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# *Ab initio* Molecular orbital and density functional studies on the ring-opening reaction of oxetene

**S. Jayaprakash · Jebakumar Jeevanandam · K. Subramani**

**Abstract** Electrocyclic ring opening (ERO) reaction of 2H-Oxete (oxetene) has been carried out computationally in the gas phase and ring opening barrier has been computed. When comparing the ERO reaction of oxetene with the parent hydrocarbon (cyclobutene), the ring opening of cyclobutene is found to exhibit pericyclic behavior while oxetene shows mild pseudopericyclic nature. Computation of the nucleus-independent chemical shift (NICS) of oxetene adds evidence for pseudopericyclic behavior of oxetene. By locking of lone pair of electrons by hydrogen bonding, it is seen that the pseudopericyclic nature of the ring opening of oxetene is converted into a pericyclic one. CASSCF(5,6)/6-311+G** computation was carried out to understand the extent of involvement of lone pair of electrons during the course of the reaction. CR-CCSD(T)/6-311+G** computation was performed to assess the energies of the reactant, transition state and the product more accurately.

**Keywords** CASSCF · CR-CCSD (T) · ERO · NICS · Pseudopericyclic

## Introduction

There are many reactions in organic chemistry that gives no evidence for involving intermediates. Absence of evidence of intermediates leads to the conclusion that the reactions are single-step processes in which bond making and bond breaking both contributes to the structure at the transition state. Such processes are called concerted reactions. An important group of concerted reactions are the concerted pericyclic reaction [1]. Pericyclic reactions must occur through cyclic transition states. The key to understanding the mechanism of the concerted pericyclic reactions was recognized by Woodward and Hoffmann [2] that the pathways of such reactions were determined by the symmetry properties of the orbital that were directly involved. There are three types of pericyclic reactions cycloaddition, sigmatropic migration reactions and electrocyclic reactions. In some pericyclic reaction non-bonding electrons also take part in the cyclic transition state, such a reaction called as pseudopericyclic reactions. Such reactions have attracted attention in recent years though they were first identified by Lemal et al. in 1976 [3]. After that there was a long gap until Birney and coworkers [4–9] later studied them in detail. These reactions are concerted transformations where primary changes in bonding encompass a cyclic array of atoms at one (or more) of which nonbonding and bonding atomic orbital interchange roles. Pseudopericyclic reactions fell into oblivion until Birney first and several other authors [10–19] later revived interest in them by showing that a number of organic syntheses involve this type of process. However, until now, no universally accepted clear-cut, absolute criterion exists for distinguishing a pseudopericyclic reaction from a normal pericyclic reaction. This has raised some controversy in classifying some reactions [20–24]. Evaluation of magnetic properties can be very useful to assess aromatization along the reaction. This fact can be interesting to study the pericyclic character of a reaction since the cyclic loop of a pericyclic reaction yields an aromatic transition state [25], as quantitatively confirmed for various reactions [26–29]. Herges et al. showed that, in the vicinity of the transition state (TS) in the Diels–Alder reaction, the magnetic susceptibility $\chi$ and its anisotropy $\chi_{anis}$ exhibit well defined minima with respect to the reactant and product

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[26]. On the other hand, the typical disconnection of pseudopericyclic reactions would have prevented this enhanced aromatization. Pseudopericyclic reactions typically have nearly-planar transition states, low activation energies, disconnections in orbital overlap and are symmetry allowed. The most widely employed method to analyze the aromaticity is the NICS index [30–36]. This magnetic-based descriptor of aromaticity was introduced by Schleyer and co-workers [37]. It is defined as the negative value of the absolute shielding computed at a ring center or at some other point, usually at 1 Å above and below the ring center. Rings with large negative NICS [37] values are considered aromatic, non-aromatic species have NICS values close to zero and positive NICS values indicates antiaromaticity. We have studied the thermolysis of oxetene and on comparison with cyclobutene, it is evident that the presence of oxygen atom substantially alters the potential energy surface for ERO. This has motivated us to look at the ERO reaction of oxetene with a view to bring out the role of oxygen in altering their pericyclic/pseudopericyclic behaviors. Locking of lone pair electron (LLPE) is used to investigate pseudopericyclic nature in addition to NICS.

Computational method

Electrocyclic ring-opening reaction of oxetene was studied using *ab initio* molecular orbital and density functional theory at different level of calculations. The levels used are B3LYP/6-311+G**, CASSCF [38, 39], and CR-CCSD(T) [40–42]. The geometries of the reactants, transition states, and the products were examined by complete structural optimization using the software PC GAMESS/Firefly QC package [43], which is partially based on the GAMESS (US) [44] source code. Transition state of this reaction was located and intrinsic reaction coordinates (IRC) calculations were performed to confirm that the transition state (TS) connects that particular reactant and product. All the frequencies of reactants and products have real values while the transition states have one imaginary frequency. NICS values were also computed with the B3LYP/6-311+G** basis using the gauge including

atomic orbital method [45, 46] (GIAO) implemented in the GAUSSIAN-03 [47] package. The magnetic shielding tensor was calculated for ghost atoms located at the ring critical points (RCP), the point of lowest density in the ring plane [48], as suggested by Cossío et al. [49]. These values are denoted as NICS (0), according to the practice described by Schleyer et al. [50] who calculated the NICS at the geometrical center (GC) of the ring. When highly symmetric molecules are studied, both points RCP and GC, usually coincide. Similarly, NICS values at 1.0 Å above the perpendicular plane of the ring, NICS (1) [51] as well as the NICS (1) zz tensor component have been calculated or at some other interesting point of the system. This quantity gives probably the best measure of aromaticity among the different NICS related definitions. These values of NICS were calculated with the aim to measure the aromaticity due to π-system, sometimes obscured by the σ-current. The graphical outputs were visualized by using MacMolplt [52] software.

## Results and discussion

Energies of the reactant, transition state, and the product for the ERO reaction of oxetene were calculated and are given in Table 1. Energy values are in hartrees and the relative energies given in kcal mol$^{-1}$.

The transition sate for the ring-opening of oxetene has one imaginary frequency and has a value of 1027.8 $i$ cm$^{-1}$ at the CR-CCSD(T)/6-311+G** level of calculation. All other frequencies were found to be positive. This shows the obtained transition state is a first order saddle point. The structure of reactant, transition state, and product in the ring opening of oxetene is shown in Fig. 1. The extents to which the bonds have been broken or formed at the transition state have been calculated from the bond order values.

The percentage of bond formation (BF$_{i/j}$) or percentage of bond cleavage (BC$_{i/j}$) at the transition state, defined by Manoharan and Venuvanalingam [53, 54] is as follows:

**Table 1** Energies in (hartrees) and relative energy in (kcal mol$^{-1}$) given in parentheses for the electrocyclic ring opening of oxetene

| Levels of calculation | Oxetene | | | Cyclobutene | | |
|---|---|---|---|---|---|---|
| | Reactant (Oxetene) | Transition sate | Product (Prop-2-en-1-al) | Reactant (Cyclobutene) | Transition sate | Product (Buta-1,2-diene) |
| B3LYP/6-311+G** | −191.926 (29.3) | −191.887 (54.1) | −191.973 (0.0) | −156.019 (11.3) | −155.966 (44.6) | −156.037 (0.0) |
| CASSCF(5,6)/6-311+G** | −190.817 (36.8) | −190.772 (64.8) | −190.875 (0.0) | −154.983 (17.6) | −154.927 (52.7) | −155.011 (0.0) |
| CR-CCSD(T)/6-311+G** | −191.431 (27.8) | −191.386 (56.7) | −191.476 (0.0) | −155.574 (8.2) | −155.517 (43.9) | −155.587 (0.0) |

**Fig. 1** Structure of the reactant, transition state and product for the ring opening reaction of oxetene



Oxetene → Transistion state → Prop-2-en-1-al
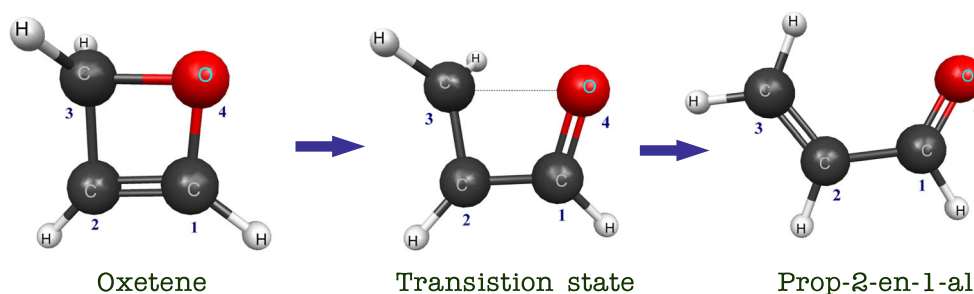
$$BF_{i/j} \text{ or } BC_{i/j} = \frac{\left(BO_{i/j}^{TS} - BO_{i/j}^{R}\right)}{\left(BO_{i/j}^{P} - BO_{i/j}^{R}\right)} * 100\% \quad (1)$$

where $BO_{i/j}^{TS}$ is the bond order between atoms i and j at the transition state, while $BO_{i/j}^{R}$ and $BO_{i/j}^{P}$ represent the bond order at the reactant and the product respectively. From this calculation it shows that the atoms $C_1$, $C_2$, $C_3$, and $O_4$ involved in the electrocyclic ring opening reaction.

Pseudopericyclic reaction

According to Birney et al. [4–9], pseudopericyclic reactions have planar or nearly planar transition states and usually exhibit small reaction barrier. Energy barrier profile for ERO of oxetene and cyclobutene calculated at various level of calculation is presented in Table 1. Experimental value for ERO of cyclobutene is 32.9 kcal mol$^{-1}$, while the computed ring opening barrier is found to be 30.6-32.7 kcal mol$^{-1}$ (including ZPE). Experimental activation enthalpy for the ring opening of oxetene has been reported by Martino and Shevlin [55] to be 24.1±1.5 kcal mol$^{-1}$, measured between 35 °C to 86.2 °C. Earlier computational ring opening for oxetene has been reported to have a barrier of 23.06 kcal mol$^{-1}$ calculated by the 4-31G method [56]. When comparing the theoretical and experimental values of cyclobutene with oxetene, the smaller energy barrier 24·8 - 29.0 kcal mol$^{-1}$ (including ZPE) of the ERO of oxetene indicates that it is pseudopericyclic nature. At the TS and dihedral angle of oxetene it is much less compared to that of cyclobutene. More planar geometry of oxetene is also an indication of pseudopericyclic character.

To understand the nature of the transition state better multi-configuration self-consistent field (MCSCF) computations were performed. The particular calculation was carried out at the complete active space self-consistent field (CASSCF). A CASSCF (5, 6) calculation was carried out using the basis functions 6-311+G**. Here the number '5' refers to the number of active orbitals and '6' refer to the number of electrons.

The other electrons are treated as core or inactive electrons. The five active orbitals in the reactant are the C-C π, π* orbitals, C-O σ, σ* orbitals, and the lone pair of electrons on the oxygen atom. The five active orbitals in the product are the two π orbitals, two π* orbitals and the lone pair. It is seen that the HOMO is the lone pair of electrons on the oxygen atom. From an analysis of the occupation of electrons in the transition state it is found that the electron occupation of the lone pair varies very little during the course of the reaction. Even at the transition state the lone pair is occupied to an extent of 1.966. This shows that the contribution of lone pair electrons during the ring opening is very minimal and the extent of pseudopericyclic nature is low. To compute the energies more accurately, structures of the reactant, transition state, and product were evaluated by complete optimization at the CR-CCSD(T)/6-311+G** level. Since analytical gradients were not available, numerical methods were employed to carry out the computation.

Nucleus-independent chemical shift (NICS)

For ERO, the choice of the points to calculate NICS is not so obvious. The points may be chosen at the center of the forming ring and/or 1 Å above or below this point to avoid spurious effects associated to σ bonds [57]. For that reason we decided to calculate NICS not only in a particular point but in a set of points defined by a line, which passes through the geometrical center of the four-membered ring. This calculation was done for the transition state (TS) and for the reactant to observe the differences between them. The results are presented in Fig. 2. The comparisons of the NICS values were made at a reference point of −0.6 Å below the plane of the molecule. In the case of reactant, the oxetene has a value of −1.7 ppm (mildly aromatic), while the corresponding value for the ring opening transition state is +2.2 ppm (mildly antiaromatic). When hydrogen bonding is used to lock the lone pair of electrons, the corresponding values for the NICS were found to be +1.7 and −0.6 ppm respectively. This shows that there is no aromatic enhancement on the ring opening of oxetene confirming pseudopericyclic nature. However, on hydrogen bonding, the lone pair of electrons is locked and the NICS value becomes aromatic on ring opening. Thus the reaction becomes pericyclic when the lone pair is locked.
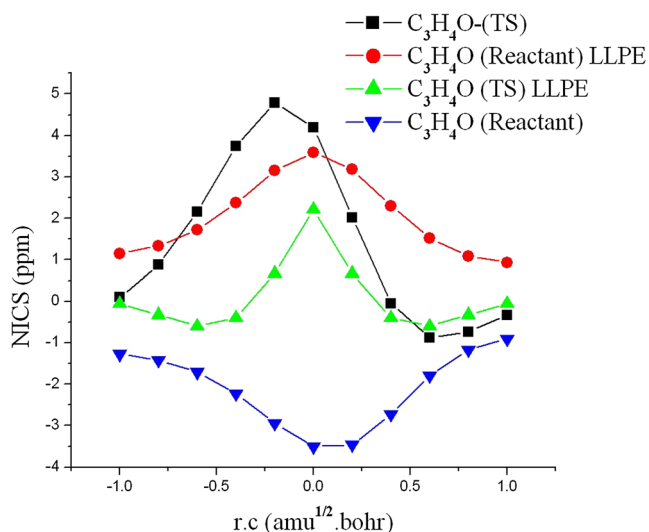
**Fig. 2** Variation of NICS along the reaction coordinates

Percentage of reaction

The ring opening of oxetene can possibly take place by two modes. The first possibility is the shifting of the double bond at $C_1-C_2$ to form a double bond at $C_1-O_4$. Synchronously the bond-pair of electrons from $C_3-O_4$ migrates to $C_2-C_3$ to form a double bond there. In this mode the lone-pair of electrons on the oxygen atom cannot get involved. In the second mode double bond at $C_1-C_2$ is shifted to $C_2-C_3$ to form a double bond there. Simultaneously the bond-pair of electrons from $C_3-O_4$ is shifted to $C_1-O_4$ to form a double bond there. The lone-pair of electrons on the oxygen atom $O_4$ competes with the above process in getting shifted to the bond at $C_1-O_4$ to form a double bond. The competition of electron pair shifting from either the bond-pair of electrons at $C_3-O_4$ or the lone-pair of electrons on the oxygen atom $O_4$ to the bond at $C_1-O_4$ to form a double bond is the cause of the pseudopericyclic nature of the transformation. When the lone-pair of electrons on the oxygen atom $O_4$ is locked by hydrogen bonding to a molecule of water. The percentage of reaction gets altered, indicating the involvement of the lone-pair of electrons and also the direction of the flow of electrons. In the absence of hydrogen bonding by water molecule, the percentage of reaction at $C_1-O_4$ is found to be 47.5. When hydrogen bonded by a molecule of water, the percentage of reaction is reduced to 44.1 as presented in Table 2. This indicates that the reaction is

pseudopericyclic. When LLPE on the oxygen atom, it reduces the percentage of reaction by almost 3.4. When the lone-pair electron on $O_4$ is locked by hydrogen bonding by water, the lone-pair is not available for shifting to $C_1-O_4$, hence the percentage of reaction at $C_1-O_4$ by bond order calculations drops from 47.5 to 44.1. LLPE conforms that the pseudopericyclic nature of ERO reaction of oxetene is due to the lone pairs of electrons present in the oxygen atom.

## Conclusions

Electrocyclic ring opening of oxetene was studied using ab initio molecular orbital and density functional theory. Transition state for this reaction was located and the energy barrier of this reaction was calculated at different levels of theory. When comparing the ring opening of oxetene with cyclobutene, the ring opening of oxetene was found to be mildly pseudopericyclic in nature, which was also found to have a more planar transition state and a lower energy barrier. To investigate the behavior of aromaticity in ring opening of oxetene, we have computed the NICS profiles which shows no enhanced aromaticity in transition state compared with reactant. This has been confirmed by the method of locking the lone-pair of electrons on the oxygen atom. The mild pseudopericyclic character in ring opening of oxetene is due to lone pair participating in the orbital overlap, though the extent of participation of the lone-pair of electrons on the oxygen atom was found to be small from CASSCF(5,6)/6-311+G** calculation. CR-CCSD(T)/6-311+G** computation was performed to assess the energies of the reactant, transition state, and the product more accurately.

**Table 2** Percentage reaction of $C_3H_4O$ with and without LLPE by $H_2O$ computed at B3LYP/6-311+G**

| Bond order between | Percentage of reaction with $H_2O$ | Percentage of reaction without $H_2O$ |
|---|---|---|
| $C_1-C_2$ | 31.4 | 33.0 |
| $C_2-C_3$ | 10.8 | 22.4 |
| $C_1-O_4$ | 44.1 | 47.5 |
| $C_3-O_4$ | 37.1 | 41.8 |

## References

1. Carey FA, Sundberg RJ (2000) Part A: structure and mechanisms. Springer, New York
2. Woodward RB, Hoffmann R (1971) The conservation of orbital symmetry. Academic, Weinheim
3. Lemal D (1976) J Am Chem Soc 98:4325
4. Birney DM, Wagenseller PE (1994) J Am Chem Soc 116:6262
5. Birney DM, Ham S, Unruh GR J Am Chem Soc 119: 4509
6. Birney DM, Xu X, Ham S (1999) Angew Chem Int Ed 38:189
7. Birney DM (2000) J Am Chem Soc 122:10917
8. Shumway WW, Dalley NK, Birney DM (2001) J Org Chem 66:5832
9. Zhou C, Birney DM (2002) J Am Chem Soc 124:5237
10. Luo L, Bartberger MD, Dolbier WRJ (1997) J Am Chem Soc 119: 12366
11. Fabian WMF, Bakulev VA, Kappe CO (1998) J Org Chem 63:5801
12. Fabian WMF, Kappe CO, Bakulev VA (2000) J Org Chem 65:47
13. Alajarin M, Vidal A, Sanchez-Andrada P, Tovar F, Ochoa G (2000) Org Lett 2:965
14. Rauhut G (2001) J Org Chem 66:5444

15. Chamorro E (2003) J Chem Phys 118:8687
16. Finnerty JJ, Wentrup C (2004) J Org Chem 69:1909
17. Zora M (2004) J Org Chem 69:1940
18. Kalcher J, Fabian WMF (2003) Theor Chem Acc 109:195
19. Chamorro E, Notario R (2004) J Phys Chem A 108:4099
20. de Lera AR, Alvarez R, Lecea B, Torrado A, Cossio FP (2001) Angew Chem Int Ed 40:557
21. Rodrıguez-Otero J, Cabaleiro-Lago EM (2002) Angew Chem Int Ed 41:1147
22. de Lera AR, Cossio FP (2002) Angew Chem Int Ed 41:1150
23. Rodrıguez-Otero J, Cabaleiro-Lago EM (2003) Chem Eur J 9:1837
24. Matito E, Poater J, Duran M, Sola M (2006) Chem Phys Chem 7:111
25. Zimmermann HE (1971) Acc Chem Res 4:272
26. Herges R, Jiao H, Schleyer PR (1994) Angew Chem Int Ed Engl 33:1376
27. Schleyer PR (1998) J Phys Org Chem 11:655
28. Manoharan M, De Proft F, Geerlings P (2000) J Org Chem 65:7971
29. Manoharan M, De Proft F, Geerlings P (2000) J Chem Soc Perkin Trans 2:1767
30. Tsipis AC, Kefalidis CE, Tsipis CA (2008) J Am Chem Soc 130:9144
31. Tsipis AC, Tsipis CA (2003) J Am Chem Soc 125:1136
32. Tsipis CA, Karagiannis EE, Kladou PF, Tsipis AC (2004) J Am Chem Soc 126:12916
33. Wannere CS, Corminboeuf C, Wang ZX, Wodrich MD, King RB, Schleyer PR (2005) J Am Chem Soc 127:5701
34. Corminboeuf C, Wannere CS, Roy D, King RB, Schleyer PR (2006) Inorg Chem 45:214–219
35. Zhang GH, Zhao YF, Wu JI, Schleyer PR (2009) Inorg Chem 48:6773–6780
36. Chen Z, Corminboeuf C, Heine T, Bohmann J, Schleyer PR (2003) J Am Chem Soc 125:13930
37. Schleyer PR, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes NJR (1996) J Am Chem Soc 118:6317–6318
38. Wahl A.C and Das.G (1977) The multiconfiguration SCF method. In Schaefer HF (1970) III edn. Methods of electronic structure theory. Plenum Press, New York. Chapt 3
39. Roos BO (1987) Adv Chem Phys 69:399
40. Piecuch P, Kucharski SA, Kowalski K, Musial M (2002) Comput Phys Commun 149:71–96
41. Kowalski K, Piecuch P (2000) J Chem Phys 113:18–35
42. Kowalski K, Piecuch P (2000) J Chem Phys 113:5644–5652
43. Alex Granovsky PC GAMESS/Firefly version 7.1.F, www http://classic.chem.msu.su/gran/gamess/index.html
44. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
45. Cheeseman JR, Trucks GW, Keith TA, Frisch MJ (1996) J Chem Phys 104:5497
46. Wolinski K, Hilton JF, Pulay P (1990) J Am Chem Soc 112:8251
47. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Scalmani G, Cossi M, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene MLX, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, ZakrzewskiVG DS, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Gonzalez C, Wong MW, Pittsburgh PA, Pople JA (2004) Gaussian Inc, Wallingford, CT
48. Bader RFW (1990) Atoms in molecules. A quantum theory. Clarendon, Oxford
49. Cossı´o FP, Morao I, Jiao HJ, Schleyer PR (1999) J Am Chem Soc 121:6737
50. Schleyer PR, Manoharan M, Jiao HJ, Stahl F (2001) Org Lett 3:3643
51. Corminboeuf C, Heine T, Seifert G, Schleyer PR, Weber J (2004) Phys Chem Chem Phys 6:273
52. Bode BM, Gordon MS (1999) J Mol Graph Model 16:133–138
53. Manoharan M, Venuvanalingam P (1997) J Mol Struct (Theochen) 41:394
54. Manoharan M, Venuvanalingam P (1997) J Chem Soc Perkin Trans 2:1799
55. Martino PC, Shevlin PB (1980) J Am Chem Soc 102:5429
56. Meer K, Mulder JJC (1975) Theoret Chim Acta (Berl) 37:159
57. Schleyer PR, Manoharan M, Wang ZX, Kiran B, Jiao H, Puchta R, Hommes NJRE (2001) Org Lett 3:2465