

our calculation (~ 10 kcal/mol) and the experimental value (~ 20 kcal/mol) of Zittel et al. In any case, the results of the calculations presented here cannot be reconciled with a singlet-triplet separation in methylene of 19.5 ± 0.7 kcal/mol deduced by Zittel et al. from their experiments.

VI. Conclusion

The use of the two-configuration singlet reference state is shown to produce results in agreement with those of the one-configuration singlet, if the estimated quadruple excitations corrections are taken into account. A trend is observed which indicates that the 3P carbon atom, the $^2\Pi$ CH radical, and 1A_1 methylene are all related, while 5S carbon, $^4\Sigma^-$ CH, and 3B_1 CH₂ are also related. Accurate calculations for C and CH show C(3P) and CH($^2\Pi$) too high by ~ 2 kcal/mol relative to C(5S) and CH($^4\Sigma^-$), respectively. This indicates that the computed large-basis 1A_1 state of methylene is still too high relative to 3B_1 . Therefore, the correct separation is most likely somewhat smaller than our lowest computed value of 10.6 kcal/mol, and may possibly be as low as 9 kcal/mol.

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The Transition State for the Epoxidation of Ethylene with Peroxyformic Acid. An ab Initio Molecular Orbital Study

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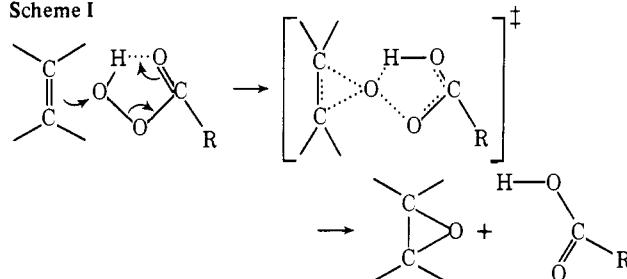
Contribution from the Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Yugoslavia. Received June 23, 1977

Abstract: Ab initio molecular orbital theory (STO-2G and STO-4G) is used to study various plausible transition states (1-5) for epoxidation of ethylene with peroxyformic acid. Unsymmetric transition states, 3 and 4 (1,1-addition mechanism), are found to be energetically more favorable than symmetric ones, i.e., 1 and 2, with the transition state 5 (1,3-dipolar addition) being somewhere in between. Previously reported nonequivalency of both olefinic carbon atoms in epoxidation of substituted styrenes seems to be not just simply a consequence of a choice of an unsymmetric olefin.

Introduction

The reaction of olefins with peroxy acids to produce epoxides (oxiranes) has been known for almost 70 years (Prilezhaev, 1908). Although a large volume of literature on the subject exists,¹⁻⁴ the question of the mechanism of this reaction is still not settled. Several mechanisms, which can accommodate the experimental data, have been proposed. The so-called "butterfly" mechanism, first proposed by Bartlett,⁵ involves nucleophilic attack of the olefin on peroxy acid according to Scheme I. Waters⁶ suggested initial attack of a hydroxyl cation, OH⁺ (not necessarily as a free ion), on the olefin via the transition state depicted in Scheme II. A recent study of the secondary deuterium isotope effect for the epoxidation of *p*-phenylstyrene and three deuterated derivatives revealed a clear

Scheme I



distinction between the α and β carbon atoms of the olefin in the transition state. On the basis of these observations, an unsymmetric transition state, as shown in Scheme III, has been

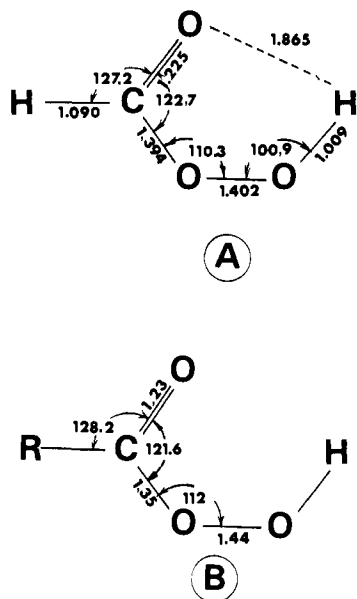


Figure 1. Optimized geometry of peroxyformic acid (A) and experimental geometry parameters of peroxypelargonic acid (B) (taken from ref 12). Bond lengths and angles are in ångströms and degrees, respectively.

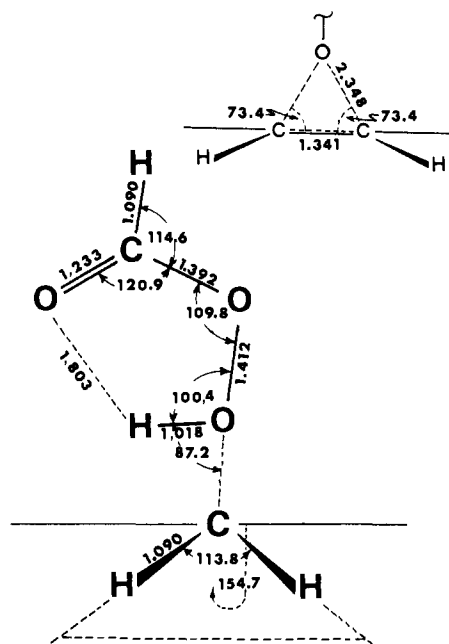
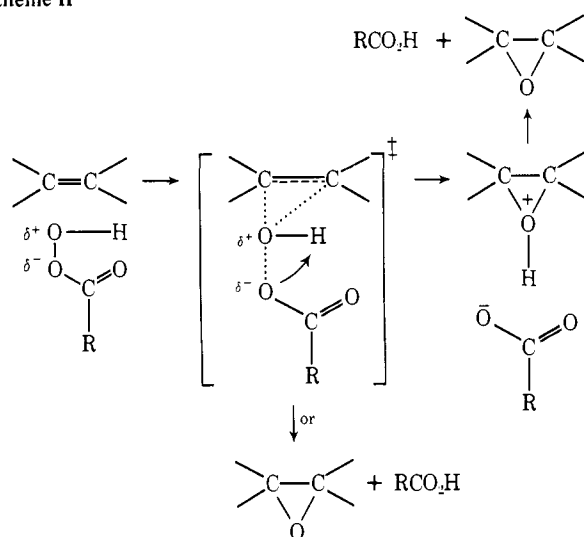
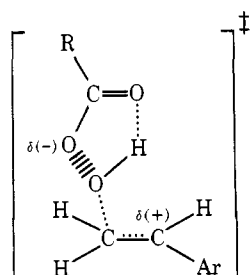


Figure 2. Optimized geometry of the transition state 1. Bond lengths and angles are in ångströms and degrees, respectively.

Scheme II



Scheme III

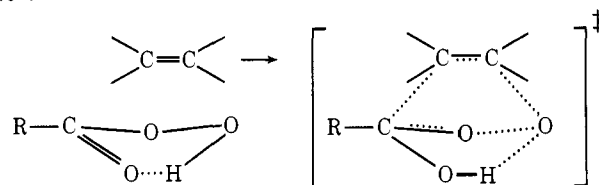


proposed by Hanzlik and Shearer.⁷ Still another mechanistic possibility, proposed by Kwart et al.,⁸ involves 1,3-dipolar addition of a hydroxycarbonyl oxide (derived from the intramolecularly hydrogen bonded peroxy acid) to the olefinic dipolarophile (Scheme IV). Owing to a great variety of plausible interpretations of available experimental results we have undertaken an ab initio molecular orbital study of various transition states in order to get more insight into the mechanism of epoxidation. We have previously already reported the results of a theoretical evaluation of 1,1- and 1,3-addition mechanism

Table I. Equilibrium Energies and Distances (r) between the Peroxy Acid (O of OH) and Olefinic Carbons in the Transition State

Transition state	r , Å	E , au (STO-4G)
1	2.35	-339.459 70
2	2.37	-339.452 79
3	2.86	-339.476 81
4	2.85	-339.476 54
5	2.47	-339.469 80
(3)	(2.00)	(-339.434 40)
(2)	(2.00)	(-339.379 92)
(4)	(2.35)	(-339.464 28)

Scheme IV



by using the Pariser-Parr-Pople (PPP) MO method but no definitive conclusion could be reached at that time.⁹

Method

In the present study, standard ab initio LCAO-SCF molecular orbital theory was used.^{10,11} Owing to the size of the molecules, the minimal STO-2G basis set was employed to calculate molecular geometries. The experience with this basis set (each Slater orbital is expanded into only two Gaussian ones) shows that it gives nearly the same geometry parameters as the STO-3G basis set. Unless otherwise stated, complete structure minimization was undertaken. Molecular energies and charge distribution were then calculated by using the STO-4G basis set. Attempts to use the extended 4-31G basis set were frustrated (for larger structures) by the limited capability of our computer facilities (CDC CYBER 72).

Results and Discussion

Peroxyformic Acid. The optimized geometry of the planar cis conformation of peroxyformic acid is shown in Figure 1. In view of rather great difficulties encountered in ab initio

Table II. The Net Atomic Charges ($\times 10^{-3}e$)^a

Atom	Transition states					HCO ₂ H	C ₂ H ₄
	1	2	3	4	5		
C(1)	-123.26	-102.53	-128.11	-124.14	-152.89		-128.67
C(2)	-123.26	-127.19	-117.01	-123.35	-111.20		-128.67
H(3)	66.09	56.53	63.60	61.56	74.52		64.33
H(4)	59.35	56.53	60.47	61.56	64.38		64.33
H(5)	59.35	61.38	59.34	62.30	63.51		64.33
H(6)	66.09	61.38	61.44	62.30	58.72		64.33
H(7)	236.24	223.35	229.77	229.92	233.23	228.04	
O(8)	-153.78	-156.19	-167.17	-168.82	-151.36	-175.00	
O(9)	-167.18	-159.65	-153.70	-152.98	-151.36	-151.64	
C(10)	246.24	247.55	249.49	249.18	259.44	254.57	
H(11)	98.70	100.04	101.93	102.19	101.05	99.93	
O(12)	-264.57	-261.22	-260.06	-259.55	-262.56	-255.89	

^a The term net atomic charge is defined as $Z - n(\text{STO-4G})$, where Z is the atomic number and n is the net electron density of an atom.

molecular orbital studies on hydrogen peroxide and its derivatives,¹³⁻¹⁹ it is surprising to find such a good agreement of calculated values with the experimental ones at this level of approximation.

Dipole moments of higher aliphatic peroxy acids ($\mu = 2.32$ D;²⁰ calculated dipole moment of peroxyformic acid is 1.433 D (STO-4G)) have previously been interpreted in terms of a nonplanar conformation (H out of the plane COOO). On the other hand, the planar cis conformation of the peroxy-carboxyl group has already been found to possess the lowest energy in a recent ab initio study of peroxyacetic acid.²¹ The planar conformation is also consistent with results of a normal coordinate analysis of force constants which shows excellent agreement with the infrared spectra of peroxyacetic and peroxyformic acid.²² Investigation of dipole moments (graphical method of analyzing the data of vectorial additive scheme)²³ of *para*-substituted peroxybenzoic acids shows that the results can be accommodated with the planar cis conformation of the peroxy-carboxyl group provided that significant contribution of the intramolecular hydrogen bond to the dipole moment is accounted for.²⁴

Ethylene. (C=C) = 1.318 Å; (H-C) = 1.089 Å; $\angle\text{HCH} = 115.4^\circ$.

Formic Acid. (H-C) = 1.090 Å (1.085 Å);²⁵ (C=O) = 1.227 Å (1.245 Å); (C-O) = 1.375 Å (1.313 Å); (O-H) = 0.994 Å (0.95 Å); $\angle\text{H-C-O} = 120.3^\circ$; $\angle\text{O=C-O} = 126.9^\circ$ (125.0°); $\angle\text{C-O-H} = 104.5^\circ$ (107.8°).

Ethylene Oxide. (C-C) = 1.490 Å (1.47 Å);²⁶ (C-O) = 1.430 Å (1.44 Å); (C-H) = 1.090 Å (1.08 Å); $\angle\text{C-C-O} = 58.6^\circ$ (59.1°); $\angle\text{HCH} = 113.2^\circ$; $\angle\text{CH}_{2\text{out}}\text{CC} = 154.1^\circ$ (159.2°).

Transition States. Five extreme, arbitrarily chosen geometries of plausible transition states for epoxidation of ethylene with peroxyformic acid were investigated. All transition states were treated as isolated molecular entities; the reaction pathway (the transformation of the transition state to products) was not investigated. Complete geometry optimization was performed only in the case of **1** (Figure 2). In all other transition states (Figure 3) the same geometry parameters were employed except for the distance, r , which was systematically varied. Orientation of peroxy acid in these cases is shown in the transition state **2** (Figure 3). Equilibrium energies of transition states **1-5** are, together with distances, r , summarized in Table I. The inspection of the optimized geometry of the transition state **1** indicates little reorganization in both participating molecules. The O-H, C=O, and O-O bonds in the peroxy acid become slightly longer while the C-O and O...H bonds shorten. These findings, if real, seem to support the intramolecular transfer of the proton during the reaction. That proton is not transferred in the transition state, but remains (more or less)

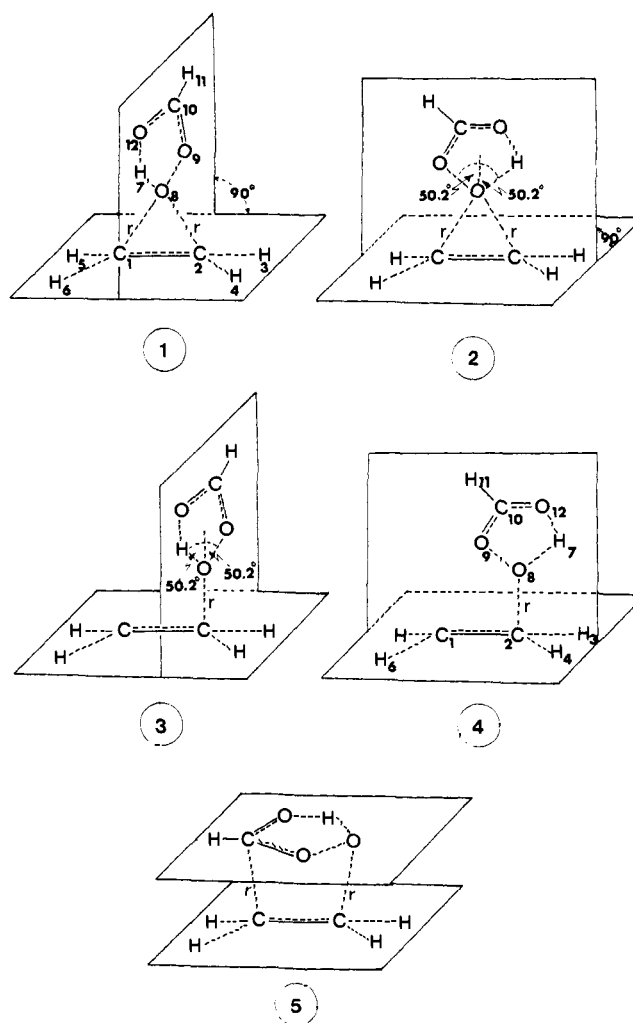


Figure 3. The geometries of transition states **1-5**.

still hydrogen bonded, is also in accord with the reported small primary peroxy acid isotope effect.⁷

The somewhat longer C-C distance in the olefin part of the transition state **1** (compared to free olefin), employed also in the transition states **3** and **4**, seems also to be not too great an approximation. Namely, only one C-O bond is beginning to form in **3** and **4**, so that syn stereospecificity of epoxidation could only be explained by the retention of a considerable amount of π -bond character of the C-C bond in the olefin part of the transition state.

Table III. Comparison of Experimental and Theoretical Energy Difference between Products and Reactants. Activation Energy of the Reaction

Compd	ΔH°_{f300} , kcal/mol exptl ^a	Calcd, au (STO-4G)
Formic acid	-90.5	-187.551 75
Ethylene oxide	-12.6	-152.011 27
Peroxyformic acid	-69.4 ^b	-261.874 09
Ethylene	12.5	-77.627 86
(Products) - (reactants)	-46.2	-0.061 07 (-38.3 kcal/mol)
Transition state (3) - (reactants)		0.025 14 (15.8 kcal/mol)

^a Values taken from S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, N.Y., 1976. ^b The estimated value for peroxyformic acid is -67.4 kcal/mol on the basis of the group values alone. An extra stabilization resulting from an internal hydrogen bonding in this species probably makes this value more negative by about 2 kcal/mol. (The theoretical energies should be compared with experimental values at 0 K corrected for zero-point vibration but in the absence of sufficient data we simply used ΔH°_{f300} .)

The distance between the oxygen atom next to the hydrogen in the peroxy acid and the olefinic carbon varies in the range of 2.35-2.86 Å. It is interesting to mention that Dewar and Thiel reported a comparable value in their study of the reaction of singlet oxygen with ethylene ($r = 2.11$ Å, symmetric transition state) by using MINDO/3.²⁷

The results in Table I show that unsymmetric transition states (3 and 4) are energetically more favorable than symmetric ones (1 and 2). That this phenomenon is not simply the consequence of shorter distance, r , in transition states 1 and 2 (compared to 3 and 4), has been demonstrated by calculating total energies of 3 and 4 with $r = 2$ and 2.35 Å, respectively.

The inspection of charges, summarized in Table II, shows that in all transition states, presumably involved in 1,1-addition mechanism (1-4), electrons are transferred from ethylene to peroxyformic acid. This is consistent with experimental observations of peroxy acids being electrophiles in epoxidation.¹⁻⁴ The largest portion of the negative charge in the peroxy acid part of the transition state is located, as expected, on both oxygen atoms next to carbon.

A comparison of the calculated and experimental energy difference between products (formic acid and ethylene oxide) and reactants (peroxyformic acid and ethylene) shows a rather good agreement (Table III). Experimental and theoretical evidence indicates an exothermic reaction of 38.3 and 46.2 kcal/mol, respectively. The relatively great exothermicity of the reaction under investigation additionally supports the above-mentioned findings, i.e., the transition state resembles the reactants more than the products (Hammond postulate). The activation energy required for the optimum reaction

pathway (3) is approximately 16 kcal/mol, which is in excellent agreement with experimental values (15-18 kcal/mol).¹

Conclusion

Although relatively large assumptions have been made in the present study, we believe that it is reasonable to conclude on the basis of the above-mentioned results that unsymmetric transition states, 3 and 4, are energetically more favorable than symmetric ones, 1 and 2. Previously reported nonequivalency of both olefinic carbon atoms in epoxidation of substituted styrenes seems to be not just simply a consequence of a choice of an unsymmetric olefin. The stability of the transition state 5, presumably involved in 1,3-addition, is somewhere in between.

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