Pergamon

Tetrahedron 58 (2002) 8751–8758

TETRAHEDRON

Is 2-oxabicyclobutane formed during the reaction of peroxyacids with cyclopropene? A high-level ab initio study

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Received 22 April 2002; revised 23 August 2002; accepted 26 August 2002

Abstract—High-level quantum chemical studies have been carried out to explain the unusual course of the reaction of peroxyacids with cyclopropene. The results of calculations at the CASSCF and UQCISD levels of theory suggest that 2-oxabicyclobutane is not formed during this reaction. An unsymmetrical transition state is formed during this reaction and is followed by the formation of a biradical intermediate which finally yields acroleine after the fast proton transfer step. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

An interaction of olefines with peracids is well-known and is a synthetically useful method applied to a variety of reactions in organic chemistry. As a rule, this reaction leads to the formation of epoxides which are widely used as intermediate compounds in the synthesis of physiologically active compounds and polymeric compositions. At the same time, there is a known example where an epoxide is not being detected during the interaction of peracids with olefins. This happens during the interactions of peracids with cyclopropene and its derivatives. There have been a number of attempts to synthesize oxabicyclobutanes using different experimental techniques.[1–3] These studies include a variation of different parameters such as the structure and nature of the substrate (alkyl-, phenyl-, ethylcarbonyl-, hydroxymethylene-substituted cyclopropenes, fused-ring cyclopropenes, and cylopropenones[3]), the nature of peroxyacid (*m*-chloroperbenzoic and peracetic acids), the nature of solvent (dichloromethane, cyclohexane, methanol), and the influence of temperature (ranging from room temperature to 0°C).

Despite the fact that oxabicyclobutanes have been postulated as intermediates in those studies, all attempts to isolate or even detect them spectroscopically have been unsuccessful.[1–3] Obviously, there are only two possible reasons why oxabicyclobutanes have not been detected in reactions of cyclopropene with peracids. Either 2-oxabicyclobutane (OBB) and its derivatives are not stable and should barrierless transform to carbonylic compounds or there is another mechanism of the title reactions which excludes the formation of oxabicyclobutanes as intermediates. Recently,[4] based on the results of ab initio calculations at the CASSCF and UQCI levels of theory, we have shown that unimolecular as well as acid-catalyzed fragmentation of OBB are characterized by high enough activation barriers. The biradical transition state of this transformation lies approximately 19.3–22.4 kcal/mol higher on the potential energy surface (PES) than the epoxide, a possible reactant in this reaction. We conclude that OBB is a thermodynamically stable molecule. In order to take into account both dynamic and nondynamic electron correlation we have additionally reinvestigated the activation barrier for unimolecular fragmentation of OBB at the MCQDPT2(12,12)/6-311+G(d)//CASSCF(10,10)/6-31G(d) level. The high value of barrier (19.3 kcal/mol) obtained at this level strongly supports the conclusions of a previous study.[4] Therefore, a theoretical analysis of the PES for the interaction reaction of peroxyformic acid with cyclopropene is required in order to shed light on the question why OBB and its derivatives have not been detected by experimental methods.

Here we report the results of the first high-level quantum chemical investigation of the PES for the interaction of cyclopropene with performic acid.

2. Computational methods

Based on our previous studies[4,5] we expect the biradical character of title reaction. Therefore, the unrestricted versions of the MP4,[6] QCISD, and QCISD(T)[7] approaches have been used to take into account the dynamic correlation effects of the reaction energetic. Structure-dependent (or

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Keywords: cyclopropene; epoxidation; peroxy acids; diradical transition state; ab initio; multiconfiguration approach.

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PII: S0040-4020(02)01087-6

nondynamical) correlation effects have been included through the calculations at the CASSCF level of theory[8] using the two following sets of orbitals in the active space: (10,10) (10 electrons on 10 orbitals) and (12,12).

The standard 6-31G(d) basis set has been used for all geometry optimizations at the UMP4, UQCISD, and CASSCF approaches. The single point calculations have been additionally performed at the UMP4(SDTQ)/6-31G(d)//UMP4(SDQ), UQCISD(T)/6-31G(d)//UQCISD/6-31G(d), and UQCISD(T)/6-311++G(d,p)//UQCISD/6-31G(d) levels of theory and at the MCQDPT2 (the multireference MP2) level[9] using the 6-31G(d) basis set for the (10,10) and the (12,12) active spaces and the 6-311+G(d) basis set for the (12,12) active space at the CASSCF/6-31G(d) reference geometry. The geometry of the local minima and transition states has been verified by establishing that the matrices of the energy second derivatives (Hessians) at the UMP2/6-31G(d)[10] and CASSCF(10,10)/6-31G(d) levels have zero and one negative eigenvalues, respectively. The total energies calculated at the UMP4, UQCISD, and UQCISD(T) levels have been corrected for the UMP2/6-31G(d) level zero-point energies scaled by a factor of 0.95. CASSCF and MCQDPT2 total energies have been corrected for the CASSCF(10,10)/6-31G(d) zero-point energies scaled by factor of 0.9.

The closed-shell synchronic mechanism (which is proceeded through symmetrical transition state) has been investigated at the RB3LYP/6-31G(d) level of theory.

Intrinsic reaction coordinate calculations (IRC)[11] have been performed at the RB3LYP/6-31G(d) and UMP4(SDQ)/6-31G(d) levels of theory.

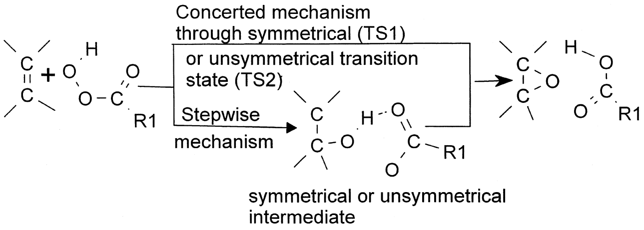
The calculations with the RB3LYP, UMP2, UMP4, UQCISD, and UQCISD(T) approaches were executed using the GAUSSIAN98 program.[12] To perturb $\alpha-\beta$ spatial symmetry of initial orbitals for calculations at the unrestricted level the HOMO and LUMO functions have been mixed. To verify the reliability of UQCI approach for the description of molecular and electronic structure of diradical transition state, the T1-diagnostic proposed by Lee and co-workers[17c] has been carried out. The weighted Euclidian norm of the converged amplitudes of the single excitation operator (T1-diagnostic) is exceed by 0.02 that according to Ref. 17c indicates large nondynamical correlation effects, and therefore a change to multireference approaches.

The CASSCF and MCQDPT2 calculations have been performed by the GAMESS program.[13]

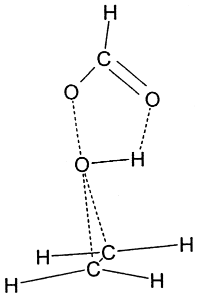
3. Results and discussion

3.1. Background: the mechanism of alkenes epoxidation by peroxy acids

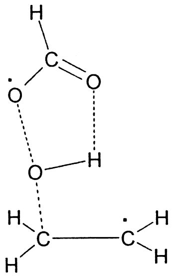
Before the results of this study are discussed, the results of theoretical and experimental investigations of the alkenes epoxidation mechanism by peracids are briefly summarized. Possible pathways of this reaction are presented in Scheme 1. Based on experimental data in 1950, Bartlett proposed a concerted ‘butterfly’ mechanism which involves the symmetrical transfer of an oxygen atom to the alkene and a proton transfer from the peroxy to the carbonyl oxygen atom in one step.[14] This mechanism is supported by results of calculations performed by Bach et al. using spin-restricted versions of the DFT, QCISD, and CCSD(T) approaches.[15] The symmetrical closed shell spiro transition state (**TS1**) has been revealed for this mechanism. This conclusion has been also supported by Singleton et al. by comparison of experimental values of kinetic isotope effects (KIEs) for epoxidation of 1-penthene by *meta*-chloroperbenzoic acid (MCPBA) in chlorobenzene with theoretical data for model reaction (gas phase epoxidation of propene by performic acid). They have shown better correspondence to the experiment of the KIEs calculated at the RB3LYP level for nearly synchronous transition states than ones calculated at RMP2 level which predict highly asymmetrical transition states.[16]



Scheme 1. Schematic representation of possible mechanisms of interaction of alkenes with peracids.



TS1



TS2

Recently[5] we have initiated a reinvestigation of the mechanism of epoxidation using high-level ab initio theory. The interaction of ethylene with performic acid has been the first considered example. Our results[5] indicate that the wave function which corresponds to the transition state of ethylene epoxidation by performic acid has a multiconfigurational character, and the methods based on single determinantal functions may be inadequate for investigations of this reaction. We expect that the quantum-chemical techniques, which include both dynamic and nondynamic electron correlation, are potentially able to describe correctly the diradical state. Thus, the results obtained by applying the CASSCF and MCQDPT2 approximations should be considered as the reference points for a comparison with the data obtained at a relatively lower level of theory.[4,5,17] In particular, we have revealed that starting with the symmetrical transition state **TS1** (preliminarily optimized at the RQCISD/6-31G(d) level),

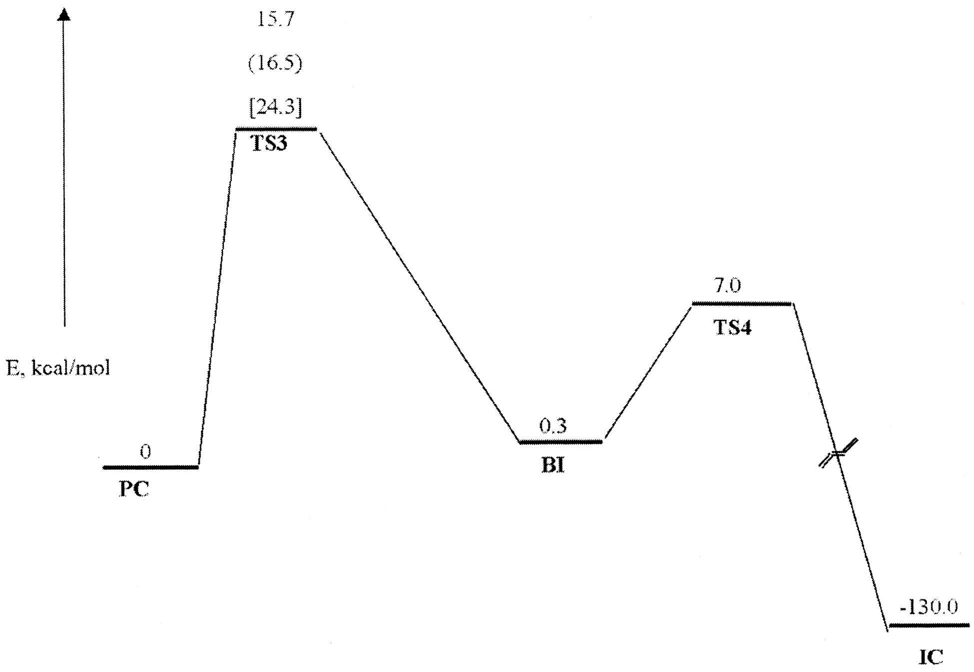


Figure 1. Potential-energy diagram of the interaction reaction of cyclopropene with performic acid calculated at MCQDPT2(12,12)/6-31G(d)//CASSCF(10,10)/6-31G(d), MCQDPT2(12,12)/6-311+G(d)//CASSCF(10,10)/6-31G(d) (in parenthesis) and UQCISD(T)/6-311+G(d)//UQCISD/6-31G(d) (in brackets) levels of theory.

optimizations at the CASSCF(12,12)/6-31G(d) level yield the highly unsymmetrical biradical transition state **TS2**. Values predicted therein of the KIEs and activation barrier (calculated d_4 secondary DKIE is equal to 0.835; the activation barrier is equal to 15.3 kcal/mol)[5] are in excellent agreement with experimental data (0.830±0.012 for DKIE[18] and 15–18 kcal/mol for activation barrier[19]). The same conclusion (unsymmetrical biradical transition state) has been obtained at the unrestricted QCISD level of theory.[5]

The current study is devoted to a comprehensive high-level ab initio theoretical analysis of the PES which represents the interaction between cyclopropene and performic acid.

3.2. The reaction pathway for interactions of cyclopropene with performic acid

3.2.1. Structures. First of all we would like to point out that both the CASSCF(10,10)/6-31G(d) and UQCISD/6-31G(d) levels of theory suggest that the symmetrical transition state which corresponds to the concerted mechanism presented in Scheme 1 is lacking. This is in complete correspondence with the results of our previous study of the interactions between ethylene and performic acid.[5]

To confirm this point, we have performed full geometry optimization at the CASSCF(10,10)/6-31G(d), UQCISD/6-31G(d), and UMP4/6-31G(d) levels of theory starting from a symmetrical transition state, initially located at the RB3LYP/6-31G(d) level. The energetic profile of the title reaction is presented in Fig. 1; the structure and geometrical parameters for all of the stationary points are collected in Fig. 2. We have found that during the optimization, the geometry smoothly transforms to the highly unsymmetrical transition structure **TS3** (Fig. 2) characterized by the C–O bond lengths of 1.882 and 2.666 Å. This transition state has a rather planar structure with a dihedral angle between the OH and C=C bonds of 22°. We have confirmed the nature of this stationary point by finding the single imaginary frequency of 951 cm^{-1} at the CASSCF(10,10)/31G(d) level of theory.

The search of the transition state at the UQCISD/6-31G(d) and UMP4/6-31G(d) levels also reveals unsymmetrical **TS3** which is characterized by very close geometrical parameters and is slightly different from the CASSCF geometry. It has a spiro rather than a planar structure (see the values of the $H_1O_1C_1C_2$ angle in Fig. 2). The UMP4 and UQCISD transition state structures have shorter peroxy O_1–O_2 and C_2–O_1 bonds compared with the corresponding transition state, optimized at the CASSCF level.

The obtained results strongly suggest the stepwise character of the reaction. Thus, we next carried out the geometry optimization of the product of the oxygen-transfer step. First of all we have performed IRC calculations for the oxygen-transfer step at the UMP4(SDQ)/6-31G(d) level starting from **TS3** in the direction of the product of this step. The calculations lead to intermediate **BI**. This result and the aforementioned CASSCF calculations clearly indicate that this step of reaction does not result in the formation of OBB but leads to the intermediate **BI**. Calculated at CASSCF(10,10)/6-31G(d) level, the reaction-coordinate vector corresponding to the single imaginary frequency of **TS3** (see Fig. 3) as well as the direct optimization of geometry starting from **TS3** have shown that the oxygen-transfer step yields the intermediate **BI** which is characterized by the cleavage of the O_1–O_2 bond and the formation of just one C_1–O_2 bond. **BI** in comparison to **TS3** is

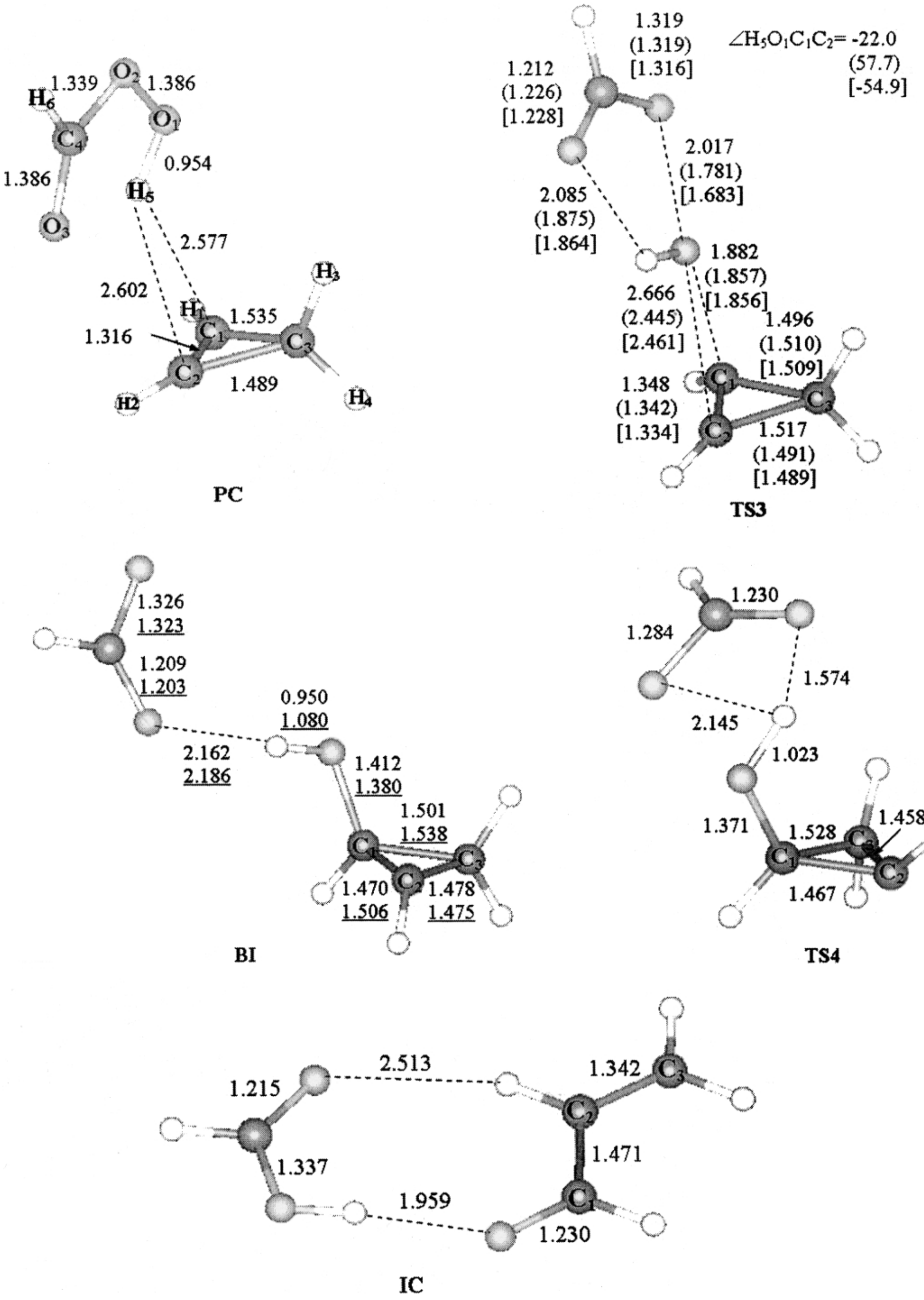


Figure 2. Geometrical parameters of the minima and transition states for interaction of cyclopropene with performic acid optimized at the CASSCF(10,10)/6-31G(d), UQCISD/6-31G(d) (in parenthesis), UMP4(SDQ)/6-31G(d) (in brackets) and CASSCF(10,10)/6-311++G(d,p) (underlined) levels of theory.

characterized by a significant elongation of the C_1-C_2 bond (by 0.122 Å). The elongation of C_1-C_3 bonds (by 0.005 Å) and the shortening of C_2-C_3 bonds (by 0.018 Å) are rather negligible. The geometry of weakly bound **BI** has been also optimized at the CASSCF(10,10)/6-311++G(d,p) level of theory. The obtained results (see Fig. 2) does not demonstrate any significant changes comparing to the 6-31G(d) level results.

The transition state for the proton-transfer step (**TS4**) has been optimized at CASSCF(10,10)/6-31G(d). It is characterized by an imaginary frequency of 1718 cm^{-1}, a value that is typical for proton-transfer reactions. As is shown in Fig. 2, the **TS4** is characterized by a significant shortening of the $H\cdots O_3$ distance, a slight elongation of the O_1-H and C_1-C_3 bonds, and a shortening of the C_1-C_2 and C_2-C_3 bonds (compare to **BI**). As displayed in Fig. 3, the reaction-coordinate vector of **TS4** indicates proton-transfer and cyclopropene-ring opening (cleaving of the C_1-C_3 bond) instead of the epoxide ring closure (formation of the C_2-O bond). Optimization of geometry for **TS4** following this vector leads to the formation of the intermolecular complex IC ‘acroleine–formic acid.’ A comprehensive analysis of the PES of the interaction of cyclopropene with performic

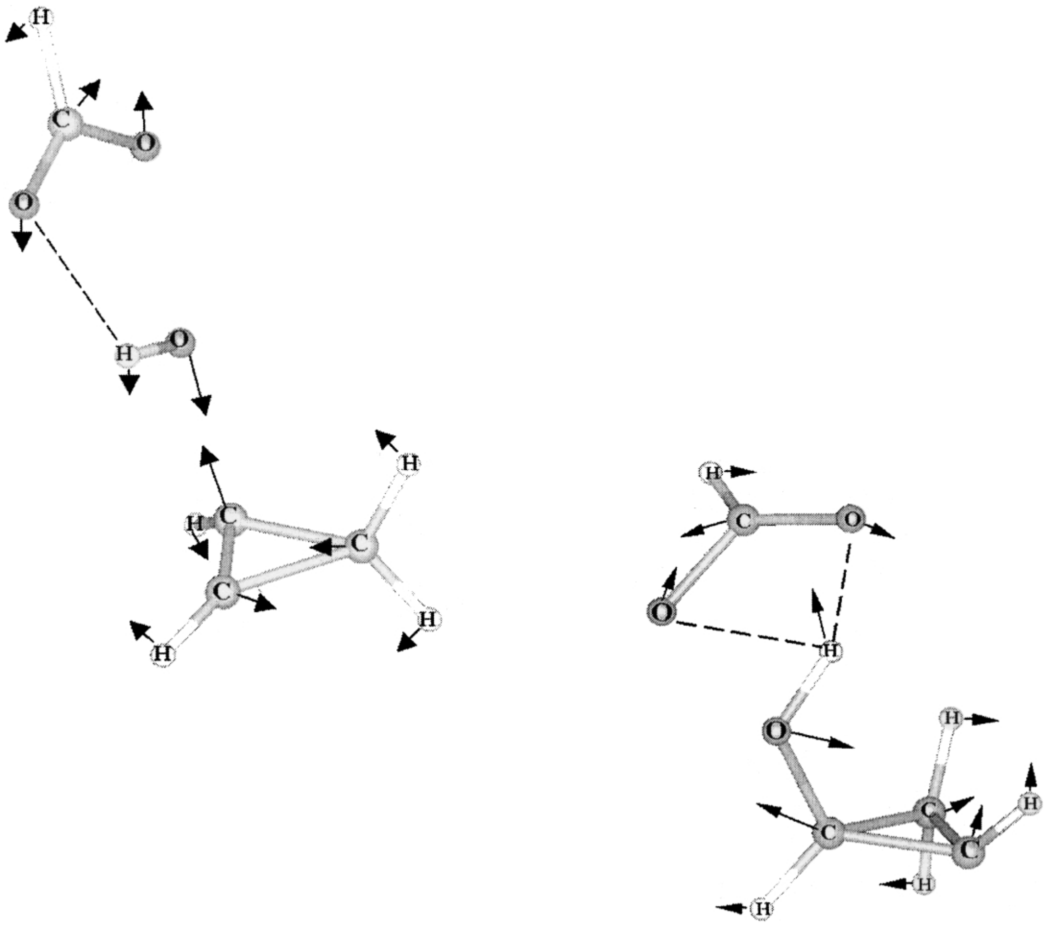


Figure 3. The reaction-coordinate vectors corresponding to the sole imaginary frequencies of **TS3** and **TS4** calculated at the CASSCF(10,10)/6-31G(d) level.

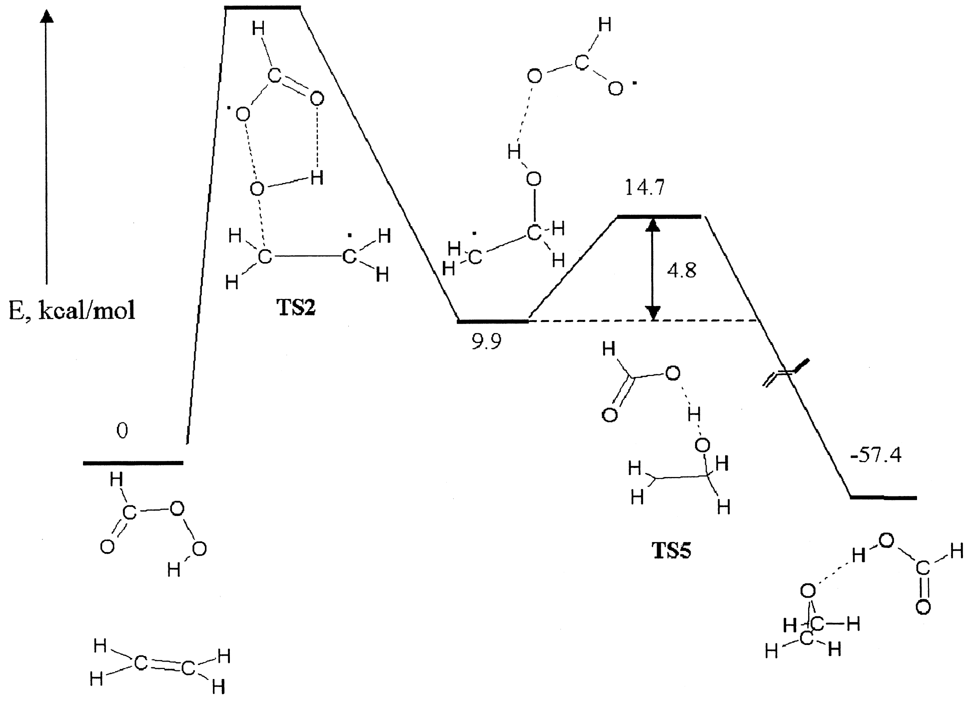


Figure 4. Potential-energy diagram of the interaction reaction of ethylene with performic acid calculated at the MCQDPT2(12,12)/6-31G(d)//CASSCF(10,10)/6-31G(d) level of theory.

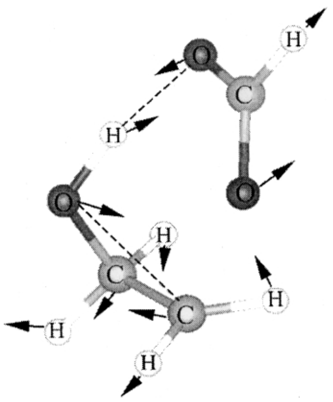


Figure 5. The reaction-coordinate vectors corresponding to the sole imaginary frequencies of **TS5** calculated at the CASSCF(10,10)/6-31G(d) level.

acid clearly shows that OBB is not formed during this reaction. This explains why OBB and its derivatives have not been obtained or even detected spectroscopically.

Because of the unusual behavior of cyclopropene in reactions with peroxyacids, it is necessary to compare the PES of the title reaction with typical epoxidation reactions which result in the formation of epoxides. We have calculated the PES for the interaction of ethylene with performic acid. As can be seen from Fig. 4, the first (oxygen-transfer) step of the reaction is similar to the interaction of cyclopropene with performic acid (see Fig. 1) and results in the formation of a biradical intermediate. At the same time, the proton-transfer steps differ dramatically for these reactions; in the case of the cyclopropene reaction, it leads to the formation of acroleine, while reactions with ethylene result in the formation of epoxide. The last statement has been supported by the reaction-coordinate vector of **TS5** which indicates proton-transfer and epoxidic ring closing (see Fig. 5). Thus, the biradical stepwise mechanism proposed here covers typical epoxidation reactions as well as reactions when epoxide is not formed as a product of interactions between peracids and olefins.

3.2.2. Energetics.

Since the oxygen-transfer step is rate-determining in the title reaction (see Fig. 1), we have applied a number of computational methods to study the barrier of this particularly important step. These calculated values are collected in Table 1. The most important conclusions are as follows.

1. The values of the activation barrier calculated at the level which includes both dynamic and nondynamic correlations (MCQDPT2 level) are in the range of the experimentally measured values.[19]
2. The activation barriers calculated at the MCQDPT2 level are not very sensitive to the size of the active space and basis set.[20]
3. The CASSCF approach remarkably overestimates this value.

Table 1. Activation barriers (in kcal/mol) for the oxygen-transfer step of the interaction reaction of cyclopropene with peroxyformic acid calculated at various computational levels

Computational level	$\Delta E^{\neq}$
CASSCF(10,10)/6-31G(d)	22.0
CASSCF(12,12)/6-31G(d)//CASSCF(10,10)/6-31G(d)	32.9
CASSCF(12,12)/6-311+G(d)//CASSCF(10,10)/6-31G(d)	29.2
MCQDPT2(10,10)/6-31G(d)	16.1
MCQDPT2(12,12)/6-31G(d)//CASSCF(10,10)/6-31G(d)	15.7
MCQDPT2(12,12)/6-311+G(d)//CASSCF(10,10)/6-31G(d)	16.7
UQCISD/6-31G(d)	29.54
UQCISD/6-311+G(d)/UQCISD/6-31G(d)	28.52
UQCISD(T)/6-31G(d)//UQCISD/6-31G(d)	26.67
UQCISD(T)/6-311+G(d)/UQCISD/6-31G(d)	25.31
UMP4(SDQ)/6-31G(d)	41.71
UMP4(SDTQ)/6-31G(d)//UMP4(SDQ)/6-31G(d)	42.21

Barrier heights are relative to the prereaction complex (**PC**).

In spite of similar geometrical parameters of **TS3** optimized at the UMP4 and UQCISD levels, the values of the activation barriers calculated at these levels differ dramatically (41.7 kcal/mol at the UMP4(SDQ)/6-31G(d) and 29.6 kcal/mol at the UQCISD/6-31G(d) levels). Such problems with the UMP*n* calculations have been reported earlier by Bally et al. in review[17b] where it was shown that for species with high spin contamination these methods significantly overestimate their energies. Inclusion of triplet excitations at the UMP4 level even increases the activation barrier. Taking into account the triplet excitations at the UQCI level leads to a decrease in the activation barrier by 2.9 kcal/mol with the 6-31G(d) basis set (see Table 1). The basis set extension (to the 6-311+G(d)) results in a modest decrease of the barrier (to 25.3 kcal/mol) at the UQCISD(T)/6-311+G(d)//UQCISD/6-31G(d) level. However, even the UQSISD(T) level of theory augmented by an extended basis set remarkably overestimates the value of the activation barrier compared to the MCQDPT2 values. Such a situation is not surprising due to large value of T1-diagnostic for **TS3** (0.0456) which clearly demonstrates the multireference character of this structure.

The energy of the intermediate **BI** is calculated to be 0.3 kcal/mol higher than that of the prereaction complex **PC**. The value of the activation barrier for the proton-transfer step calculated at the MCQDPT2(12,12)/6-31G(d)//CASSCF(10,10)/6-31G(d) level of theory (6.7 kcal/mol) indicates rapid transformation of **BI** to the product of the reaction. The reaction energy, i.e., the difference between the **PC** and **IC** amounts to −130.0 kcal/mol. However, this reaction is much more exothermic in comparison to typical epoxidation reactions (experimental value for ethylene amounts to −46.2 kcal/mol[21]).

3.2.3. Wave function's character of local minima and transition states.

An inspection of the configuration state functions (CSFs) and natural orbitals occupancies (Table 2) reveals that the wave functions of prereaction complex **PC** and intermolecular complex **IC** possess a single configuration closed-shell character. In contrast, both the transition states (**TS3** and **TS4**) and intermediate **BI** have an open-shell character. According to our calculations, the (10,10) active space is sufficient to describe this reaction since occupancies of the additional σ_{C1C2C3} and σ^{*}_{C1C2C3} orbitals added to form the (12,12) active space remain close to 2 and 0, respectively, for all of the stationary structures. The **TS3** is characterized by noticeable electron transfer from OMO5 and HOMO to LUMO (population of these orbitals are 1.90,

Table 2. Occupation numbers of the MCSCF natural orbitals of all stationary structures in the interaction reaction of cyclopropene with performic acid

	OMO6	OMO5	OMO4	OMO3	OMO2	HOMO	LUMO	UMO2	UMO3	UMO4	UMO5	UMO6
PC	1.9789	1.9723	1.955	1.9802	1.9823	1.9298	0.0701	0.0200	0.0452	0.0188	0.0267	0.0207
TS3	1.9779	1.9039	1.9665	1.9795	1.9496	1.537	0.4665	0.0944	0.0329	0.0503	0.0205	0.0211
BI	1.9781	1.9828	1.9758	1.9797	1.9476	1.0054	0.9951	0.0243	0.0203	0.0523	0.0222	0.0165
TS4	1.978	1.9667	1.9769	1.9761	1.9649	1.4312	0.5828	0.0348	0.0234	0.0229	0.0180	0.0243
IC	1.9808	1.9492	1.9504	1.9796	1.9775	1.9038	0.1009	0.0495	0.0465	0.0228	0.0205	0.0185

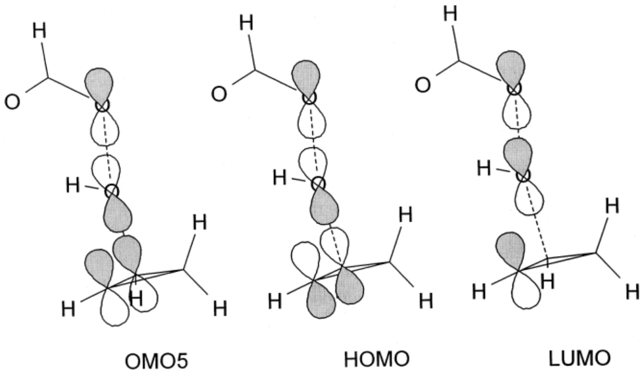


Figure 6. Schematic representation of frontier natural orbitals of **TS3**.

1.54, and 0.47, correspondingly). The OMO5 and HOMO orbitals are a linear combination of the $\pi_{C1=C2}$ orbital of cyclopropene and the σ_{O1-O2} orbital of performic acid, while LUMO is a combination of the $p_y(C_2)$ orbital and the σ^*_{O-O} orbital of performic acid (see Fig. 6 for schematic representation of natural orbitals included in the active space). It should be mentioned that in the case of bonding combination of the $\pi_{C1=C2}$ and σ_{O1-O2} orbitals (OMO5), the predominate contribution is from the $p_y(C_1)$ orbital, while in the case of antibonding combination (HOMO and LUMO) the $p_y(C_2)$ orbital predominates. Such composition of molecular orbitals corresponds to the formation of only one C_1-O_1 bond and agrees with mechanism described above of the investigated reaction. In addition, we would like to mention that the values of spin densities at both UMP4 and UQCISD levels (see Table 3) also characterize **TS3** as a diradical species.

Table 3. Total atomic spin densities for **TS3**

Atom	UMP4/6-31G(d)	UQCISD/6-31G(d)
O_1	−0.4848	−0.5416
O_2	0.7625	0.8572
O_3	−0.0259	−0.0268
C_1	0.6237	0.6162
C_2	−0.9324	−0.9710
C_3	0.0596	0.0670
C_4	−0.0484	−0.0562
H_1	−0.0451	−0.0431
H_2	0.0637	0.0669
H_3	−0.0171	−0.0195
H_4	−0.0176	−0.0192
H_5	0.0215	0.0261
H_6	0.0403	0.0439

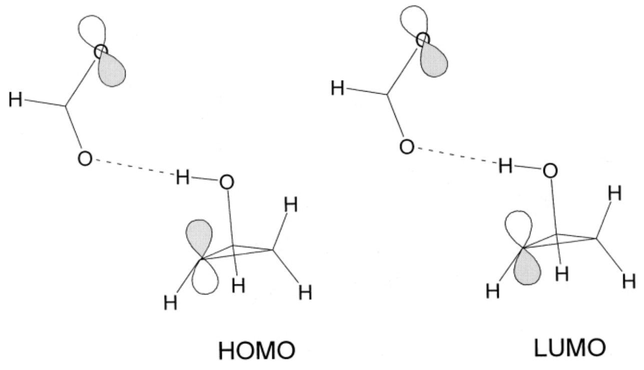


Figure 7. Schematic representation of frontier natural orbitals of **BI**.

Let us now analyze the **BI** intermediate and the **TS4** transition state. The **BI** can be characterized as pure diradical molecule with half-filled HOMO and LUMO. This corresponds to localization of spin density on the C_2 and O_2 atoms (see Table 2 and Fig. 7). As shown in Table 2, the **TS4** has significant depopulation of HOMO and population of LUMO. It indicates that **TS4** also has biradical character.

4. Conclusions

In this study, we have investigated the PES which corresponds to the biradical mechanism of the interaction of cyclopropene with performic acid. The PES of the title reaction calculated by high-level ab initio methods (CASSCF, UQCISD, and UMP4) reveals the following features.

1. The oxygen-transfer (rate-determining) step for the reaction of cyclopropene with performic acid proceeds through a highly unsymmetrical transition state (**TS3**) which possesses biradical character. This step yields the biradical intermediate (**BI**) which is characterized by the cleavage of the O_1-O_2 bond and the formation of just one C_1-O_2 bond.
2. The formation of an intermediate is followed by the second transition state (**TS4**) for the proton transfer and cyclopropene ring opening. This step has a small activation barrier and leads to the formation of the intermolecular complex acroleine–formic acid without the formation of OBB as an intermediate. Thus, a possible reason why oxabicyclobutanes were not isolated or even detected spectroscopically during the reactions of peroxyacids with cyclopropenes is that they were not formed during those reactions.
3. Based on the present results and the results of investigations of model epoxidation reactions of ethylene by performic acid,[5] we conclude that the stepwise mechanism which proceeds trough unsymmetrical biradical transition state on the oxygen-transfer stage is a common mechanism for the reactions of alkenes oxidation with peracids.

Acknowledgements

This work was facilitated by the NSF EPSCoR grant No 94-4-756-01 and NSF CREST Grants No. 9805465 & 9706268 and by the support of the Army High Performance Computing Research Center under the auspices of the Department of the Army, Army Research Laboratory cooperative agreement number DAAH04-95-2-0003/ contract number DAAH04-95-C-0008, the content of which does not necessarily reflect the position or policy of the government, and no official endorsement should be inferred.

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