fold greater occupation than the C_s LUMO but a similar percentage of all virtual electrons (70%). The C_1-TS (LUMO+1) is occupied by 0.09 e (15% of virtual electrons) and can be characterized as an antibonding combination of $\pi^*_{C=C}$ and σ^*_{O1-O2}. Thus, one may suggest a greater diradicaloid character of the unsymmetrical transition structure. The fact that the reactants, isolated ethylene and DO, have 0.35 electrons in the virtual space [0.16 and 0.19 electrons, according to CAS(10,10)/6-31G(d) calculations], whereas C_s and C_1 structures have 0.38 and 0.60 electrons [CAS(12,12)/6-31G(d)], also supports the suggestion of a greater diradicaloid character of the C_1-TS. The C_s orbital (LUMO+1) and all other virtual orbitals of the C_s and C_1 structures have occupation numbers less than 0.03. Nevertheless, in the case of the C_s structure, the role of LUMO+1 and LUMO+2 is still important because of the relatively large percentage (10% each) of electrons residing in these virtual orbitals. This emphasizes the importance of the virtual orbitals of the lp*(O1)+$\pi^*_{C=C}$ and σ^*_{C3-O1} in the stabilization of the symmetrical structure by back-donation of the oxygen lone-pair into the $\pi^*_{C=C}$ orbital. Although the CASSCF method does suggest diradicaloid character for the unsymmetrical C_1-TS, the corresponding constrained symmetrical structure has comparable electron density in the virtual orbitals of both reactants and the C_s "transition structure."

Interestingly, the methods providing the more symmetrical TS structures, CCSD/6-31G* and B3LYP/6-311+G(3df,2p), give the best agreement with the experimental microwave-structural data for DO (R_{O-O} = 1.516 Å),[1e] whereas the higher-level CCSD(T) and CASSCF calculations result in a slightly longer OO bond (Figure S1 in the Supporting Information). Our experience with CASSCF calculations on these very electron rich systems has suggested to us that the CASSCF method is not necessarily the most reliable affordable method unless the active space comprises essentially a full valence shell calculation of the electron/orbitals to ensure a balanced correlation of *all* of the oxygen lone pairs.

TABLE 4: Most Active Molecular Orbitals (from HOMO-3 to LUMO+3) Selected from the Active Space of the Symmetrical (C_s) Saddle Point of Second-Order and the Unsymmetrical (C_1) Transition Structure for Ethylene Epoxidation with Dioxirane Optimized at the CAS(12,12)/6-31G(d) Level of Theory[a]

orbital	C_s	C_1 - TS
LUMO+3	 0.02 (6%)	 0.03 (5%)
LUMO+2	 0.03 (10 %)	 0.03 (5%)
LUMO+1	 0.03 (10%)	 0.09 (15%)
LUMO	 0.21 (67% of "virtual" electrons)	 0.42 (70 % of "virtual" electrons)
HOMO	 1.81	 1.66
HOMO-1	 1.96	 1.88
HOMO-2	 1.97	 1.96
HOMO-3	 1.97	 1.96

[a] The numbers given with each orbital are corresponding electron occupations.

TABLE 5: Classical Reaction Barriers for the Ethylene Epoxidation with Dimethyldioxirane (DMDO) at Various Levels of Theory

method	$\Delta E^{\ddagger}$, kcal/mol
B3LYP/6-31G(d)	18.2
B3LYP/6-31+G(d,p)	17.7
B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p)[a]	19.6
B3LYP/6-311+G(3df,2p)	19.1
QCISD(T)//QCISD/6-31G(d)	19.4
QCISD/6-31+G(d,p)	22.3
QCISD(T)//QCISD/6-31+G(d,p)	15.2
B3LYP/6-311+G(3df,2p)//QCISD/6-31G+(d,p)	18.9
QCISD(T)/6-31G+(d,p)//B3LYP/6-311+G(3df,2p)	14.9
CCSD/6-31G*	28.5
CCSD(T)//CCSD(T)/6-31G*	18.4
CCSD(T)/6-31+G(d,p)//CCSD(T)/6-31G*[b]	15.5

[a] The TS geometry was optimized at B3LYP/6-31+G(d,p) with a single-point energy correction at B3LYP/6-311+G(3df,2p). [b] Geometry optimization with the triples contribution gave an asymmetric approach to the double bond with DMDO (Figure 2).

Cremer has shown that the activation enthalpy for O−O bond cleavage of dioxirane (DO) of 18 kcal/mol is increased to 23 kcal/mol for dimethyldioxirane (DMDO).[19] We have also provided evidence that the strain energy of DMDO is reduced from 18 kca/mol in DO to only 11 kcal/mol in DMDO.[20] These observations suggest that we also look at their differences in transition structures for oxygen atom transfer. Single-reference methods such as B3LYP, CCSD, and QCISD applied to the optimization of transition structures for the ethylene epoxidation with dimethyldioxirane (DMDO) typically lead to an almost symmetrical *spiro* geometry.[21] The B3LYP barriers for DMDO epoxidation of ethylene vary from 17.7 to 19.1 kcal/mol suggesting only a marginal basis set effect (Table 5). At the QCISD level, single-point QCISD(T) calculations show that the contribution of the triples also markedly reduces the barrier as noted previously with peracid epoxidation. However, in the case of DMDO epoxidation, the B3LYP method slightly overestimates the classical activation barriers relative to QCISD(T) barriers. The opposite effect has been generally noted for B3LYP peracid epoxidation.[18] A comparison of B3LYP barrierrs on QCISD geometries with QCISD barriers on B3LYP geometries supports our earlier contention[21] that the latter protocol is the most economical route to accurate epoxidation barriers.

As in the above case of peracid epoxidation, we observe that the triples contribution also has a pronounced effect upon the magnitude of the activation barrier for ethylene epoxidation with dioxirane (Table 5). We see the same effect of the triples contribution on the geometry for oxygen atom transfer from DMDO.

Although the transition structure for DMDO/ethylene epoxidation optimized at the CCSD/6-31G* level of theory has an essentially symmetrical *spiro* geometry, when the triples contribution was included [CCSD(T)/6-31G*], a highly unsymmetrical C_1-TS (C−O =1.83 and 2.30 Å) was obtained albeit with an approximate *spiro* orientation (Figure 2). The CCSD(T)/6-31G* total energy of the essentially symmetrical structure optimized at the CCSD/6-31G* level of theory is 1.9 kcal/mol higher in energy (Figure 2) than the unsymmerical C_1-TS [CCSD(T)/6-31G*].

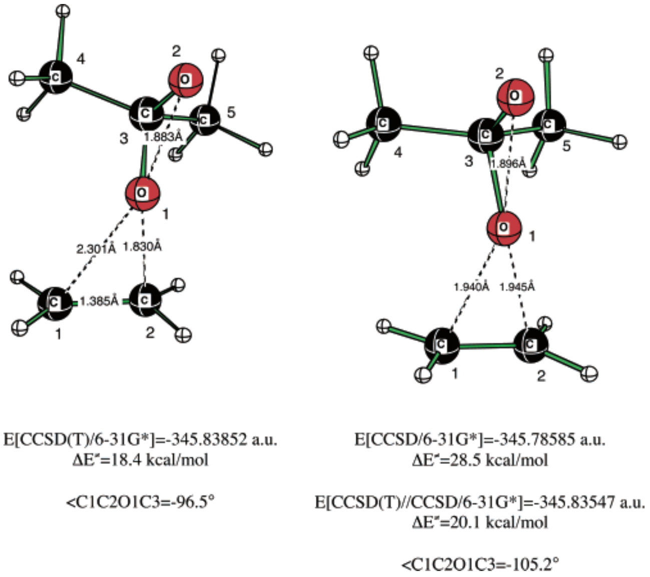


Figure 2. CCSD(T)/6-31G* unsymmetrical and CCSD/6-31G* symmetrical transition structures for ethylene epoxidation with dimethyldioxirane (both fully optimized without symmetry constraint).

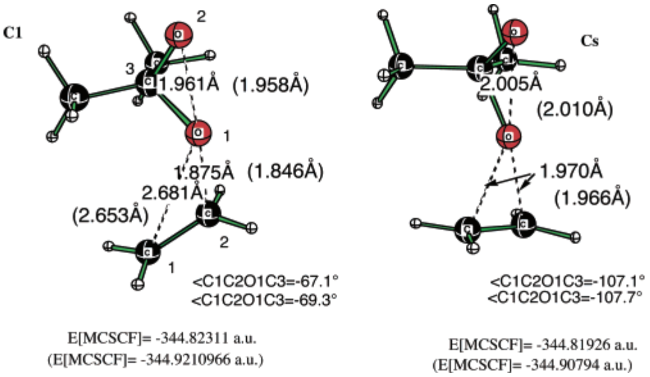


Figure 3. Unsymmetrical (C_1) transition structure and symmetrical (C_s) structure (constrained) for ethylene epoxidation with dimethyldioxirane optimized at the CAS(8,8)/6-31+G(d) level of theory. Numbers in parentheses correspond to the CAS(8,8)/6-311+G(d,p)-optimized structures.[22]

These observations prompted a series of CASSCF calculations to assess the multireference character of these TSs. This is a delicate problem since the CASSCF method tends to exaggerate the apparent diradical character (and stabilizes the unsymmetrical structure) and a CAS(MP2) calculation is needed to correct this overemphasis. In this instance, we have chosen the active orbitals by looking at the MOs from a typical NBO analysis of the symmetrical B3LYP TS. With an (8,8)/6-31+G(d) CAS, starting with a symmetrical B3LYP geometry, we could obtain either a symmetrical (C−O = 1.97 Å) or an unsymmetrical TS (C−O = 2.68, 1.87 Å) (Figure 3) depending upon the choice of the active space. This dilemma points to one of the major problems with CASSCF calculations; the choice of active space is very subjective!

At the CAS(8,8)/6-311+G(d,p) level, an unsymmetrical C_1-TS (Figure 3) is also preferred for the DMDO epoxidation of ethylene by 9.4 kcal/mol after a CAS(MP2) correction. With a BD(T)/6-31G(d) single-point energy correction, that energy difference is reduced to 0.6 kcal/mol. Consistent with this observation, the configuration coefficient for this CAS(8.8) calculation is 0.82 for the C_1-TS and 0.85 for the symmetrical TS. These values are typically smaller for dioxirane epoxidation than for peracid epoxidation[18a] reflecting the greater multireference character of the dioxirane wave function. The virtual orbital population of the C_1-TS is also greater than for the C_s-TS as evidenced by the HOMO−LUMO occupation of 1.52−0.48 for the unsymmetrical TS and 1.77−0.23 e for the symmetrical DMDO TS. These observations are consistent with the contention that the CASSCF method tends to favor energetically the TS with greater biradicaloid character.

We suggest that the approach of DMDO to a symmetrically substituted alkene should result in an essentially symmetrical transition structure. The B3LYP method proves adequate for the study of dioxirane epoxidation reactions.

Conclusions

From these collective data, we may conclude that the potential energy surface is very soft for both DO and DMDO alkene epoxidation. The energies of C_1 and C_s transition structures typically differ by a kcal/mol or two. Depending on the theoretical method, one may get either a symmetrical or an unsymmetrical approach. The geometries of the C_1 and C_s structures also show a strong dependence on the method applied (Table 3).

In general, B3LYP and CCSD methods gave essentially symmetrical *spiro* transition structures. Geometry optimization with CASSCF gave unsymmetrical *spiro* transition structures. In contrast to the other single reference methods, geometry *optimization* of the dioxirane/ethylene TS (Figure 1) *with the triples contribution* [CCSD(T) method] gave a highly unsymmetrical transition structure that was favored by 1.4 kcal/mol relative to the constrained C_s structure. With BD(T) and BD(TQ)/6-311+G(d,p), single-point corrections to the CCSD(T) geometries the energy difference is reduced to only 0.5 and 1.2 kcal/mol. All three CASSCF calculations with varying size active space [(8,8) (10,10), and 12,12)] suggest an unsymmetrical transition structure for DO epoxidation. The C_s DO/ethylene structure is not a transition structure since at the CASSCF(8,8)/6-31G(d) level of theory it is characterized by two imaginary frequencies (saddle point of second-order). RSPT2 calculations on CAS(8,8)/6-31G(d)-optimized structures lead to the almost equal energies of C_1 and C_s ($\Delta\Delta E^{\ddagger} = -0.1$ kcal/mol in favor of C_s). CAS(MP2) corrections on the optimized transition structures suggest a 2.1, 5.4, and 5.5 kcal/mol preference for the unsymmetrical C_1-TS. It is also worthy of note that the MP2 corrections are essential to reduce these very large energy differences (Table 2).

However, BD(T)/6-311+G(d,p) calculations on the (12,12) geometries result in an energy difference of only 0.6 kcal/mol in favor of the C_1-TS. The BD(T) single point correction to the CAS(10,10) C_1-TS differs from the CAS(MP2) barrier by less than a kcal/mol suggesting this as a possible complimentary method to correct the CAS barriers.

In general, it is found that the C_s approach with corrections at different levels of theory is more often higher in energy than a C_1 unsymmetrical attack. The CASSCF method exhibits a tendency to overemphasize the stability of the unsymmetrical diradicaloid structure. The DFT method (B3LYP) has the opposite tendency, strongly favoring the symmetrical approach with no discernible diradicaloid character in either the ground or transition state. The B3LYP-optimized structure with a C_s constraint is a first-order saddle point, and its geometry is almost identical to the C_1-TS optimized without any constraints. Single-point energy calculations using the B3LYP/6-311+G(3df,2p) method on CCSD(T)/6-31G*-optimized C_1 and C_s structures suggest a 2.6 kcal/mol preference for the symmetrical approach of DO to ethylene.

In contrast to the case of peroxyformic acid epoxidation, the size of the basis set has a lesser effect on the reaction barrier and geometry of the DO/ethylene TS. The resulting active space of the CAS(8,8)-C_1-TS re-optimized with the more flexible 6-311+G** basis set, and geometry were not affected markedly by the larger basis set.

The lp(O1) lone-pair molecular orbital and its interaction with the $\pi^*_{C=C}$ orbital is largely responsible for the symmetrical approach to the C=C.

For the DMDO epoxidation of ethylene, we suggest that the approach of DMDO to a symmetrically substituted alkene should result in an essentially symmetrical transition structure. On balance, the B3LYP method proves adequate for the study of dioxirane epoxidation reactions.

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Supporting Information Available: Total energies, Cartesian coordinates, and active space TSs optimized at the CCSD(T), B3LYP, and CAS(o,e) with o (number of orbitals) and e (number of electrons) varying from 8 to 12. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Plesnicar, B. In *The Chemistry of Peroxides*; Patai, S., Ed.; John Wiley and Sons: New York, 1983; p 521. (b) Finn, M. G.; Sharpless, K. B. *Asymmetric Synth.* **1986**, *5*, 247. (c) *Organic Peroxides Vol. II*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Chapter 5. (d) Frohn, M.; Zhou, X.; Zhang, J.-R.; Tang, T.; Shi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 7718. (e) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890.

(2) For an excellent review on substrate-directable chemical reactions, see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.

(3) (a) Bartlett, P. D. *Rec. Chem. Prog.* **1950**, 47. (b) Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 4093.

(4) (a) Bach, R. D.; Willis, C. L.; Domagals, J. M. In *Applications of MO Theory in Organic Chemistry*; Csizmadia, I. C., Ed.; Elsevier: Amsterdam, 1977; Vol. 2, p 221. (b) Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275. (c) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1410.

(5) (a) Koerner, T.; Slebocka-Tilk, H.; Brown, R. S. *J. Org. Chem.* **1999**, *64*, 4, 196. (b) Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M.; Rastelli, A. *J. Org. Chem.* **2002**, *67*, 8519. (c) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385.

(6) (a) Yamabe, S.; Kondou, C.; Minato, T.*J. Org. Chem.* **1996**, *61*, 616. (b) Okovytyy, S.; Gorb, L.; Leszczynski, J. *Tetrahedron Lett.* **2002**, *43*, 4215.

(7) Bach, R. D.; Dmitrenko, O. *J. Phys. Chem. A* **2003**, *107*, 4300.

(8) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Pople, J. A.; Head-Gordon, M.; Raghavchari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (c) Handy, N. C.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185. (d) Dykstra, C. E. *Chem. Phys. Lett.* **1977,** *45*, 466. (e) Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Phys. Chem.* **1990**, *94*, 5579.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) Stevens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(14) (a) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (b) Schlegel, H. B. *Adv. Chem. Phys.* **1987**, *67*, 249. (c) Schlegel, H. B. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 459.

(15) ACES II is a program product of the Quantum Theory Project, University of Florida. Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Kucharski, S. A.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K. K.; Rozyczko, P.; Sekino, H.; Hober, C.; Bartlett, R. J.

(16) (a) Hegerty, D.; Robb. M. A. *Mol. Phys.* **1979**, 38, 1795. (b) The GAMESS (General atomic and molecular electronic structure system) program: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347. (c) Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. *Adv. Chem. Phys.* **1999**, *110*, 267.

(17) MOLPRO is a package of ab initio programs designed by H.-J. Werner and P. J. Knowles. The authors are R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklaβ, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone R. Tarroni, T. Thorsteinsson and H.-J. Werner.

(18) (a) Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estévez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem. A* **1997**, *101*, 6092. (b) Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C. *J. Am. Chem. Soc.* **1998**, *120*, 9902. (c) Bach, R. D.; Dmitrenko, O.; Adam, W.; Schambony, S. *J. Am. Chem. Soc.* **2003**, *125*, 924. (d) Bach, R. D.; Glukhovtsev, M. N.; Canepa, C. *J. Am. Chem. Soc.* **1998**, *120*, 775.

(19) Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.* **1998**, *292*, 97.

(20) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 2588. Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 3884.

(21) Glukhovtsev, M. N.; Canepa, C.; Bach, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10258.

(22) Unsymmetrical (C_1) transition structure was fully optimized at the CAS(8,8)/6-311+G(d,p)level of theory. The optimization of the C_s structure as a saddle point of second order was stopped when the maximum gradient reached 0.0002 instead of the default gradient convergence tolerance, 0.0001 (see ref 16b); the total energy was not significantly changed for many cycles.