Theor Chem Acc (2009) 123:59–66
DOI 10.1007/s00214-009-0541-0

REGULAR ARTICLE

Density functional methods in the study of oxygen transfer reactions

Carles Acosta-Silva · Vicenç Branchadell

Received: 11 February 2009 / Accepted: 11 February 2009

Abstract The oxygen transfer reactions from heterocyclic compounds such as oxaziridine, methyldioxirane and ethylene oxide to ethylene and phosphine have been studied using different computational methods, and the results have been compared to those obtained with CASPT2 and CBS-QB3 methods. The results show that the generalized gradient approximation (GGA) functionals BLYP and PBEPBE, highly underestimate the barriers. On the other hand, the hybrid meta-GGA functionals (BB1K, M05 and M05-2X) and BHandHLYP tend to overestimate the barriers. Finally, the B3LYP and OPBE functionals provide reasonable barriers. Nevertheless, none of the tested functionals describes all the studied reactions with the same accuracy.

Keywords Density functional theory · Oxygen transfer

1 Introduction

The Kohn–Sham density functional theory (DFT) [1–6] is the most widely used method by computational and theoretical chemists. The key of this success has been its capacity to predict important aspects of a large range of chemical systems with a low computational cost in comparison with post-Hartree–Fock methods.

The development of new exchange–correlation functionals has allowed the use of DFT in the study of chemical reactivity. In particular, hybrid functionals, such as B3LYP [7–9], have been successfully used for many chemical reactions [6, 10–18]. However, there are certain types of reactions in which the most popular DFT methods underestimate potential energy barriers [16, 19–41].

In the last years, new density functionals have been developed specially designed to reproduce accurate potential energy barriers by Zhao and Truhlar [29, 33, 42, 43]. This purpose can be achieved by varying the amount of exact exchange in the exchange–correlation functional. More recently, the same authors have developed a new generation of functionals with broad applicability in chemistry [44–48].

The performance of different functionals in thermochemical kinetics is generally tested for datasets of different barrier heights corresponding to hydrogen-transfer reactions of small systems [27, 29, 32, 43], showing that the hybrid functionals with a large amount of exact exchange such as BB1K [43, 49, 50] (42% of exact exchange) and mPW1K [42, 51, 52] (42.8% of exact exchange) give the best results. The studies comprising non hydrogen-transfer reactions [32, 37, 39] also demonstrate the good performance of the BB1K functional.

Small heterocycles such as oxaziridines and dioxiranes (see Fig. 1) are used in oxygen transfer reactions to alkenes and other species. In the last years, reactions of this kind have been the object of theoretical studies [53–64].

The transition states of these reactions may have a diradical character, so that monodeterminantal methods might not be appropriate for their study. However, in the literature there are several examples in which density functional methods lead to results in good agreement with post-Hartree–Fock methods for this kind of systems [56, 59, 63, 65–70].

Dedicated to Professor Santiago Olivella on the occasion of his 65th birthday and published as part of the Olivella Festschrift Issue.

C. Acosta-Silva · V. Branchadell (✉)
Departament de Química, Universitat Autònoma de Barcelona, Edifici Cn, 08193 Bellaterra (Barcelona), Spain
e-mail: vicenc.branchadell@uab.cat; vicenc@klingon.uab.es

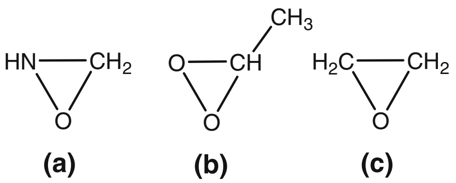

Fig. 1 Oxaziridine (**a**), methyldioxirane (**b**) and ethylene oxide (**c**)

Bach et al. [56] have shown that for reactions of dioxirane and dimethyldioxirane the B3LYP method leads to transition state geometries similar to QCISD. However, the B3LYP energy barriers are underestimated with respect to QCISD(T) results. On the other hand, the MP2 method is not adequate for the optimization of the transition state.

For the reaction between oxaziridine and ethylene, Houk et al. [57] have analyzed the diradical character of the transition state from spin-unrestricted B3LYP calculations, which lead to a breaking of the symmetry between α and β spin densities. However, these UB3LYP calculations seem to exaggerate the diradical character of the transition state.

Baboul et al. [59] have also studied the oxygen transfer between dioxirane and phosphine showing that B3LYP and MP2 lead to a similar energy barriers, but these values are lower than the QCISD(T) result.

In this work we have studied the oxygen transfer reactions of oxaziridine and methyldioxirane with ethylene and phosphine using different density functional methods and comparing the results with CASPT2 and CBS-QB3 calculations. For purpose of comparison, reactions of ethylene oxide have also been studied.

2 Computational details

The structures of reactants and transition states have been optimized at the CASSCF [71] and B3LYP levels of theory with the 6-31G(d) basis set [72]. In all cases, harmonic vibrational frequencies have been computed to characterize each structure. In the CASSCF calculations the active space consists in four electrons and four orbitals for oxaziridine, methyldioxirane and ethylene oxide (σ_{XO}, σ_{CO}, σ^*_{XO} and σ^*_{CO} orbitals, where X is N, O or C, respectively) and two electrons in two orbitals for ethylene (π and π^*) and phosphine (the P lone pair and one of the σ^*_{PH} orbitals). For the transition states, this leads to an active space of six electrons in six orbitals.

For all structures single point calculations have been carried out at the CASPT2 [73, 74], CCSD(T) [75] and MP2 [76] levels of calculation and different density functional methods using the 6-311++G(2df,2pd) basis set. Several functionals have been tested: three generalized gradient approximation (GGA) functionals (BLYP [8, 49], PBEPBE [77, 78] and OBPE [77–79]), three hybrid GGA functionals (B3LYP [7–9], BHandHLYP [8, 49, 80] and PBE1PBE [77, 78, 81]) and three meta-GGA hybrid functionals (BB1K [43, 49, 50], M05 [44] and M05-2X [45]). Finally, we have also done calculations with a high accurate monodeterminantal method such as CBS-QB3 [82].

CASSCF, density functional and CBS-QB3 calculations have been done using the Gaussian-03 program [83], whereas the MOLCAS program [84] has been used for CASPT2 calculations.

3 Results and discussion

The geometries of reactants and transitions states of each reaction have been optimized at the CASSCF and B3LYP levels of calculation. Figures 2 and 3 show the structures of the transition states of the reactions of the three model oxygen donors with ethylene and phosphine, respectively. When different transition state conformers have been found, we have chosen the most stable ones at each level of calculation.

As we can observe, there are significant differences between CASSCF and B3LYP geometries, especially in the reactions with ethylene. The values of the C–O interatomic distances corresponding to the forming bonds show that the CASSCF transition states are asynchronous. Regarding the B3LYP transition states, we can observe a decrease of asynchronicity for the reaction of oxaziridine and, specially, for the reaction of methyldioxirane, which is nearly synchronous. On the other hand, the asynchronicity does not change for the reaction of ethylene oxide. Another significant difference between CASSCF and B3LYP structures is observed in the torsion angle around the shortest forming C–O bond (C–O–C–C dihedral angle) for the reactions of oxaziridine (53.6° for CASSCF and 102.3° for B3LYP) and ethylene oxide (58.7° for CASSCF and 11.5° for B3LYP).

Regarding the phosphine reactions, the most significant differences between CASSCF and B3LYP geometries correspond to the P–O distance in the reactions of oxaziridine (0.168 Å) and ethylene oxide (0.160 Å) and to the O–O distance (0.166 Å) for the reaction of methyldioxirane.

The diradical character of these transition states can be measured through the weight of the diexcited configuration in a CASSCF(2,2)/6-31G(d) calculation. These weights are shown in Table 1 along with T1 diagnostic [85] in the CCSD/6-31G(d) calculation.

From the weights of diexcited configurations, we can observe that the diradical character of transition state of a given reaction depends on the method used in its location. For the reaction of oxaziridine with ethylene the diradical

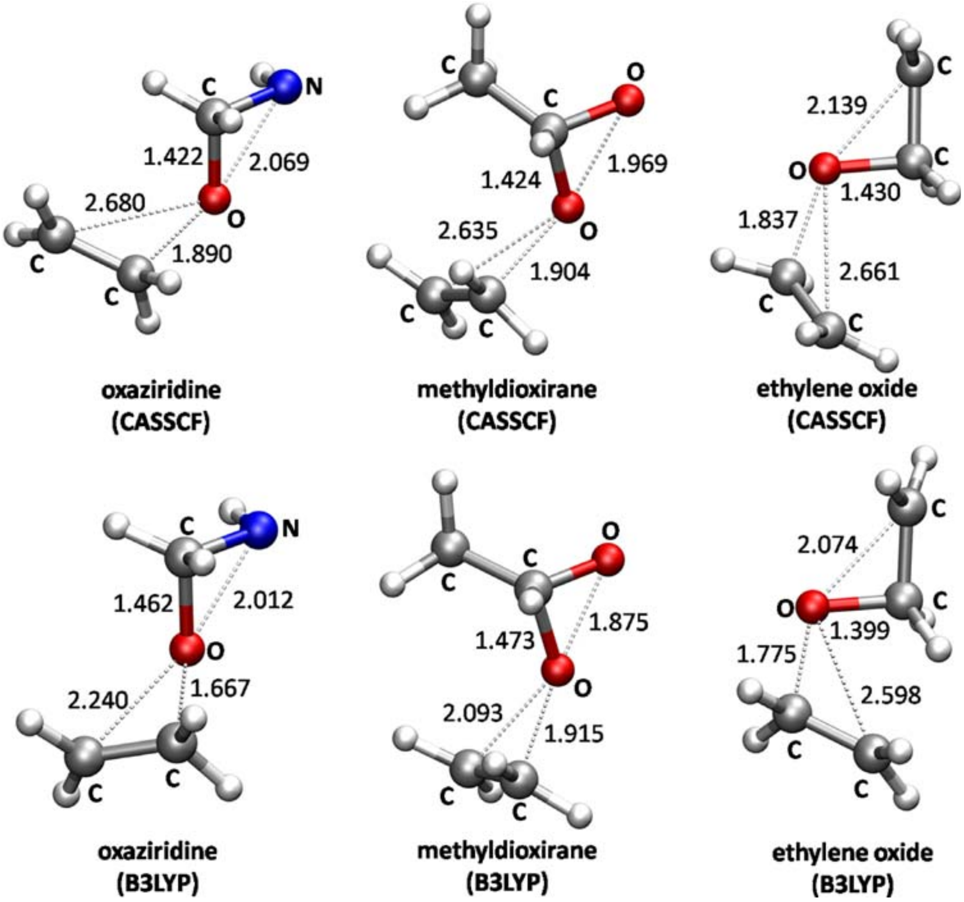

Fig. 2 Geometries of the transition states for the reactions of oxaziridine, methyldioxirane and ethylene oxide with ethylene obtained at the CASSCF(6,6)/6-31G(d) and B3LYP/6-31G(d) levels of theory. Selected interatomic distances in angstrom

character of the transition state is larger for the B3LYP structure than for the CASSCF one. On the contrary, for the reactions of ethylene with methyldioxirane and ethylene oxide the diradical character is larger for CASSCF than for B3LYP. A similar behavior is observed for the reaction between phosphine and methyldioxirane, whereas both CASSCF and B3LYP methods lead to similar diradical characters for the reactions of phosphine with oxaziridine and ethylene oxide.

Regarding the T1 diagnostics, all values are >0.02 except the one corresponding the B3LYP transition state of the reaction between ethylene oxide and phosphine.

Table 2 presents the potential energy barriers of the studied reactions computed at the CBS-QB3 levels of theory for geometries optimized at the CASSCF/6-31G(d) and B3LYP/6-31G(d) levels.

Although the geometries of the transition states depend on the level of calculation, the potential energy barriers computed for each reaction at the CBS-QB3 level are similar, with a mean unsigned difference of 1.7 kcal mol^{-1} and a maximum difference of 3.0 kcal mol^{-1} for the reaction between oxaziridine and phosphine.

As we have seen, potential energy barriers computed with a given method are reasonably similar regardless of the method used in the geometry optimization. For this reason, we will examine the results obtained by different density functionals using only geometries optimized at the B3LYP level of calculation.

For the DFT calculations, we have also considered the possibility of symmetry breaking between α and β spin densities through spin-unrestricted calculations. In the cases in which this leads to a solution different from the restricted one, the energy has been projected to annihilate the contamination from the triplet state [86, 87].

Tables 3 and 4 present the potential energy barriers computed at different levels of calculation for the reactions of ethylene and phosphine, respectively.

Table 3 shows how the CBS-QB3 and CASPT2 methods lead to similar barriers, with a maximum difference of 1.3 kcal mol^{-1} for the reaction with methyldioxirane. These results provide ranges of values that can be used as a reference for each reaction. Regarding the CCSD(T) results, we can observe that the computed energy barriers lie slightly above the reference range for oxaziridine (28.0–28.3 kcal mol^{-1}), between the CBS-QB3 and CASPT2 results for methyldioxirane and >2 kcal mol^{-1} above the CBS-QB3 result for ethylene oxide. The MP2 method provides values slightly lower than CCSD(T) for

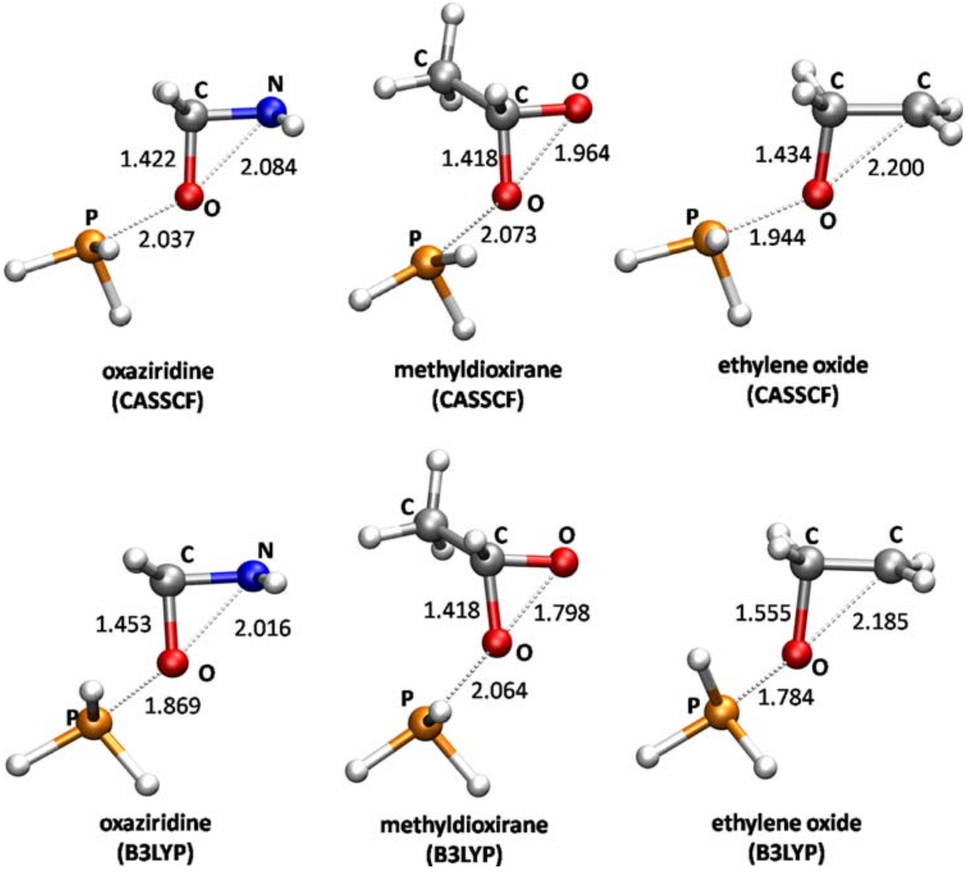

Fig. 3 Geometries of the transition states for the reactions of oxaziridine, methyldioxirane and ethylene oxide with phosphine obtained at the CASSCF(6,6)/6-31G(d) and B3LYP/6-31G(d) levels of theory. Selected interatomic distances in angstrom

Table 1 Weight of the diexcited configuration in the CASSCF(2,2)/6-31G(d) wave-function and T1 diagnostic in the CCSD/6-31G(d) calculation for the transition states of reactions of oxaziridine, methyldioxirane and ethylene oxide with ethylene and phosphine optimized at the CASSCF(6,6)/6-31G(d) and B3LYP/6-31G(d) levels of calculation

	C_2H_4				PH_3			
	CASSCF		B3LYP		CASSCF		B3LYP	
	W_D	T1	W_D	T1	W_D	T1	W_D	T1
Oxaziridine	19.2	0.0212	28.0	0.0236	20.5	0.0225	20.1	0.0210
Methyldioxirane	19.0	0.0282	12.4	0.0270	19.5	0.0256	12.5	0.0206
Ethylene oxide	25.8	0.0314	21.2	0.0309	21.1	0.0331	20.5	0.0195

W_D values are given in %

dimethyloxirane and ethylene oxide, but it clearly underestimates the barrier for the reaction of oxaziridine.

Regarding the reactions of phosphine (Table 4), we can observe that CBS-QB3 and CASPT2 methods also lead to similar energy barriers. However, the maximum difference increases to 2.2 kcal mol^{-1} for the reaction with oxaziridine. The CCSD(T) energy barriers lie between 1.2 and 3.1 kcal mol^{-1} above the CBS-QB3 results. On the other hand, the MP2 method underestimates the barriers for the reactions of oxaziridine and methyldioxirane, whereas for the reaction with ethylene oxide provides a barrier similar to CASPT2.

Let us now analyze the potential energy barriers computed for all reactions with the different density functionals.

In general, GGA functionals tend to underestimate energy barriers, especially those corresponding to the methyldioxirane reactions which have the lower diradical character (see Table 1). For the reaction between methyldioxirane and phosphine, BLYP and PBEPBE functionals place the transition state below the reactants. On the other hand, for the reactions of oxaziridine with ethylene and phosphine, the results obtained with these two functionals are similar to the MP2 values.

Table 2 Potential energy barriers for the reactions of oxaziridine, methyldioxirane and ethylene oxide with ethylene and phosphine computed with the CBS-QB3 method for geometries optimized at the CASSCF/6-31G(d) and B3LYP/6-31G(d) levels of calculation

	Oxaziridine		Methyldioxirane		Ethylene oxide	
	CASSCF	B3LYP	CASSCF	B3LYP	CASSCF	B3LYP
C_2H_4	29.7	28.3	18.7	16.0	51.1	53.5
PH_3	20.7	17.7	6.9	6.9	43.2	42.4

Values are given in kcal mol^{-1}

It is to be noted that the OPBE functional has a different behavior than the other two GGA functionals, since it yields a reasonable energy barrier for the reaction of methyldioxirane with ethylene, whereas it slightly overestimates energy barriers for the reaction between methyldioxirane and phosphine and the reactions of oxaziridine and ethylene oxide. This behavior is similar to that of B3LYP and PBE1PBE hybrid GGA functionals. On the other hand, BHandHLYP clearly overestimates energy barriers. Finally, the energy barriers computed with the three hybrid meta-GGA functionals, are also too large.

The results obtained up to now show that none of the used density functionals provides completely satisfactory results for all reactions. However, OPBE and, specially, B3LYP lead generally to the best results in comparison with CBS-QB3 and CASPT2. The inclusion of exact exchange in an amount greater than that of B3LYP does not improve the results. On the other hand, the used hybrid meta-GGA functionals do not seem to be appropriate for this kind of reactions. The performance of the different density functionals does not have a direct relation with the diradical character of the transition states.

Table 3 Potential energies of transition states relative to reactants for the reactions of oxaziridine, methyldioxirane and ethylene oxide with ethylene computed at different levels of theory

Method	Oxaziridine	Methyldioxirane	Ethylene oxide
BLYP	23.3	7.9	47.5
B3LYP	33.7 (23.1)	16.4	56.8 (52.3)
BHandHLYP	48.4 (21.4)	27.7	70.2 (53.4)
OPBE	32.8 (31.7)	17.3	56.8
PBEPBE	22.1	6.2	45.4
PBE1PBE	36.0 (21.7)	17.9	58.0 (50.1)
BB1K	46.7 (27.9)	26.5	68.4 (58.5)
M05	41.2 (25.6)	20.4 (19.3)	66.9 (55.9)
M05-2X	46.0 (25.1)	25.8 (19.7)	66.4 (55.5)
MP2	22.9	15.5	53.5
CCSD(T)	29.4	16.5	55.7
CBS-QB3	28.3	16.0	53.5
CASPT2	28.0	17.3	52.7

Values are given in kcal mol^{-1}. In parentheses values obtained from symmetry broken unrestricted calculations. Geometries obtained at the B3LYP/6-31G(d) level of theory. Using the 6-311++G(2df,2pd) basis set except in CBS-QB3

Table 4 Potential energies of transition states relative to reactants for the reactions of oxaziridine, methyldioxirane and ethylene oxide with phosphine computed at different levels of theory

Method	Oxaziridine	Methyldioxirane	Ethylene oxide
BLYP	12.1	−0.1	36.0
B3LYP	20.9 (14.0)	7.1 (6.9)	45.9 (40.4)
BHandHLYP	33.6 (12.5)	17.5 (2.3)	59.8 (42.2)
OPBE	22.3	8.3	48.0
PBEPBE	11.6	−1.3	36.3
PBE1PBE	23.5 (13.4)	8.9 (5.4)	49.3 (40.5)
BB1K	32.8 (18.5)	16.7 (8.3)	59.4 (47.9)
M05	28.8 (19.8)	11.3 (9.8)	57.0 (47.8)
M05-2X	30.3 (15.4)	15.6 (7.7)	55.8 (42.9)
MP2	12.9	4.3	40.2
CCSD(T)	19.8	8.1	45.5
CBS-QB3	17.7	6.9	42.4
CASPT2	15.5	5.8	40.8

Values are given in kcal mol^{-1}. In parentheses values obtained from symmetry broken unrestricted calculations. Geometries obtained at the B3LYP/6-31G(d) level of theory. Using the 6-311++G(2df,2pd) basis set except in CBS-QB3

For all density functional methods, we have done spin-unrestricted calculations by breaking the symmetry of α and β spin densities. For the transition states of the reactions of oxaziridine and ethylene oxide, all hybrid functionals may lead to broken symmetry solutions. Regarding the GGA functionals, calculations converge to the spin restricted solution, with the exception of the OPBE results for the reaction between oxaziridine and ethylene. For the reaction of methyldioxirane with ethylene the broken symmetry result is only found with the M05 and M05-2X functionals.

Spin-projection has been applied to the broken symmetry energies to annihilate contamination form the triplet state. For the reactions of oxaziridine, where the hybrid functionals overestimate energy barriers, the projected broken symmetry barriers are generally too low. However, for the reaction with phosphine, corrected BB1K and M05 barriers are still too high and the M05-2X barrier is very close to the CASPT2 result. For the reaction with ethylene, the corrected barrier at the BB1K level of theory is close to the CASPT2 result.

For the reaction between methyldioxirane and phosphine the corrected B3LYP barrier coincides with the CBS-QB3 result, whereas the PBE1PBE functionals leads to a result very close to the CASPT2 value. The three hybrid meta-GGA functionals yield corrected barriers that are higher than the CBS-QB3 result. Finally, for the reaction between ethylene oxide and ethylene both B3LYP and BHandHLYP functionals lead to results within the reference range. On the other hand, for the reaction with phosphine, B3LYP and PBE1PBE functionals provide results close to the CASPT2 value, whereas the corrected BHandHLYP barrier is close to the CBS-QB3 barrier. The corrected barriers obtained with the three hybrid meta-GGA functionals are still too high, with the exception of M05-2X functional which overestimates the CB-QB3 result in only 0.5 kcal mol^{-1}.

As we have observed, energy barriers obtained from spin-projected unrestricted DFT calculations on transition states may be closer to the reference values than the restricted results. Excellent results are obtained from UB3LYP calculations for the reactions of ethylene oxide with ethylene and phosphine, from the UBB1K method for the reaction of oxaziridine with ethylene, and from UM05-2X for the reactions of phosphine with oxaziridine and ethylene oxide. However, it is not possible to predict when this improvement will be observed.

4 Concluding remarks

We have studied the oxygen transfer reactions of three heterocyclic compounds (oxaziridine, methyldioxirane and ethylene oxide) to ethylene and phosphine using different computational methods, and the results have been compared to those obtained with the CASTP2 and the CBS-QB3 methods.

The structures of the minima and transition states have been obtained at the CASSCF and B3LYP levels. The potential energy barriers calculated for each reaction with CBS-QB3 are similar regardless the method used in the optimization.

In general, for B3LYP geometries, CBS-QB3 and CASPT2 provide similar energy barriers, which can be used as reference values. In most of the cases, CCSD(T) slightly overestimates the barriers.

Several GGA, hybrid GGA and hybrid meta-GGA functionals have been tested. In general, GGA functionals tend to clearly underestimate the barriers, with the exception of OPBE, which behaves as a hybrid GGA functional. In contrast, BHandHLYP functional and the hybrid meta-GGA functionals BB1K, M05 and M05-2X highly overestimate the barriers. OBPE and B3LYP are the functionals which provide the lowest errors, when all the barriers are considered. However, none of the tested functionals is accurate in the same way for the six studied reactions. Thus, we recommend a careful previous selection of the DFT functional before a computational study of a given oxygen transfer reaction.

Acknowledgments This work has been financially supported by Ministerio de Educación y Ciencia (CTQ2004-01067/BQU) and Generalitat de Catalunya (2005SGR-103). Access to computational facilities of Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged.

References

1. Hohenberg P, Kohn W (1964) Phys Rev B 136:864. doi:10.1103/PhysRev.136.B864
2. Kohn W, Sham LJ (1965) Phys Rev A 140:1133. doi:10.1103/PhysRev.140.A1133
3. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, New York
4. Chong DP (1996) Recent advances in density functional methods, part I. World Scientific, Singapore
5. Koch W, Holthausen MC (2000) A chemist's guide to density functional theory. Wiley-VCH, Weinheim
6. Cramer CJ (2002) Essentials of computational chemistry: theories and model. Wiley, Chichester
7. Becke AD (1993) J Chem Phys 98:5648. doi:10.1063/1.464913
8. Lee CT, Yang WT, Parr RG (1988) Phys Rev B 37:785. doi:10.1103/PhysRevB.37.785
9. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623. doi:10.1021/j100096a001
10. Svensson M, Matsubara T, Morokuma K (1996) Organometallics 15:5568. doi:10.1021/om960535u
11. Guha S, Francisco JS (1997) J Phys Chem A 101:5347. doi:10.1021/jp970166v
12. Branchadell V, Muray E, Oliva A, Ortuño RM, Rodríguez-García C (1998) J Phys Chem A 102:10106. doi:10.1021/jp981689l
13. Shustov GV, Rauk A (1998) J Org Chem 63:5413. doi:10.1021/jo9802877
14. Nguyen MT, Chandra AK, Sakai S, Morokuma K (1999) J Org Chem 64:65. doi:10.1021/jo980723p
15. Wiest O (1999) J Phys Chem A 103:7907. doi:10.1021/jp991917r
16. Poater J, Solà M, Duran M, Robles J (2002) Phys Chem Chem Phys 4:722. doi:10.1039/b108910m
17. Isobe H, Takano Y, Kitagawa Y, Kawakami T, Yamanaka S, Yamaguchi K, Houk KN (2003) J Phys Chem A 107:682. doi:10.1021/jp021125o
18. Ess DH, Houk KN (2005) J Phys Chem A 109:9542. doi:10.1021/jp052504v
19. Deng LQ, Branchadell V, Ziegler T (1994) J Am Chem Soc 116:10645. doi:10.1021/ja00102a034
20. Glukhovtsev MN, Bach RD, Pross A, Radom L (1996) Chem Phys Lett 260:558. doi:10.1016/0009-2614(96)00923-2
21. Gritsenko OV, Ensing B, Schipper PRT, Baerends EJ (2000) J Phys Chem A 104:8558. doi:10.1021/jp001061m
22. Parthiban S, De Oliveira G, Martin JML (2001) J Phys Chem A 105:895. doi:10.1021/jp0031000
23. Lynch BJ, Truhlar DG (2001) J Phys Chem A 105:2936. doi:10.1021/jp004262z
24. Gonzales JM, Cox RS, Brown ST, Allen WD, Schaefer HFIII (2001) J Chem Phys A 105:11327. doi:10.1021/jp012892a
25. Kormos BL, Cramer CJ (2002) J Phys Org Chem 15:712. doi:10.1002/poc.548
26. Gonzales JM, Pak C, Cox RS, Allen WD, Schaefer HFIII, Császár AG, Tarczay G (2003) Chem Eur J 9:2173. doi:10.1002/chem.200204408

27. Zhao Y, Pu JZ, Benjamin JL, Truhlar DG (2004) Phys Chem Chem Phys 6:673. doi:10.1039/b316260e
28. Grüning M, Gritsenko OV, Baerends EJ (2004) J Phys Chem A 108:4459. doi:10.1021/jp031227u
29. Zhao Y, Truhlar DG (2004) J Phys Chem A 108:6908. doi:10.1021/jp048147q
30. Swart M, Ehlers AW, Lammertsma K (2004) Mol Phys 102:2467. doi:10.1080/0026897042000275017
31. Vayner G, Houk KN, Jorgensen WL, Brauman JI (2004) J Am Chem Soc 126:9054. doi:10.1021/ja049070m
32. Zhao Y, González-García N, Truhlar DG (2005) J Phys Chem A 109:2012. doi:10.1021/jp045141s
33. Zhao Y, Truhlar DG (2005) J Phys Chem A 109:5656. doi:10.1021/jp050536c
34. Bento AP, Solà M, Bickelhaupt FM (2005) J Comput Chem 26:1497. doi:10.1002/jcc.20261
35. Van Bochove MA, Swart M, Bickelhaupt FM (2006) J Am Chem Soc 128:10738. doi:10.1021/ja0606529
36. Swart M, Solà M, Bickelhaupt FM (2007) J Comput Chem 28:1551. doi:10.1002/jcc.20653
37. Riley KE, Op't Holt BT, Merz KM Jr (2007) J Chem Theory Comput 3:407. doi:10.1021/ct600185a
38. Sousa SF, Fernandes PA, Ramos MJ (2007) J Phys Chem A 111:10439. doi:10.1021/jp0734474
39. Acosta-Silva C, Branchadell V (2007) J Phys Chem A 111:12019. doi:10.1021/jp075708f
40. Bento AP, Solà M, Bickelhaupt FM (2008) J Chem Theory Comput 4:929. doi:10.1021/ct700318e
41. Zhao Y, Truhlar DG (2008) Acc Chem Res 41:157. doi:10.1021/ar700111a
42. Lynch BJ, Fast PL, Harris M, Truhlar DG (2000) J Phys Chem A 104:4811. doi:10.1021/jp000497z
43. Zhao Y, Lynch BJ, Truhlar DG (2004) J Chem Phys A 108:2715. doi:10.1021/jp049908s
44. Zhao Y, Schultz NE, Truhlar DG (2005) J Chem Phys 123:161103. doi:10.1063/1.2126975
45. Zhao Y, Schultz NE, Truhlar DG (2006) J Chem Theory Comput 2:364. doi:10.1021/ct0502763
46. Zhao Y, Truhlar DG (2006) J Chem Phys 125:194101. doi:10.1063/1.2370993
47. Zhao Y, Truhlar DG (2006) J Phys Chem A 110:13126. doi:10.1021/jp066479k
48. Zhao Y, Truhlar DG (2008) Theor Chem Acc 120:215. doi:10.1007/s00214-007-0310-x
49. Becke AD (1988) Phys Rev A 38:3098. doi:10.1103/PhysRevA.38.3098
50. Becke AD (1996) J Chem Phys 104:1040. doi:10.1063/1.470829
51. Perdew JP (1991) In: Ziesche P, Eschrigh H (ed) Proceedings of the 21st annual international symposium on the electronic structure of solids. Akademie Verlag, Berlin
52. Adamo C, Barone V (1998) J Chem Phys 108:664. doi:10.1063/1.475428
53. Bach RD, Wolber GJ (1984) J Am Chem Soc 106:1410. doi:10.1021/ja00317a036
54. Bach RD, Coddens BA, McDouall JJW, Schlegel HB (1990) J Org Chem 55:3325. doi:10.1021/jo00297a062
55. Bach RD, Andrés JL, Owensby AL, Schlegel HB, McDouall JJW (1992) J Am Chem Soc 114:7207. doi:10.1021/ja00044a037
56. Bach RD, Glukhovtsev MN, Gonzalez C, Marquez M, Estévez CM, Baboul AG, Schlegel HB (1997) J Phys Chem A 101:6092. doi:10.1021/jp970378s
57. Houk KN, Liu J, DeMello NC, Condroski KR (1997) J Am Chem Soc 119:10147. doi:10.1021/ja963847x
58. Jenson C, Liu J, Houk KN, Jorgensen WL (1997) J Am Chem Soc 119:12982. doi:10.1021/ja971766a
59. Baboul AG, Schlegel HB, Glukhovtsev MN, Bach RD (1998) J Comput Chem 19:1353. doi:10.1002/(SICI)1096-987X(199809)19:12<1353::AID-JCC4>3.0.CO;2-H
60. Deubel DV, Frenking G, Senn HM, Sundermeyer J (2000) Chem Commun (Camb) 2469. doi:10.1039/b006280o
61. Washington I, Houk KN (2000) J Am Chem Soc 122:2948. doi:10.1021/ja993724n
62. Armstrong A, Washington I, Houk KN (2000) J Am Chem Soc 122:6297. doi:10.1021/ja000237v
63. Crehuet R, Anglada JM, Cremer D, Bofill JM (2002) J Phys Chem A 106:3917. doi:10.1021/jp0142031
64. Brodsky BH, DuBois J (2005) J Am Chem Soc 127:15391. doi:10.1021/ja055549i
65. Lee TJ (1990) Chem Phys Lett 169:529. doi:10.1016/0009-2614(90)85642-P
66. Goldstein E, Beno B, Houk KN (1996) J Am Chem Soc 118:6036. doi:10.1021/ja9601494
67. Gräfenstein J, Kraka E, Cremer D (1998) Chem Phys Lett 288:593. doi:10.1016/S0009-2614(98)00335-2
68. Gräfenstein J, Hjerpe AM, Kraka E, Cremer D (2000) J Phys Chem A 104:1748. doi:10.1021/jp993122q
69. Gräfenstein J, Cremer D (2000) Chem Phys Lett 316:569. doi:10.1016/S0009-2614(99)01326-3
70. Gräfenstein J, Cremer D (2000) Phys Chem Chem Phys 2:2091. doi:10.1039/a909905k
71. Roos BO (1987) Adv Chem Phys 69:399. doi:10.1002/9780470142943.ch7
72. Hehre WJ, Radom L, Schleyer PV, Pople JA (1986) Ab Initio molecular orbital theory. Wiley, New York
73. Andersson K, Malmqvist P-Å, Roos BO, Sadlej AJ, Wolinski K (1990) J Phys Chem 94:5483. doi:10.1021/j100377a012
74. Andersson K, Malmqvist P-Å, Roos BO (1992) J Chem Phys 96:1218. doi:10.1063/1.462209
75. Raghavachari K, Trucks GW, Pople JA, Headgordon M (1989) Chem Phys Lett 157:479. doi:10.1016/S0009-2614(89)87395-6
76. Moller C, Plesset MS (1934) Phys Rev 46:618. doi:10.1103/PhysRev.46.618
77. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865. doi:10.1103/PhysRevLett.77.3865
78. Perdew JP, Burke K, Ernzerhof M (1997) Phys Rev Lett 78:1396. doi:10.1103/PhysRevLett.78.1396
79. Handy NC, Cohen AJ (2001) Mol Phys 99:403. doi:10.1080/00268970010018431
80. Becke AD (1993) J Chem Phys 98:1372. doi:10.1063/1.464304
81. Adamo C, Barone V (1999) J Chem Phys 110:6158. doi:10.1063/1.478522
82. Montgomery JA, Frisch MJ, Ochterski JW, Petersson GA (1999) J Chem Phys 110:2822. doi:10.1063/1.477924
83. 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, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Shida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li, Knox JE, Hratchian HP, Cross JB, Bakken V, 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, Zakrzewski VG, Dapprich S, 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, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, revision E.01. Gaussian, Inc., Wallingford

84. Karlström G, Lindh R, Malmqvist P-Å, Roos BO, Ryde U, Veryazov V, Widmark P-O, Cossi M, Schimmelpfennig B, Neogrady P, Seijo L (2003) Comput Mater Sci 28:222. doi:10.1016/S0927-0256(03)00109-5
85. Lee TJ, Taylor PR (1989) Int J Quantum Chem Symp 23:199
86. Yamaguchi K, Jensen F, Dorigo A, Houk KN (1988) Chem Phys Lett 149:537. doi:10.1016/0009-2614(88)80378-6
87. Takano Y, Kubo S, Onisi T, Isobe H, Yoshioka Y, Yamaguchi K (2001) Chem Phys Lett 335:395. doi:10.1016/S0009-2614(01)00067-7