

Relative Reactivity of Peracids versus Dioxiranes (DMDO and TFDO) in the Epoxidation of Alkenes. A Combined Experimental and Theoretical Analysis

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Abstract: Comparative analysis of the calculated gas-phase activation barriers (ΔE^\ddagger) for the epoxidation of ethylene with dimethyldioxirane (DMDO) and peroxyformic acid (PFA) [15.2 and 16.4 kcal/mol at QCISD(T)//QCISD/6-31+G(d,p)] and *E*-2-butene [14.3 and 13.2 kcal/mol at QCISD(T)/6-31G(d)//B3LYP/6-311+G(3df,2p)] suggests similar oxygen atom donor capacities for both oxidants. Competition experiments in CH_2Cl_2 solvent reveal that DMDO reacts with cyclohexene much faster than peracetic acid/acetic acid under scrupulously dried conditions. The rate of DMDO epoxidation is catalyzed by acetic acid with a reduction in the classical activation barrier of 8 kcal/mol. In many cases, the observed increase in the rate for DMDO epoxidation in solution may be attributed to well-established solvent and hydrogen-bonding effects. This predicted epoxidative reactivity for DMDO is not consistent with what has generally been presumed for a highly strained cyclic peroxide. The strain energy (SE) of DMDO has been reassessed and its moderated value (about 11 kcal/mol) is now more consistent with its inherent gas-phase reactivity toward alkenes in the epoxidation reaction. The unusual thermodynamic stability of DMDO is largely a consequence of the combined *geminal* dimethyl- and dioxa-substitution effects and unusually strong C–H and C–CH₃ bonds. Methyl(trifluoromethyl)dioxirane (TFDO) exhibits much lower calculated activation barriers than DMDO in the epoxidation reaction (the average $\Delta\Delta E^\ddagger$ values are about 7.5 kcal/mol). The rate increase relative to DMDO of $\sim 10^5$, while consistent with the higher strain energy for TFDO (SE ~ 19 kcal/mol) is attributed largely to the inductive effect of the CF₃ group. We have also examined the effect of alkene strain on the rate of epoxidation with PFA. The epoxidation barriers are only slightly higher for the strained alkenes cyclopropene ($\Delta E^\ddagger = 14.5$ kcal/mol) and cyclobutene ($\Delta E^\ddagger = 13.7$ kcal/mol) than for cyclopentene ($\Delta E^\ddagger = 12.1$ kcal/mol), reflecting the fact there is little relief of strain in the transition state. Alkenes strained by twist or π -bond torsion do exhibit much lower activation barriers.

Introduction

In recent years cyclic peroxides such as dimethyldioxirane (DMDO) and methyl(trifluoromethyl)dioxirane (TFDO) have found increasing utility as oxidizing agents for alkenes, heterocyclics, and saturated hydrocarbons.¹ Chiral dioxiranes are also becoming increasingly important in the asymmetric epoxidation of complex alkenes.^{1c} It is generally assumed within the experimental community that dioxiranes, as typified by DMDO, are more reactive than peracids in the epoxidation of alkenes. For example, Curci^{1b} has reported a rate ratio for the epoxidation of cyclohexene with DMDO (acetone) versus perbenzoic acid (CH_2Cl_2) of 74. The reactivity of dioxiranes as oxygen-atom donors has typically been ascribed largely to their strain energy (SE). Strain is a fundamental concept in organic chemistry and

is considered a major factor in determining structure, energy, and reactivity. Traditional analysis of strain effects on reactivity assumes that any observed rate enhancement stems from destabilization of the ground state (GS) of the strained compound. The presumed high rates of epoxidation by three-membered-ring peroxides have been attributed to the driving force for O-atom transfer due to the relief of ring strain and the favorable enthalpy change attending the formation of a strong C=O π -bond. The even greater reactivity of TFDO (≥ 1000 -fold) compared to DMDO has been credited largely to the inductive effect of the CF₃ substituent on the dioxirane ring. However, since very little actual rate data were available, the “high” reactivity of dioxiranes was attributed in the early literature to the fact that these cyclic peroxides could readily oxidize saturated hydrocarbons even at low temperatures; this level of reactivity is not observed for other oxidizing agents such as peracids. Recent rate-data estimates^{1b} suggest that the reactivity of DMDO toward alkenes exceed that of a typical peracid such as peroxybenzoic acid (PBA) by a factor ranging up to 10^2 .

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We have recently completed a comprehensive study of the SE of small-ring compounds,^{2a} including dioxiranes.^{2b} Strain energies of simple unsubstituted cyclic hydrocarbons have traditionally been measured relative to all-anti linear hydrocarbons in their minimum-energy conformations.³ However, when the small-ring compound bears a highly substituted carbon atom such as that in DMDO, special consideration must be given to the effects of substitution on the inherent strain energy. The SE of the parent dioxirane DO has recently been revised downward from 26.4 kcal/mol at the CCSD(T)⁴ level to 18 kcal/mol based upon several high-level ab initio (G2) methods.^{2b} The relative SEs of DO, DMDO, and TFDO have been estimated by combination of the dioxirane with cyclopropane to form the corresponding 1,3-dioxacyclohexane reference compound. The relative SE predicted for DMDO is 7 kcal/mol lower than that of DO, a value that is more consistent with theoretical predictions⁵ of dioxirane reactivity toward alkenes. The SE for DMDO was also predicted to be only about 11 kcal/mol, based upon several other computational schemes.^{2b} The most reactive dioxirane, methyl(trifluoromethyl)dioxirane, has an estimated SE just 1 kcal/mol more than that of DO, but 8 kcal/mol greater than that of DMDO.² The thermodynamic stability of DMDO is largely a consequence of the combined dioxa and dimethyl geminal effects and its relatively strong C–H and C–CH₃ bonds.² While a CF₃ substituent has only a minimal effect upon the stability of a cyclopropane ring,² it has a large impact upon the reactivity of a dioxirane; e.g., TFDO is estimated to be 7.7 kcal/mol more strained than DMDO. The average difference in epoxidation barriers given below is $\Delta\Delta E^\ddagger = 7.5$ kcal/mol, which perhaps suggests that this increase in the rate of oxidation comes from relief of ring strain in the dioxirane ring. Whatever the origin of TFDO reactivity, the predicted relative reactivity of these two oxidizing agents is clearly supported by the experimental facts.⁶

Results and Discussion

(a) Comparative Theoretical Rate Studies for Peracids and Dioxiranes. As part of a comprehensive theoretical study on the relative reactivity of peracids and dioxiranes toward simple alkenes, we found that theoretical gas-phase activation barriers for alkene epoxidation with these two oxidants appear to be quite comparable. Many of the more recent theoretical studies on these epoxidation reactions have been carried out with density functional theory (DFT) using the B3LYP method and quite often using the relatively small 6-31G* basis set. It is also commonly believed that B3LYP calculations often underestimate

Table 1. Classical Reaction Barriers (ΔE^\ddagger , kcal/mol) for the Ethylene Epoxidation with Peroxyformic Acid (PFA) and Dimethyldioxirane (DMDO) at Various Levels of Theory

method	ethylene + PFA	ethylene + DMDO
B3LYP/6-31G(d)	14.1	18.2
B3LYP/6-31+G(d,p)	14.9	17.7
B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) ^a	17.0	19.6
B3LYP/6-311+G(3df,2p)	16.9	19.1
QCISD(T)//QCISD/6-31G(d)	18.8	19.4
QCISD/6-31+G(d,p)	23.4	22.3
QCISD(T)//QCISD/6-31+G(d,p)	16.4	15.2
B3LYP/6-311+G(3df,2p)//QCISD/6-31G+(d,p)	17.0	18.9
QCISD(T)/6-31G+(d,p)//B3LYP/6-311+G(3df,2p)	16.2	14.9
CCSD(T)//CCSD(T)/6-31G*	19.4	18.4
CCSD(T)/6-31+G(d,p)//CCSD(T)/6-31G* ^b	17.1	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 a symmetrical TS for PFA epoxidation but an asymmetric approach to the double bond with DMDO (C–O bonds of 1.830 and 2.301 Å).

Table 2. Summary of the Reaction Barriers (kcal/mol) for the Epoxidation of Simple Alkenes with Peroxyformic Acid (PFA) and Dimethyldioxirane (DMDO)

reaction	ΔE^\ddagger	method
ethylene + PFA	16.4	QCISD(T)//QCISD/6-31+G(d,p)
	18.7	QCISD(T)//B3LYP/6-31G(d) ^a
	18.8	QCISD(T)//QCISD/6-31G(d) ^b
	17.4	QCISD(T)//B3LYP/6-311G(d,p) ^b
	18.6	QCISD(T)/6-311+G(3df,2p)//QCISD/6-31+G(d,p)
propene + PFA	15.9	QCISD(T)//B3LYP/6-31G(d) ^b
	16.0	QCISD(T)//QCISD/6-31G(d) ^b
isobutene + PFA	13.7	QCISD(T)//B3LYP/6-31G(d) ^a
	13.8	QCISD(T)//QCISD/6-31G(d) ^a
E-2-butene + PFA	13.3	QCISD(T)//B3LYP/6-31G(d) ^a
	13.4	QCISD(T)//QCISD/6-31G(d)
	10.8	QCISD(T)/6-31+G(d,p)//QCISD/6-31G(d)
	11.2	CBS-Q//QCISD/6-31G(d) ^c
	13.2	QCISD(T)/6-31G(d)//B3LYP/6-311+G(3df,2p)
1,3-butadiene + PFA	15.9	QCISD(T)//QCISD/6-31G(d)
E-2-butene + DMDO	14.6	QCISD(T)//B3LYP/6-31G(d)
	14.6	QCISD(T)//QCISD/6-31G(d)
	14.3	QCISD(T)/6-31G(d)//B3LYP/6-311+G(3df,2p)
ethylene + DMDO	9.7	CBS-Q//QCISD/6-31G(d) ^c
	15.2	QCISD(T)//QCISD/6-31+G(d,p)
	19.3	QCISD(T)//B3LYP/6-31G(d) ^b
	19.4	QCISD(T)//QCISD/6-31G(d) ^b

^a Reference 5b. ^b References 5c,d. ^c Based upon CBS-Q energy calculations on the QCISD/6-31G(d) optimized geometries of TS and corresponding isolated reactants (see Supplemental Information).

activation barriers. Since our observations on the relative reactivity of these two classes of oxidizing agents appear to be at odds with conventional wisdom, this point of contention must be addressed at a higher level of theory. With B3LYP calculations the classical activation barriers (Table 1) for DMDO epoxidation of ethylene are systematically higher than peroxyformic acid (PFA) epoxidation with the smaller 6-31G(d) basis set ($\Delta\Delta E^\ddagger = 4.1$ kcal/mol), the intermediate 6-31G(d,p) (2.8 kcal/mol), and the more flexible 6-311+G(3df,2p) basis set (2.2 kcal/mol). However, this predicted trend is reversed with QCISD methods that provide a better treatment of electron correlation effects. It is also essential that the triples contribution to the total energies be included since they provide a marked reduction

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Table 3. B3LYP/6-31G(d) Activation Barriers (ΔE^\ddagger , kcal/mol) for the Epoxidation of a Series of Alkenes with Peroxyformic Acid (PFA), Dimethyldioxirane (DMDO), and Methyl(trifluoromethyl)dioxirane (TFDO)^a

alkene	PFA	DMDO	TFDO
ethylene	14.1 (14.9) 17.0 ^b [16.4] ^c	18.2 (17.7) [15.2] ^a	11.3 (11.1)
propene	12.0 (12.6) 14.8 ^b [16.0] ^d	16.6 (16.0)	9.6 (9.1)
<i>tert</i> -butylethylene	11.2 (12.3) 14.0 ^b		
1-octene	11.2 (12.2) 14.1 ^b	15.8 (15.2)	8.2 (8.0)
isobutene	10.8 (11.2) 13.0 ^b [13.7] ^d	15.3 (14.0) 16.0 ^b	7.3 (6.8)
<i>E</i> -2-butene	10.5 (11.0) 12.8 ^b [13.4] ^d	15.5 (14.8) [14.6] ^d	6.9 (6.9)
<i>Z</i> -2-butene	10.0 12.1 ^b	14.1 (13.4)	5.6 (5.6)
<i>Z</i> -2-pentene	9.3 (10.0) 11.6 ^b		
cyclopropene	12.0 (12.5) 14.5 ^b		
cyclobutene	11.0 (11.5) 13.7 ^b		
cyclopentene	9.3 (9.7) 12.1 ^b		
cyclohexene	9.7 (10.1) 12.1 ^b	13.5 (12.6) 14.7 ^b	5.3 (5.2)
cycloheptene	9.8 (10.2) 12.2 ^b		
<i>Z</i> -cyclooctene	9.1 (9.6) 11.5 ^b		
<i>E</i> -cyclooctene	5.6 (6.1) 8.2 ^b		
1-methyl- <i>E</i> -cyclooctene	4.0 (4.3) 5.9 ^b		
norbornene (<i>exo</i>)	9.7 (10.3) 12.9 ^b	13.3 (13.0)	5.5 (5.5)
norbornene (<i>endo</i>)	12.5 (13.2) 15.4 ^b	15.9 (15.8)	
benzonorbornadiene (<i>exo</i>)	9.6 (10.2) 12.2 ^b		
benzonorbornadiene (<i>endo</i>)	14.6 (15.1) 17.0 ^b		
bicyclo[3.3.1]non-1-ene	5.2 (5.7) 7.7 ^b		
trimethylethylene	8.9 (9.1) 11.0 ^b	13.7 (12.8)	4.8 (4.9)
tetramethylethylene	7.8 (7.9) 9.8 ^b	14.0 (12.8)	4.8 (4.7)
1,3-butadiene	11.7 (12.4) 14.3 ^b [15.9] ^d	14.9 (14.6)	7.6 (7.3)
<i>trans</i> -2-cis4-hexadiene	9.4 (9.6) 11.5 ^b		
<i>E</i> -stilbene	13.2 (13.3) 15.1 ^b		
<i>Z</i> -stilbene	11.8 (12.6) 14.6 ^b		
styrene	11.2 (11.7) 14.2 ^b	14.3 (13.8)	6.7 (6.3)
<i>Z</i> -3-methyl-3-penten-2-ol	9.2 ^f		
allyl alcohol	7.5 ^f 11.4 ^g		

^a The barriers in parentheses are at the B3LYP/6-31+G(d,p) level of theory. Other computational approaches are indicated by footnotes. The barriers have been computed with respect to isolated reactants. ^b Classical activation barriers computed at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level. ^c The numbers in brackets for ethylene are at the QCISD(T)//QCISD/6-31+G(d,p). ^d The numbers in brackets for propene, isobutene, *E*-2-butene, and 1,3-butadiene entries are at the QCISD(T)//QCISD/6-31G(d) level of theory; CBS-Q//QCISD/6-31G(d) gas-phase intrinsic barriers (ΔE^\ddagger) for the epoxidation of *E*-2-butene with dimethyldioxirane (DMDO) and peroxyformic acid are 9.7 and 11.2 kcal/mol, respectively. ^e Classical activation barrier computed at the B3LYP/cc-pVTZ level. ^f Classical activation barrier computed at the B3LYP/6-311G(d,p) level. ^g Classical activation barrier computed at the QCISD(T)//QCISD/6-31G(d) level.

in activation energy (Table 1). QCISD(T)/6-31+G(d,p) energy corrections to either QCISD/6-31+G(d,p) or B3LYP/6-311+G(3df,2p) geometries suggest that DMDO is slightly more reactive than PFA ($\Delta\Delta E^\ddagger = 1.3$ kcal/mol). Thus, the most consistent results at an electron-correlated level [QCISD(T)//QCISD/6-31+G(d,p)] suggest classical activation barriers for the epoxidation of ethylene by PFA and DMDO of 16.4 and 15.2 kcal/mol (Table 1). A similar picture emerges when the geometry optimization step also includes the triples contribution and the CCSD(T)/6-31+G(d,p)//CCSD(T)/6-31G* barriers favor the DMDO TS ($\Delta\Delta E^\ddagger = 1.6$ kcal/mol) in quite good agreement with the experimental rate ratio of 74 given above.

At the DFT level the order of the gas-phase reactivity is reversed for the epoxidation of *E*-2-butene (Table 2) since PFA is slightly faster (1.1 kcal/mol). Similar results are predicted for the epoxidation of cyclohexene by PFA (12.1 kcal/mol) and DMDO (14.7 kcal/mol) when DFT methods are used [B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p), Table 3]. However, we again see a reversal in relative barriers when *E*-2-butene epoxidation is studied at a more highly correlated level. The DMDO barrier for epoxidation of *E*-2-butene is 1.5 kcal/mol lower than that for PFA at the CBS-Q level (on QCISD/6-31G* geometries).

In summary, relative to the electron-correlated QCISD(T)/QCISD calculations, the B3LYP method [with the smaller 6-31G(d) basis set] typically *underestimates* epoxidation barriers of peracids by some 4–6 kcal/mol, while it slightly *overestimates* epoxidation barriers for DMDO (Table 3). For example, the ΔE^\ddagger value for the epoxidation of propene with PFA at the

QCISD(T)/6-31G(d) level of theory is 16.0 kcal/mol, which corresponds to a B3LYP barrier of 12.6 kcal/mol (Table 2); the ΔE^\ddagger value for the epoxidation of *E*-2-butene at the QCISD(T)/6-31G(d) level of theory is 14.6 kcal/mol, which corresponds to a B3LYP/6-31G(d) barrier of 15.5 kcal/mol. The most sensible conclusion from this entire set of calculations at various levels is that *the gas-phase oxygen atom donor propensity of these two classes of reagents are essentially comparable*. This predicted epoxidative reactivity of DMDO is not consistent with what is generally assumed for a highly strained cyclic peroxide. Hence, we must look elsewhere for the origin of the observed increase in rate for DMDO epoxidation in the condensed versus the gas phase.

Earlier studies on the rates of electrophilic addition to alkenes typically resorted to relative rates with very few examples of absolute rate measurements. With modern computational methods, we may estimate the rates of epoxidation in a more economic, convenient fashion.⁵ This is particularly true for the rates of highly strained or unique structurally elaborate alkenes, which are not readily available and prove difficult to prepare. A direct comparison of the activation barriers for the PFA, DMDO, and TFDO epoxidation of a typical range of alkenes used in such reactions also suggested that the gas-phase reactivity of DMDO appeared to be less than anticipated (Table 3).

B3LYP/6-31+G(d,p) calculations predict that each additional alkyl group on the alkene double bond increases the rate of PFA epoxidation by about an order of magnitude. With DMDO and TFDO, the activation barriers are also sensitive to the number of alkyl substituents on the C=C bond and the rate

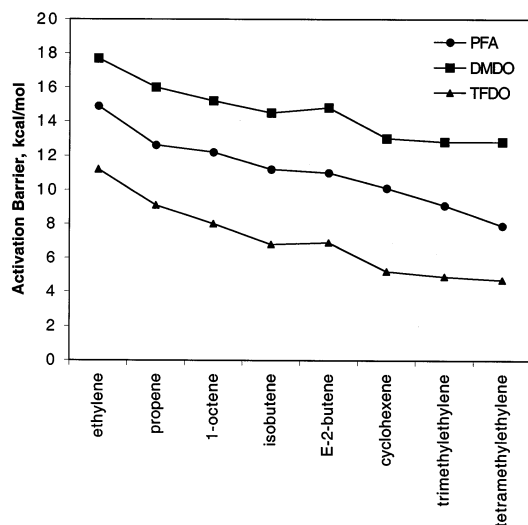


Figure 1. Graphic comparison of the calculated activation barriers [B3LYP/6-31+G(d,p)] for the epoxidation of a series of simple alkenes with peroxyformic acid (PFA), dimethyldioxirane (DMDO), and methyl(trifluoromethyl)dioxirane (TFDO).

increases in a similar fashion (Figure 1). The situation is somewhat confusing since an increase in the size of the basis set [to 6-311+G(3df,2p)] or the level of theory (QCISD) has the opposite effect on the DMDO and PFA activation barriers (Table 3). However, the general trends are consistent and the classical activation barriers (ΔE^\ddagger) decrease with increasing substitution in a nearly monotonic fashion. The DMDO barriers are consistently higher and the TFDO barriers consistently lower than those of PFA. The observed faster rate of DMDO epoxidation of *E*- versus *Z*-2-butene has been interpreted as a steric effect. In the gas-phase steric inhibition of the approach of DMDO to the more highly substituted alkenes does not appear to be a problem.

The gas-phase activation barriers for the epoxidation of this series of alkenes are systematically higher for DMDO than peroxyformic acid by an average $\Delta\Delta E^\ddagger$ of about 3 kcal/mol, which corresponds to a rate difference of ca. 200. However, B3LYP/6-31+G(d,p) barriers for PFA are typically greater than QCISD(T) barriers by an average of 2.7 kcal/mol. B3LYP/6-31+G(d,p) DMDO barriers are slightly smaller than QCISD(T) activation energies for ethylene and *E*-2-butene/DMDO (Table 3). When this correction is applied, we predict comparable gas-phase reactivity for peroxyformic acid and DMDO. As anticipated on the basis of experimental data,⁶ the trifluoromethyl-substituted TFDO exhibits much lower calculated activation barriers than DMDO in the epoxidation reaction. The theoretically predicted average $\Delta\Delta E^\ddagger$ of about 7.5 kcal/mol [B3LYP/6-31+G(d,p), Table 3] corresponds to a rate increase relative to DMDO of $\sim 10^5$ in excellent agreement with experiment. Since we presume that the QCISD(T) gas-phase epoxidation barriers are the most accurate, we had suggested that the traditionally assumed SE for dioxiranes are too high and that the predicted level of DMDO reactivity in the epoxidation is more consistent with our recent reassessment of the SE of DMDO.² The conclusion that DFT methods underestimate activation barriers, in general, should be amended, and each type of reaction must be examined individually.

(b) Gas-Phase Epoxidation of Selected Alkenes. Mechanistic studies of electrophilic addition to alkenes has been a

Table 4. B3LYP/6-31+G(d,p) Calculated Activation Barriers (ΔE^\ddagger , kcal/mol) and Reaction Exothermicities (ΔE , kcal/mol) for the Epoxidation of *E*-2-Butene with a Series of Diverse Oxidizing Agents^a

oxidizing agents	ΔE^\ddagger , kcal/mol	ΔE , kcal/mol	ΔS^\ddagger , e.u.	im freq, cm^{-1}	$E_{\text{H-bond}}$ (reactant) ^b	$E_{\text{H-bond}}$ (TS) ^b
FCO ₃ H	6.4	-54.5	-37.2	-370.4	1.1	5.3
trifluoroperacetic acid	6.4	-53.1	-37.5	-371.1	1.9	5.8
sila-DMDO ^c	6.9			-306.9		
TFDO ^d	6.9		-42.9	-363.6		
HOO(C=O)OH	9.0 ^e		-37.7	-400.8		
<i>m</i> -CPBA ^f	11.0		-37.8	-417.9		
peroxyformic acid	11.0 ^g	-50.8	-37.3	-411.1	2.9	8.3
CH ₃ OCO ₃ H	12.8	-49.5	-38.4	-409.1	3.2	10.0
peroxyacetic acid	13.5	-49.2	-36.1	-424.1	4.6	10.5
DMDO ^h	14.8 ^h		-39.6	-481.9		

^a The activation entropies (ΔS^\ddagger) and imaginary frequencies (im freq) have been calculated with a 6-31G(d) basis set. The estimated energies for OH...O hydrogen bonding [kcal/mol, B3LYP/6-31+G(d,p)] in the reactant and the corresponding transition structures are given in the last two columns. ^b The intramolecular hydrogen bonding to the carbonyl oxygen atom, $E_{\text{H-bond}}$ (reactant/TS), was estimated as the relative energy of the rotamer with the OH group pointing away ($\angle\text{OCOH}$ is 180°) with respect to the intramolecularly H-bonded, lowest-energy reactant/TS. ^c Dimethyldioxasilacyclopropane. ^d Methyl(trifluoromethyl)dioxirane. ^e The barriers have been calculated at the B3LYP/6-31G(d) level of theory. ^f *m*-Chloroperbenzoic acid. ^g The activation barrier at the QCISD(T)/B3LYP/6-31G(d) level of theory is 13.3 kcal/mol. ^h Dimethyldioxirane; the activation barrier at the QCISD(T)/B3LYP/6-31G(d) level of theory is 14.6 kcal/mol.

major area of research for many years.⁷ We are now in the fortunate position to visualize *computationally* the transition structures for many such reactions. It is important to note that hybrid density functional calculations are able to produce *relative* rates of epoxidation in good agreement with experiment. For instance, on the basis of calculated barriers for PFA epoxidation reactions listed in Table 3, we found that the ratio of the reaction rates for epoxidation of 1-octene/styrene is 1.2 [gas phase, B3LYP/6-31+G(3df,2p)//6-31+G(d,p)], whereas the corresponding experimental value reported by Perrin is 1.5 (MCPBA epoxidation).^{7a} Our relative rate data are also quite consistent with the series of epoxidation reactions reported by Shea^{7b} with the exception of highly strained alkenes. Several such unique transition structures calculated for peracid epoxidation are presented in Figure 2.

The epoxidation barriers are only slightly higher for the strained alkenes cyclopropene (SE \sim 55.2 kcal/mol)^{3c} and cyclobutene (SE \sim 28.4 kcal/mol) than for cyclopentene (SE \sim 4.1 kcal/mol), which presumably reflects the fact that the resulting epoxide products are also strained. The SE for the simplest epoxide, namely, oxirane, is 26.3 kcal/mol,^{3b} with an accompanying reduction in SE with each alkyl substituent.^{2a} The lack of correlation of the rate with strain energy is quite evident in the $\Delta\Delta E^\ddagger$ value of 0.8 kcal/mol for cyclopropene versus cyclobutene. The TS for epoxidation of the highly strained cyclopropene actually comes later along the reaction coordinate than that for cyclobutene (even more so for cyclopentene) as evidenced by the developing C–O bond distances (Figure 2, part 1 (first three structures)). All three TSs exhibit a highly symmetrical approach to the alkene double bond, with a spiro^{8a,b} orientation (90°) of the plane of the peracid with

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 (8) (a) Bach, R. D.; Willis, C. L.; Domagala, J. M. In *Progress in Theoretical Organic Chemistry*, Vol. II; Ciszmadia, I. G., Ed.; Elsevier: New York, 1977; p 221. (b) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1410.

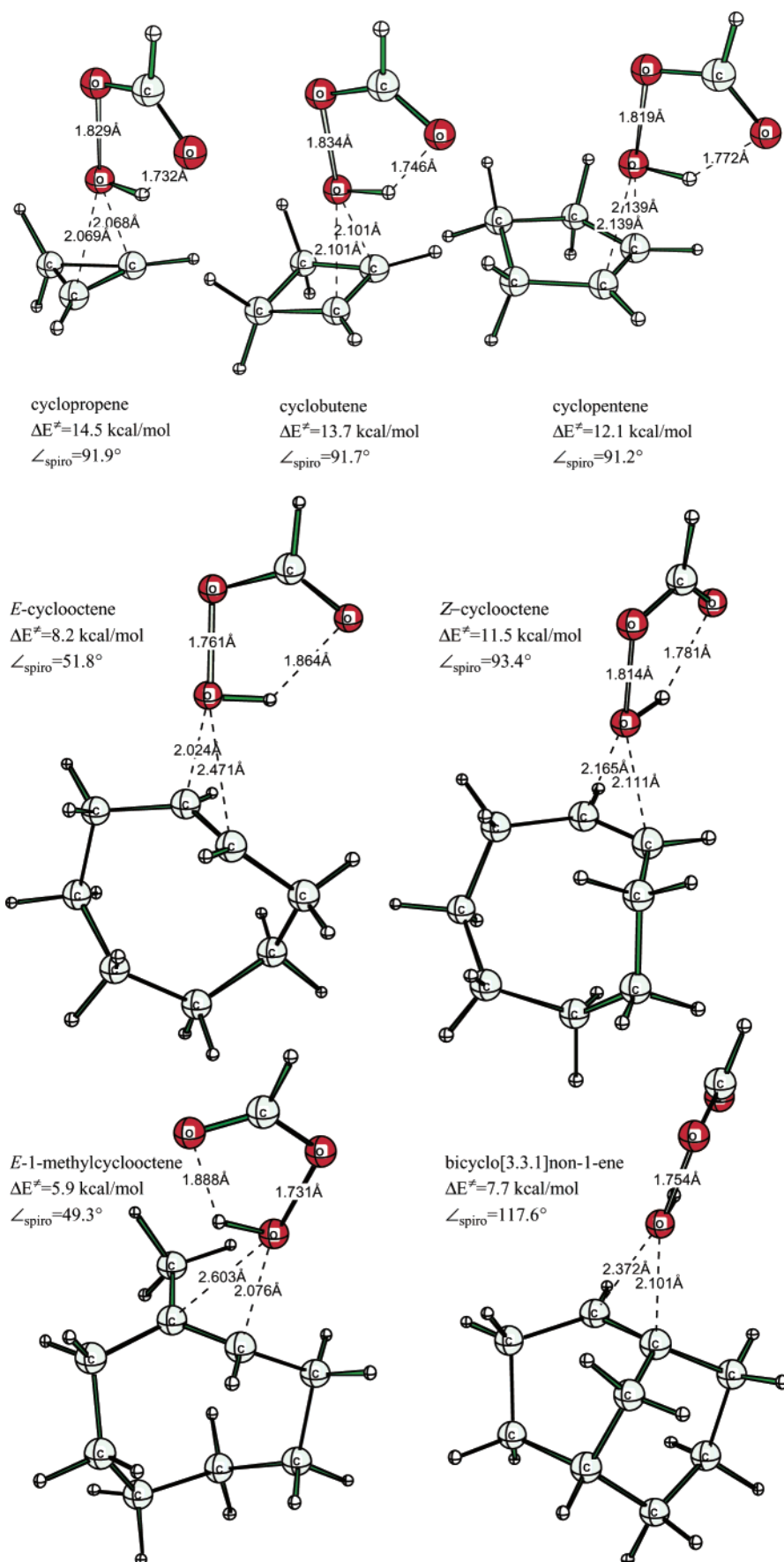


Figure 2. Transition structures for the epoxidation of cyclic alkenes with peroxyformic acid, optimized at the B3LYP/6-31+G(d,p) level of theory. The classical activation barriers are given at B3LYP/6-311+G(3df,2p)/B3LYP/6-31+G(d,p). Dihedral angles (\angle_{spiro} represents $\angle\text{HOCC}$) indicate the deviation from an ideal *spiro* approach (\angle_{spiro} is 90°) of the HO group in PFA onto the C=C bond of the alkene.

Table 5. Calculated (B3LYP/6-311+G(d,p)) Activation Parameters for the Epoxidation of Cyclohexene and Isobutene with Dimethyldioxirane (DMDO), Peroxybenzoic Acid (PBA) *m*-Chloroperoxybenzoic Acid (*m*-CPBA), and Peroxyformic Acid (PFA)^a

	DMDO/cyclohexene	PBA/cyclohexene	<i>m</i> -CPBA/cyclohexene	PFA/isobutene	DMDO/isobutene
ΔE^\ddagger	12.6 (14.7) ^b	12.0 (14.3) ^b	10.9 (13.4) ^b	11.2 (13.0) ^b	14.0 (16.0) ^b
ΔH_{298}^\ddagger	12.6	11.9	10.9		14.2
ΔG_{298}^\ddagger	24.0	23.1	22.2		25.0
ΔS_{298}^\ddagger	-38.1	-37.6, -32.9 ^c	-38.1, -27.8 ^c		-36.3
$\Delta E^\ddagger(\text{CHCl}_3)$	11.3				
$\Delta H_{298}^\ddagger(\text{CHCl}_3)$	11.4, 5.0 ^c				
$\Delta G_{298}^\ddagger(\text{CDCl}_3)$	16.9 ^c				
$\Delta E^\ddagger(\text{CH}_2\text{Cl}_2)$		12.2	11.4		
$\Delta H_{298}^\ddagger(\text{CH}_2\text{Cl}_2)$		12.1	11.3, 10.9 ^c		
$\Delta E^\ddagger(\text{acetone})$	10.7		10.6		10.9
$\Delta H_{298}^\ddagger(\text{acetone})$	10.7, 7.4 ^c		10.6		11.1, 9.3 ^f
$\Delta G_{298}^\ddagger(\text{acetic acid})$	16.6 ^c				
$\Delta E^\ddagger(\text{benzene})$		12.2			
$\Delta H_{298}^\ddagger(\text{benzene})$		12.1, 10.4 ^c			

^a Solvent corrections were performed with the COSMO model. The numbers in italics are experimental values. ^b Numbers in parentheses are at the B3LYP/6-311+G(3df,2p)//B3LYP/6-311+G(d,p) level of theory. ^c Reference 11. ^d References 11b,c. ^e Reference 11d. ^f Reference 12b.

Table 6. Calculated Energies and Enthalpies of the Alkene Epoxidation Reactions with Peroxyformic Acid (PFA), Dimethyldioxirane (DMDO), and Methyl(trifluoromethyl)Dioxirane (TFDO)

alkene	PFA		DMDO		TFDO	
	ΔE^\ddagger	ΔH^\ddagger	ΔE^\ddagger	ΔH^\ddagger	ΔE	ΔH
ethylene	-47.7	-48.3	-51.4	-52.0	-50.7 ^c -49.9 ^e	-50.9 ^d -50.1 ^f
propene	-50.2	-50.6	-53.9	-54.4		
isobutylene	-52.0	-52.4	-55.7	-56.2		
trimethylethylene	-55.1	-55.1	-58.8	-58.8	-58.0 ^c	-57.6 ^d
tetramethylethylene	-58.2	-58.6	-61.9	-62.4		
<i>E</i> -2-butene	-53.0	-53.5	-56.7	-57.3		
<i>Z</i> -2-butene	-53.1	-53.5	-56.8	-57.3		
butadiene	-46.9	-47.3	-50.6	-51.1		
acrylonitrile	-44.4	-44.8	-48.2	-48.6		

^a G2 (0 K). ^b G2 (298.15 K). ^c G2(MP2) (0 K). ^d G2(MP2) (298.15 K). ^e G3 (0 K). ^f G3 (298.15 K).

respect to the center of the C=C bond axis. This idealized approach allows a modest back-bonding of the oxygen lone pair with the π^* orbital of the alkene.

In both cases relatively high negative entropies of activation are observed (Tables 4 and 5), suggesting a highly ordered transition state. For peracid epoxidation there is an intramolecular H-bond of the OOH moiety to the carbonyl oxygen in the ground state (GS) of PFA (2.9 kcal/mol) that gets markedly stronger in the TS for oxygen transfer (8.3 kcal/mol, Table 4). Additionally, the spiro orientation contributes to the experimental entropy of ≈ -30 entropy units (e.u., Table 4). The calculated entropies range from 36 to 43 e.u., and the energy difference between the spiro (first-order) and planar (constrained second-order saddle point) attack of peroxyformic acid on *E*-2-butene is 2.6 kcal/mol. The spiro orientation for DMDO epoxidation of *E*-2-butene is favored by 5.8 kcal/mol [B3LYP/6-311G(d,p)], providing a rationale for its relatively high activation entropy of 40 e.u.

Alkenes strained by twist or π -bond torsion, such as *E*-cyclooctene, exhibit much lower barriers due to relief of strain in the TS for the oxygen-transfer step. The dihedral angle of the allylic substituents ($\text{CH}_2\text{-C}=\text{C}-\text{CH}_2$) in this twisted alkene is 133°, while the *trans*-hydrogen atoms on the double bond are essentially in the plane, with a dihedral angle of 178°. Whereas the epoxidation of symmetrically substituted alkenes normally involves a symmetrical approach onto the π -bond, the TSs for epoxidation of *E*-cyclooctene and *E*-1-methylcyclooctene exhibit highly asymmetric transition structures. We have no obvious explanation for the asymmetric approach onto *E*-cyclooctene, since the above dihedral angle for the carbon

skeleton has only been decreased by 3° in the TS. The $\Delta\Delta E^\ddagger$ value of 3.3 kcal/mol for *E*- versus *Z*-cyclooctene is clearly a reflection of the relative SE of these two medium-ring alkenes (16.4 vs 4.2 kcal/mol).^{3c} The activation barrier (ΔE^\ddagger) for the highly strained bicyclo[3.3.1]non-1-ene is also quite low (Figure 2, part 2 (fourth and fifth structures)). In these twist-strain alkenes the approach of the peracid deviates markedly from the idealized spiro one, which suggests that this part of the potential energy surface is quite soft. The back-bonding of the attacking oxygen lone pair to the π^* -orbital of the carbon-carbon double bond is obviously reduced when the approach is so asymmetric.

Although it is generally accepted that the *exo* approach to norbornene is favored over the *endo* one, the magnitude of the $\Delta\Delta E^\ddagger$ value is rarely measurable, unless some fraction of the *endo* product can be detected. The *exo* approach to norbornene is favored over the *endo* orientation by nearly 3 kcal/mol for both PFA and DMDO, while the *exo* TS for benzonorbornadiene is favored by nearly 5 kcal/mol (Figure 3).

The preferred *exo* approach does not appear to result from steric interactions. It is of particular relevance that the ΔE^\ddagger value for norbornene is only 0.9 kcal/mol greater than that for cyclohexene despite an SE value of 19.2 kcal/mol for the strained bicyclic alkene. Thus, except for twist strain, we observe surprisingly little rate enhancement due to ring strain. The asymmetric approach onto conjugated alkenes resembles the TS for a Michael-like addition due to the polarization of the α,β -unsaturated carbon-carbon bond and attack of the electrophilic oxygen of the oxidant at the β -carbon of the double bond. As anticipated, conjugated alkenes have greater π -bond ionization potentials and hence exhibit higher activation barriers (Figure 4).

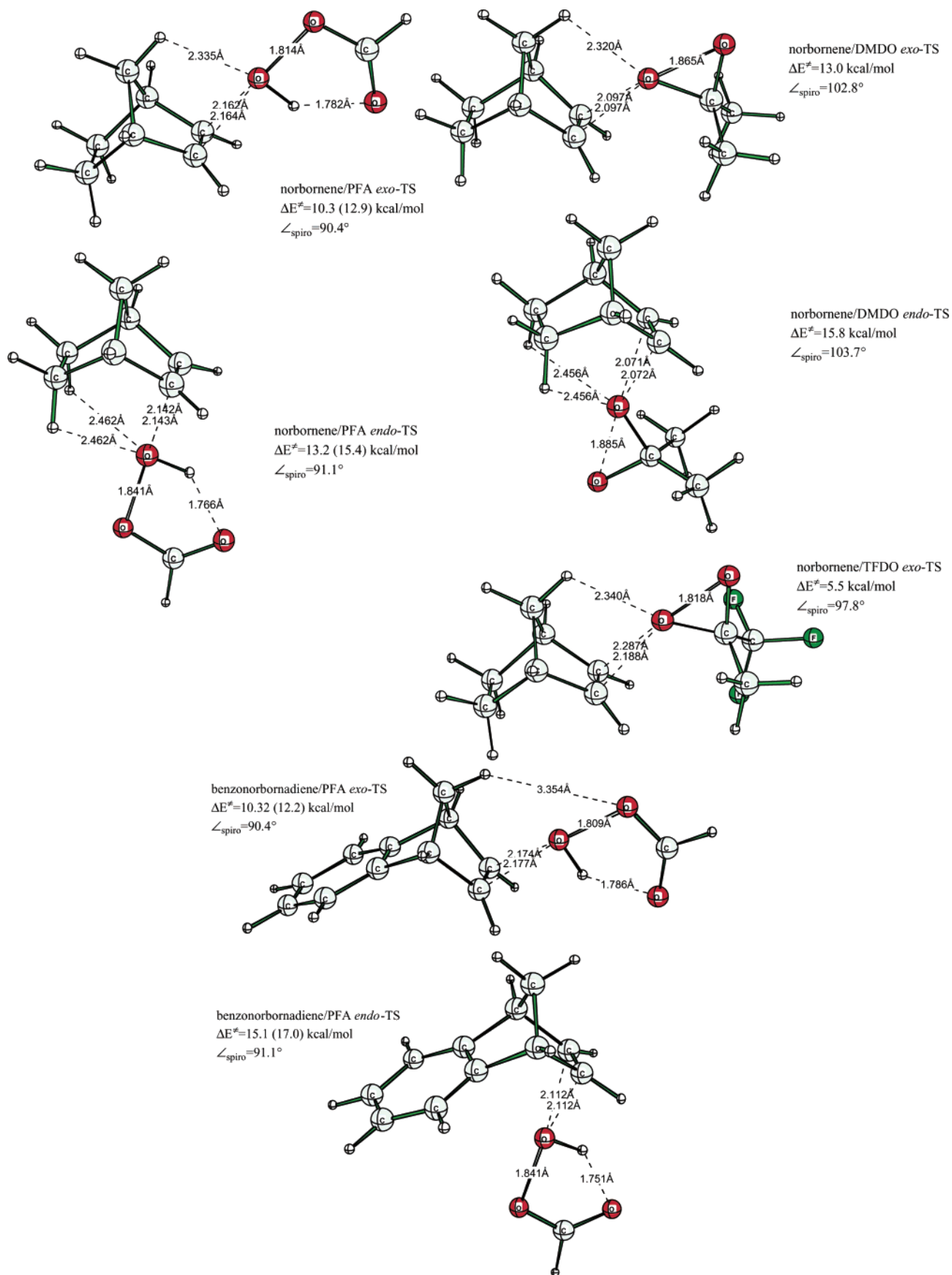


Figure 3. Transition structures for the epoxidation of norbornene and benzonorbornadiene, optimized at the B3LYP/6-31+G(d,p) level of theory. The classical activation barriers are given at B3LYP/6-31+G(d,p). The barriers in parentheses are at B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p). Dihedral angles (\angle_{spiro} represents $\angle\text{HOCC}$ for the PFA TSs or $\angle\text{COCC}$ for DMDO and TFDO TSs) indicate the deviation from an ideal *spiro* approach (\angle_{spiro} is 90°).

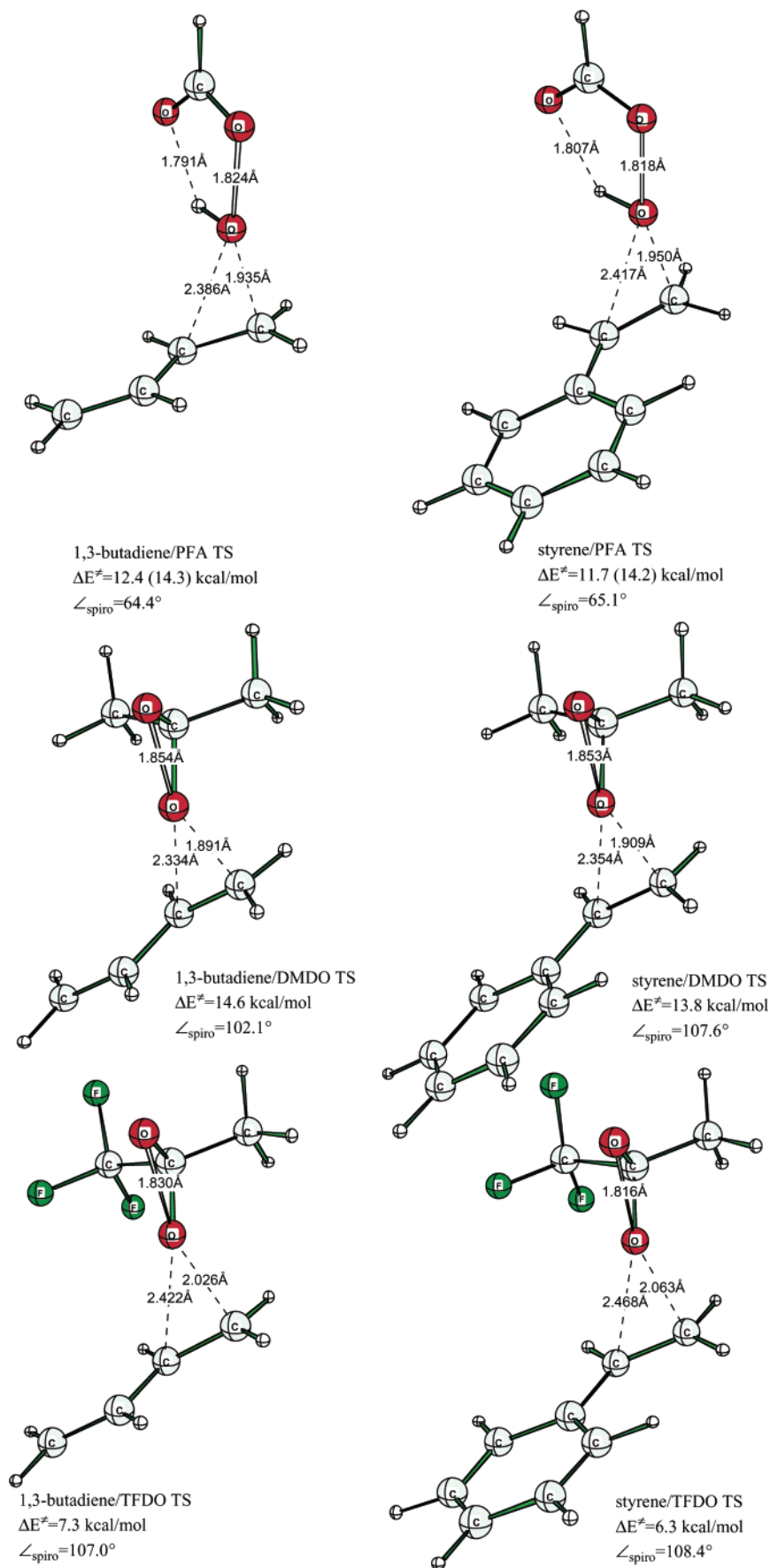


Figure 4. Transition structures for the epoxidation of 1,3-butadiene and styrene, optimized at the B3LYP/6-31+G(d,p) level of theory. The classical activation barriers are given at B3LYP/6-31+G(d,p). The B3LYP/6-311+G(3df,2p)/B3LYP/6-31+G(d,p) barriers are in parentheses. Dihedral angles (\angle_{spiro} represents $\angle\text{HOCC}$ for PFA TSs or $\angle\text{COCC}$ for DMDO and TFDO TSs) indicate the deviation from an ideal *spiro* approach (\angle_{spiro} is 90°).

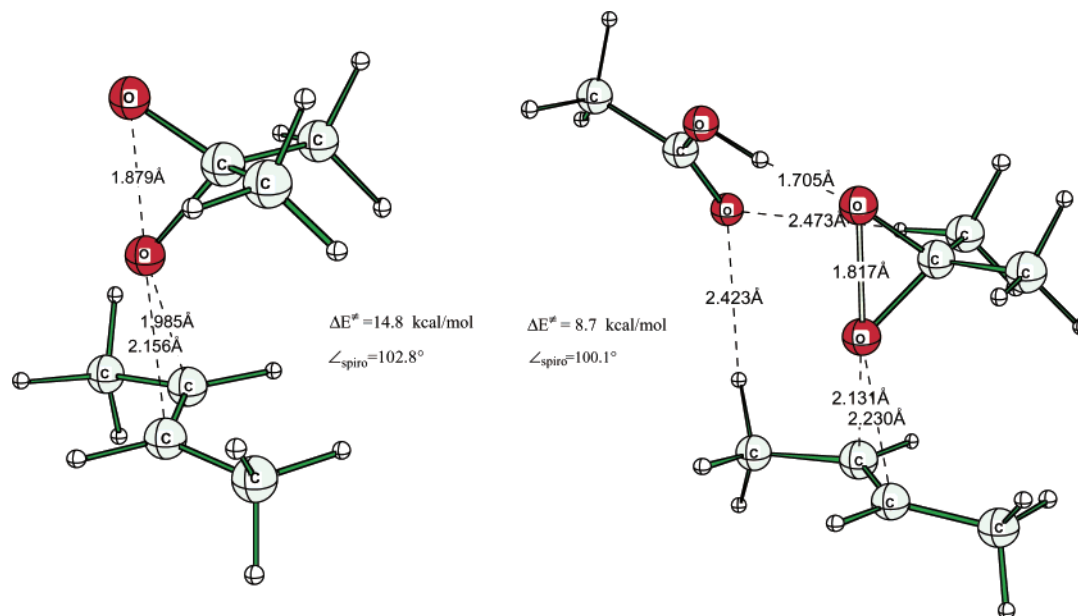


Figure 5. (a, left) Transition structure for the epoxidation of *E*-2-butene with DMDO, optimized at the B3LYP/6-31+G(d,p) level of theory. (b, right) Transition structure for the epoxidation of *E*-2-butene with DMDO in the presence of acetic acid, optimized at the B3LYP/6-31+G(d,p) level of theory.

Similar epoxidation barriers for PFA and DMDO prompted us to take a closer look at the relative reactivity of a more extensive series of classical oxidizing agents at a common level of theory [B3LYP/6-31+G(d,p)]. While the reactivity of DMDO in epoxidations was generally considered to be at least equal or even greater than that of a peroxy acid,⁹ our theoretical data suggest that DMDO actually has the lowest oxygen atom donor propensity of the entire series of examined peroxide–oxygen atom donors (Table 4). By using *E*-2-butene as a standard substrate, we observe a range of activation barriers from 6.4 to 14.8 kcal/mol. As anticipated, the fluoro-substituted peracids FCO₃H and CF₃CO₃H gave the lowest barriers, while DMDO gave the highest, much to our surprise. Sila-DMDO also proved to be a very effective potential oxygen donor, as a consequence of its high strain energy (36.4 kcal/mol).^{10a}

These striking computational results demand revision of our traditional views on the origin of DMDO reactivity, namely, that DMDO is a “highly strained cyclic peroxide”. This view appears to be fallacious and rests on the remarkable ability of DMDO to oxidize saturated hydrocarbons by oxygen atom insertion into CH bonds. Quite evidently, the reactivity of the versatile DMDO oxidant must be ascribed to reasons other than its strain energy and should be attributed to well-established solvent and hydrogen-bonding effects.^{9,14}

In a two-electron oxidation such as alkene epoxidation, in which the transfer of an oxygen atom by DMDO involves a S_N2-like displacement of an acetone molecule, the relief of strain

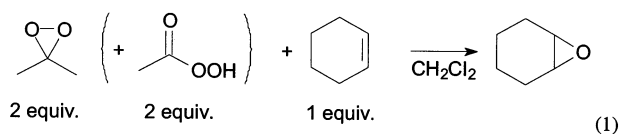
is obviously less than previously presumed. The peracid epoxidation of ethylene reactions involves the cleavage of a relatively weak O–O bond (48 kcal/mol) and the formation of an oxirane, albeit strained, that has two much stronger C–O bonds ($\Delta H_{298} = 52.0$ kcal/mol). Thus, another measure of the oxygen atom donor capacity can be estimated from the overall exothermicity of the reaction. These data at the G2 and G3 levels of theory (Table 6) should provide highly reliable energetics for these epoxidation reactions. The exothermicity of peracid epoxidation increases systematically with increasing alkyl substitution as evidenced by the difference in reaction enthalpy for epoxidation of tri- versus tetramethylethylene (3.5 kcal/mol). This is consistent with an earlier TS and the noted greater reactivity of the more highly substituted double bonds. This rate increase has traditionally been attributed to a higher lying HOMO for the tetra-substituted alkene. The anticipated relief of ring strain energy on the activation barriers for DMDO epoxidation is simply not in evidence. The $\Delta\Delta H_{298} = 3.8$ kcal/mol for PFA versus DMDO epoxidation does not support the long assumed contention that relief of strain makes a major contribution to the reactivity of “highly strained dioxiranes”. It is even more striking that the reaction enthalpy for the more strained TFDO (SE = 19 kcal/mol)² is *actually slightly lower than that of DMDO!* Thus, it is the inherent electrophilicity of dioxiranes due to their unique structure and a relatively low-lying O–O σ^* -orbital that is mainly responsible for dioxirane reactivity. The origin of the increased reactivity of TFDO appears to reside largely in its electronegative CF₃ substituent.

(c) Relative Rates of Epoxidation in Solution. These composite theoretical data strongly support the contention that the inherent gas-phase reactivity of DMDO is comparable to that of peroxyformic acid. How then may we resolve the observed greater reactivity of DMDO in relatively polar or protic solvents? It is well-established experimentally that protic solvents disrupt the internal H-bond in a peracid and markedly slow the rate of epoxidation. Moreover, the rate of oxygen transfer from a peracid responds only modestly to acid

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catalysis.^{10b} In contrast, Baumstark^{9a} reported that protic solvents enhance the rate of DMDO epoxidation of *p*-methoxystyrene. Murray^{11a} showed that the protic solvents methanol and acetic acid increase the rate of epoxidation of cyclohexene by DMDO at 25 °C by factors of 5 and 7.5 faster than in acetone. In moist acetone, the rate is enhanced both by the polarity of the medium and the effects of hydrogen bonding on the distal oxygen of DMDO in the TS for epoxidation. Indeed, Curci^{1b} has reported a rate ratio of 74 for the epoxidation of cyclohexene with DMDO (acetone) versus perbenzoic acid (PBA in CH₂Cl₂).

A competition experiment was conducted to estimate the relative rates of the epoxidation of cyclohexene by DMDO and peracetic acid (eq 1); also the role of water catalysis was assessed under these conditions. When equimolar amounts of



acetone-free¹³ DMDO (2 equiv) and peroxyacetic acid (2 equiv) were allowed to react with cyclohexene (1 equiv) under rigorously dried conditions, 53% of the DMDO was consumed after 15 min, whereas essentially all of the peracid remained (see Experimental Section in Supporting Information). These results are quite similar to those that we have observed in not rigorously dried acetone, the usual conditions for DMDO epoxidations. Thus, DMDO reacts much faster (ca. 100-fold) than peracetic acid, even under meticulously dried conditions.

For this purpose, an acetone-free DMDO solution in dichloromethane was prepared,¹³ dried first over P₂O₅ (3 h) and subsequently over K₂CO₃ (2 h), and stored at -20 °C under dry argon gas. All other solvents and solutions were carefully dried. Under these conditions, DMDO alone reacts rapidly with cyclohexene, as monitored photometrically and by iodometric titration; after 15 min, 56% of the DMDO was consumed. In the presence of equimolar amounts of DMDO and peroxyacetic acid, the amount of DMDO was determined photometrically and the total peroxide content (DMDO + peracid) was determined by iodometric titration. After 15 min, 53% of the DMDO was consumed within the experimental error (ca. 5%), whereas essentially all of the peracid remained (no conversion). These results are quite similar to those, which we have observed in not especially dried acetone. These data reveal that DMDO reacts much faster than peracetic acid, even under meticulously dried conditions. The solubility of H₂O in CH₂Cl₂ is maximally 1.3%, such that a 2-mL sample contains only 26 μL (1.4 mmol) of water; this amount of H₂O would increase the reaction rate of the DMDO epoxidation maximally by a factor of 1.2–1.7;¹⁴ however, under our meticulously dried conditions, the water concentration is much lower, probably below 5 ppm.

This leaves open the question of catalysis by acetic acid, the solvent for the peroxyacetic acid. The role of acetic acid catalysis can be best examined computationally as discussed below. We find that in the presence of 1 equiv of peroxyacetic acid (see transition structure in Figure 5), the barrier for the DMDO epoxidation of *E*-2-butene is reduced from 14.8 to 8.7 kcal/mol.

For the HOAc-catalyzed epoxidation, the bimolecular barrier was calculated with respect to isolated *E*-2-butene and the pre-

reaction complex of DMDO + acetic acid. The competition experiment in eq 1 exemplifies the problems associated with the determination of relative rates in this way, because the presence of acetic acid (a potential catalyst in the DMDO epoxidation) is unavoidable; even if acetic-acid-free peroxyacetic acid were used, epoxidation by AcOOH would release AcOH and be available as a catalyst.

We calculate a ΔE^\ddagger barrier of 12.6 kcal/mol for the gas-phase DMDO epoxidation of cyclohexene (Table 5), which is reduced by 4.1 kcal/mol when a single water molecule is hydrogen-bonded to the distal oxygen of DMDO (a *bimolecular* process relative to a pre-reaction cluster of DMDO·H₂O) and by 6.3 kcal/mol with two complexed water molecules [B3LYP/6-311+G(d,p)]. The calculated barriers for the DMDO epoxidation of *E*-2-butene with and without water catalysis are 11.0 and 14.4 kcal/mol at the same level of theory. Protic-solvent catalysis was reported earlier by Miaskiewicz and Smith,¹⁵ who, on the basis of theoretical work, suggested that the barrier for the DMDO epoxidation of 2-methyl-2-butene may be reduced from 13.6 kcal/mol to just 0.8 kcal/mol^{15b} by the action of just one methanol molecule, H-bonded to the distal oxygen of DMDO (B3LYP/6-31G*). However, this much reduced activation barrier was calculated relative to isolated reactants, a *termolecular* process relative to separated reactants (DMDO, CH₃OH, and 2-methyl-2-butene).¹⁵ The H-bonded DMDO·CH₃OH pre-reaction cluster has a stabilization energy of -6.9 kcal/mol, which actually places this activation barrier at 7.7 kcal/mol, based upon a bimolecular process.

These composite data strongly suggest that the presence of adventitious water or other hydrogen donors affect the observed rate of epoxidation. For example, Murray has reported $\Delta H^\ddagger = 5.0$ kcal/mol for the DMDO epoxidation of cyclohexene in CDCl₃ and 7.4 kcal/mol in acetone as solvent.^{11a} Curci et al. also reported an *E_a* value of 9.3 for the DMDO epoxidation of isobutene in acetone.¹² These barriers are significantly lower than the 13–18 kcal/mol gas-phase barriers that we calculate at the B3LYP level of theory (Tables 1 and 2). We estimate activation barriers of 12.6, 11.3, and 10.7 kcal/mol for the DMDO epoxidation of cyclohexene in the gas phase, CHCl₃, and acetone by using the COSMO solvent model [B3LYP/6-311+G(d,p), Table 5]. However, the current solvent correction models do not explicitly treat hydrogen bonding interactions. Importantly, the calculated activation barriers for peracid cyclohexene epoxidation, 12.0 (PBA, gas phase) and 10.9 (MCPBA, gas phase), are not as sensitive to the solvent as is DMDO. For example, estimated barriers for the PBA/cyclohexene in CH₂Cl₂ and in benzene both had the same calculated ΔE^\ddagger values of 12.2 kcal/mol. These results and the comparison with experimental data are given in Table 6. As is evident, the activation enthalpies for the peracid epoxidation of cyclohexene in CH₂Cl₂ and benzene are in very good agreement with experiment.

Conclusions

The gas-phase reactivities of peroxyformic acid and DMDO have been shown to be comparable on the basis of a series of high-level ab initio calculations. Solvent polarity and hydrogen

(15) (a) Miaskiewicz, K.; Smith, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 1872. (b) The activation barrier with respect to isolated 2-methyl-2-butene and complexed DMDO with methanol is 7.7 kcal/mol at the B3LYP/6-31G(d) level of theory.

bonding effects have a profound effect upon the rate of dioxirane epoxidation but a relatively small impact upon the activation barriers for peracid epoxidation. The increased reactivity noted for DMDO epoxidation in protic solvents may be traced directly to a lowering of the energy of the transition state due to hydrogen bonding to the distal dioxirane oxygen. Under the usual experimental reaction conditions in solution, adventitious water in the acetone solvent may also increase the rate of epoxidation by hydrogen-bonding catalysis about as much as 100-fold. In contrast, in the gas phase, the oxygen-atom-donor propensity of peroxyformic acid toward simple alkenes is, after correction for the computational method, comparable to that of DMDO. These data suggest that in addition to the inductive effects of electronegative substituents, such H-bonding effects could be exploited by the experimentalist to achieve faster rates of dioxirane epoxidation.

When *gem*-dimethyl substitution is present in a dioxirane, as in DMDO, the inherent strain energy is reduced (ca. 11 kcal/mol),^{2b} and this ground-state stabilization energy is reflected in a lower intrinsic reactivity toward alkenes. The overall exothermicity of peracid and DMDO epoxidation differ by only 3.8 kcal/mol, suggesting that relief of ring strain energy in the TS has only a minor influence upon the barrier for alkene epoxidation. Although TFDO is more highly strained and more reactive as an oxygen-atom donor than DMDO ($\Delta SE = 7.7$ kcal/mol), its enthalpy of reaction is actually lower by 1.2 kcal/mol. The increased reactivity of TFDO relative to DMDO ($\Delta\Delta E^\ddagger = 7.5$ kcal/mol) is clearly not due to relief of ring strain but must be attributed largely to the inductive effect of its electronegative CF₃ group.

The lower reactivity of DMDO toward alkenes in the gas phase should not be confused with the facile DMDO oxidation of alkanes. The hydroxylation of saturated alkanes proceeds in a different manner involving a biradicaloid transition state in a concerted oxygen-atom insertion.¹⁶ As reported by Cremer,⁴ the parent dioxirane decomposes at 298 K with an activation enthalpy of 18 kcal/mol to the bis-oxomethylene diradical, whereas the barrier to the comparable ring opening of DMDO is as much as 23 kcal/mol, which accounts for its persistence and its capacity to serve as a useful chemical oxidant.

The rate of epoxidation of alkenes with a highly strained ring, such as cyclopropene, is increased surprisingly little relative to cyclopentene, but the twist strain in alkenes such as *E*-cyclooctene results in a substantial increase in the rate of epoxidation. The *exo* approach of peroxyformic acid to norbornene is favored by 3 kcal/mol over *endo* oxidation, while the *exo* epoxidation of benzonorbornadiene is preferred by some 5 kcal/mol. Conjugated dienes experience a reduced rate of epoxidation relative to isolated double bonds and exhibit very asymmetric transition structures.

Computational Methods

Ab initio molecular orbital calculations¹⁸ were performed with the Gaussian 98 system of programs.¹⁹ The Becke three-parameter hybrid functional,^{20a,21a} combined with the Lee, Yang, and Parr (LYP) correlation functional,^{20b} denoted B3LYP,^{21b} was employed in the

calculations by using density functional theory (DFT). Geometries were optimized²² at the B3LYP and QCISD levels by 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 by using the ACES II program²³ that implements the coupled-cluster and many-body-perturbation-theory methods. The reaction enthalpies and strain energies were calculated by using G2, G3, and in some cases G2(MP2) theories.²⁴ Zero-point energies (ZPE) and thermal corrections to obtain reaction enthalpies at 298 K in the G2, G3, and G2(MP2) series were by convention computed at the HF/6-31G* level. The stationary points on the potential energy surfaces were characterized by calculations of vibrational frequencies at the B3LYP/6-31G* level of theory. Corrections for solvation were made by means of polarizable conductor COSMO model calculations.²⁵

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Supporting Information Available: Table S1–S5 listing total energies of the isolated reactants and TSs for the oxidation of ethylene and the epoxidation of *E*-2-butene with DMDO and peroxyformic acid at the different levels of theory, the total energies of the oxidizing agents and transition structures for the epoxidation of *E*-2-butene at the B3LYP/6-31+G(d,p) level of theory, Cartesian coordinates of the TSs for the oxidation reaction of ethylene and *E*-2-butene with DMDO and peroxyformic acid, and the total energies of the alkenes and transition structures for the epoxidation with peroxyformic acid at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level, figures showing Cartesian coordinates of the TSs, and text giving the Experimental Section. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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