

Ab initio multireference study of Hetero-Diels-Alder reaction of buta-1,3-diene with alkyl glyoxylates

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Abstract Hetero-Diels-Alder (HDA) reaction of methyl glyoxylate with buta-1,3-diene has been investigated using multireference methods (complete active space SCF and multi-reference perturbation theory) and compared with several single-reference methods (including DFT) often used in calculations of catalysed [4+2] cycloadditions. Concerted and stepwise mechanisms, found in the literature, are compared. It is shown, that the stepwise mechanism may be a result of choosing unbalanced active space. Such choice leads to very close singlet and triplet states in the intermediate geometry - an artificial effect, that disappears if properly balanced active space is used (here, we use active space of 12 orbitals and 12 electrons). Conclusions concerning the mechanism and usefulness of the applied methodology are drawn, which might be important for theoretical investigation of stereoselectivity and specificity of catalysts for the HDA reaction.

Keywords Complete active space · self consistent field method · [4+2] cycloaddition · Density functional theory · Hetero-Diels-Alder reaction mechanism

Introduction

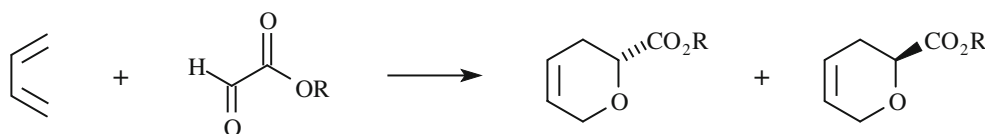
Hetero-Diels-Alder (HDA) reaction is a [4+2] cycloaddition reaction of great importance for organic chemistry. Due to its specific nature, HDA reaction is used in synthesis of fine chemicals, for example drugs or natural products [1–3]. Desired biological activity usually implies synthesis or separation of one of the enantiomers, because in many cases only one enantiomer is active, whereas the other one may be inactive or even toxic [4, 5]. Naturally, stereoselective synthesis of single enantiomer would be preferred over separation from racemic mixture of products, due to economical and ecological reasons. Various enantioselective catalysts have been developed for HDA reaction [6, 7], one of the most promising being salen complexes of the transition metals. [8]. Kwiatkowski et al. achieved good yields and very high enantiomeric excess in [4+2] cycloaddition of 1-methoxybuta-1,3-diene with glycoaldehyde and glyoxylate derivatives (Fig. 1), under high-pressure conditions and using various complexes of salen ligands with chromium and cobalt ions [9, 10]. The design of highly enantioselective catalysts is a great challenge for theoretical chemistry, however proper description of this type of systems requires application of sophisticated quantum-chemical methods. Routine calculations of catalytic systems at the multireference level are beyond present capabilities of computational chemistry, therefore single-reference (mostly DFT) methods are commonly used for modelling of catalysed reactions [11–14]. High-level quantum chemical calculations on the Diels-Alder reaction of ethylene with buta-1,3-diene suggest that multireference treatment would be needed for exact description of [4+2] cycloaddition [15].

In this paper, we use various levels of theory to describe model HDA reaction (see Fig. 1) and we focus on the

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Fig. 1 [4+2] cycloaddition of alkyl glyoxylate to buta-1,3-diene (R=Pr^t, Buⁿ, Bu^t)



cycloaddition of methyl glyoxylate to buta-1,3-diene. Single-reference reaction pathways for HDA reaction are confronted with multireference results at complete active space SCF (CASSCF) and multi-reference Møller-Plesset 2 (MRMP2) levels of theory, probably for the first time employing large (up to 12 orbitals and 12 electrons) active spaces. It is shown, in particular, that choosing too small and not properly balanced active space may lead to a wrong mechanism of the reaction and insufficient separation of the singlet and triplet states.

Methods

Cycloaddition reaction of methyl glyoxylate to buta-1,3-diene was calculated using several methods. Three DFT functionals were used: a hybrid B3LYP functional, [16] Perdew-Burke-Ernzerhof [17] (PBE) and Becke88 exchange [18] plus Perdew86 correlation [19] functional (also known as BP86). DFT results were tested against ab initio methods including electron correlation: second-order Møller-Plesset (MP2) method and multireference methods — CASSCF [20] and a multiconfigurational quasidegenerate perturbation theory (MCQDPT) by Nakano [21] (here applied to single state, therefore called MRMP2). In all cases LANL2dz basis set was used. DFT and MP2 calculations were done using Gaussian 03 package [22]. The CASSCF and MRMP2 calculations were done in GAMESS package [23], using three different active spaces: 6 orbitals/6 electrons — including π and π^* orbitals taking part in the cycloaddition; 8 orbitals/8 electrons — including additional π/π^* orbital pair from the carboxyl group of glyoxylate; 12 orbitals/12 electrons — including also π and π^* orbitals along two carbon-oxygen double bonds. The number of orbitals and electrons included in the active space will be indicated in brackets, e.g. CASSCF(12,12). The computations at DFT, MP2 and CASSCF levels included optimization and normal mode calculations; MRMP2 calculations at the CASSCF optimized geometry have been performed, except for the smallest active space, where MRMP2 optimizations have also been performed. In the MRMP2 calculations 10 core orbitals were frozen, i.e. not included in the perturbation calculation. Energy of the substrates (buta-1,3-diene and methyl glyoxylate) was calculated for the optimized van der Waals complex of the two molecules. In this way, the basis set superposition error was excluded, which would appear if the substrates were optimized separately.

To identify the stationary points along the reaction coordinate, the following symbols are used: R — denoting the complex of the reactants, P — denoting the product (these are the same for both mechanisms); TS — denoting the transition state of the concerted mechanism, TS1 and TS2 — denoting the first and the second transition state of the stepwise mechanism and I — denoting the intermediate between TS1 and TS2 in the stepwise mechanism.

Results and discussion

Energetics and mechanism of the reaction The CASSCF calculations of the reaction using two different active spaces 6 orbitals/6 electrons and 8 orbitals/8 electrons led to two possible mechanisms — concerted and stepwise with similar energetics (see Tables 1 and 2). Sakai has calculated mechanisms of [4+2] cycloaddition of ethylene to buta-1,3-diene [24] and formaldehyde to buta-1,3-diene [25], using in the latter case 6–31G(d,p) basis set and two active spaces: 6 electrons/6 orbitals and 8 electron/7 orbitals (including orbital corresponding to the lone pair at oxygen atom). He found two mechanisms (concerted and stepwise) with slightly higher energy barriers than found here: 46.3 kcal/mol for concerted mechanism (42.3 kcal/mol here) and 47.8, 49.6 kcal/mol for the two steps of stepwise mechanism (41.9, 40.1 kcal/mol here). Both, Sakai's and our results predict differences in the energy barrier heights between concerted and stepwise mechanism of few kcal/mol. Such differences are comparable with accuracy of the method, therefore at this level one cannot decide which mechanism is more likely to happen.

Table 1 Energies of the reactants (R), transition states (TS) and products (P) for the concerted mechanism at various levels of theory; all values are in kcal/mol

	R	TS	P
CASSCF(6,6)	0.0	42.3	-5.2
CASSCF(12,12)	0.0	42.7	-2.8
MRMP2(6,6), sp	0.0	20.5	-11.7
MRMP2(12,12), sp	0.0	19.8	-13.1
MRMP2(6,6)	0.0	21.7	-11.2
DFT/PBE	0.0	7.2	-31.4
DFT/BP86	0.0	7.6	-29.6
DFT/B3LYP	0.0	14.7	-27.5
MP2	0.0	19.8	-15.8

Table 2 Energies of the reactants (R), first (TS1) and second transition state (TS2), intermediate (I) and product (P) for the stepwise mechanism in the singlet state. ‘sp’ means the single point energy MRMP2 calculation at the CASSCF-optimized geometry; all values are in kcal/mol

	R	TS1	I	TS2	P
CASSCF(6,6)	0.0	41.9	39.4	40.1	-5.2
CASSCF(8,8)	0.0	42.7	40.0	40.7	-4.6
CASSCF(12,12)	0.0	—	<i>a</i>	—	-2.8
MRMP2(6,6) sp	0.0	30.9	40.5 ^b	34.4	-11.7
MRMP2(8,8) sp	0.0	31.4	41.3 ^b	35.2	-10.8
MRMP2(12,12) sp	0.0	—	—	—	-13.1
MRMP2(6,6)	0.0	—	<i>a</i>	—	-11.1

^a No minimum; the geometry optimization converges to the reactant or product state. ^b The energy of the intermediates is higher than the energy of TS’s, since the MRMP2 values are single point calculations for CASSCF optimized geometries. The intermediate does not exist at MRMP2 level.

Increasing the size of the active space to 8 orbitals/8 electrons does not alter the barriers significantly, although when the biggest active space is applied (12 orbitals/12 electrons) the stepwise mechanism is no longer possible. At this level, the geometry of the singlet intermediate (Table 2) converges either to the reactant or product geometry. Despite several attempts, the singlet transition states for the stepwise mechanism could not be located at the CASSCF(12,12) level. However, at the CASSCF(12,12) level, the stepwise path can be found in the triplet state (see Table 3). Similarly, triplet paths may be found if 6 orbitals/6 electrons or 8 orbitals/8 electrons active space is used. Although we do not completely exclude the possibility of overlooking the right structure while searching for stepwise transition states and an intermediate at the CASSCF(12,12) level, it seems, that these two saddle points, found in the singlet state using 6 orbitals/6 electrons and 8 orbitals/8 electrons active spaces, are simply an artifact of using an unbalanced active space. In these cases singlet and triplet intermediates are very close in energy: compare values of the energy of intermediate (I) in Tables 2 and 3 — at CASSCF(6,6) 39.4 and 40.7 kcal/mol, at CASSCF(8,8) 40.0 and 41.2 kcal/mol for singlet and triplet state, respectively. Note, that when the size of the active space is increased in the triplet state (Table 3), the energy of the intermediate is the one that is most affected. Increasing the size of the active space does not affect the energy of the reactant, product and TS (they change by 2 kcal/mol at most), but it does affect the energy of the triplet intermediate which increases from 40.7 at CASSCF(6,6) level and 41.2 at CASSCF(8,8) level to 47.0 kcal/mol when the largest active space is used (12 orbitals/12 electrons), leading to a better separation of the singlet and triplet potential energy surfaces. The triplet state intermediate is a true minimum on the potential energy surface and has a

strongly biradical nature. Its energy at the CASSCF(12,12) level is 4.3 kcal/mol higher than the energy of the concerted TS. It has to be noted, that the singlet state intermediates found at the CASSCF(6,6) and CASSCF(8,8) levels have energies very close to the corresponding triplet states (Table 2) and are dominated by biradical configurations. The ground state configuration of CASSCF(8,8) singlet state intermediate has about 20% contribution in the CI wavefunction and the CASSCF(6,6) ground state configuration has a contribution of 55%, therefore cannot be described by a single-reference method. The triplet states, on the other hand, are dominated by the ground state configuration, which is an open-shell biradical. This is the reason, why we were not able to find the stepwise singlet path using single-reference methods (DFT and MP2), but we were able to calculate these paths in the triplet state, using all methods, including the single-reference techniques (Table 3). It is worth to recall at this point, that a proper description of degenerate states is beyond the capabilities of traditional DFT formalism, based on the Kohn-Sham equations [26, 27]. We have also optimized the intermediate of the cycloaddition of formaldehyde to buta-1,3-diene investigated by Sakai [25], using CASSCF(6,6) method and 6–31G(d,p) basis set (the same as in work of Sakai). He has found, that both mechanisms (concerted and stepwise) are valid for this reaction, but he did not consider the triplet state. We have found stable geometries of singlet and triplet state of the intermediate, that have almost the same energy — the difference is 0.3 kcal/mol. It seems, that our conclusions concerning the proper choice of the active space in the CASSCF calculations of the stepwise mechanism could probably be extended to the cycloaddition of formaldehyde to buta-1,3-diene investigated by Sakai.

Lischka et al. have shown [15], that the dynamical correlation component reduces the barrier calculated at CASSCF level considerably. In order to assess the contribution of the dynamical correlation to the barriers

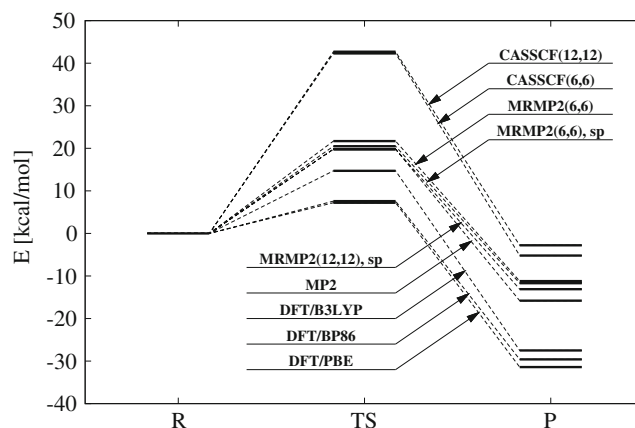


Fig. 2 Energy diagram of the singlet state concerted mechanism. Labels are ordered according to the energy of the product

Table 3 Energies of the reactants (R), first (TS1) and second transition state (TS2), intermediate (I) and product (P) for the stepwise mechanism in the triplet state

	R	TS1	I	TS2	P
CASSCF(6,6)	52.2	66.0	40.7	77.2	60.4
CASSCF(8,8)	52.0	66.7	41.2	77.6	60.9
CASSCF(12,12)	52.0	67.8	47.0	79.6	62.6
MRMP2(6,6) sp	54.3	58.6	45.1	66.6	56.8
MRMP2(8,8) sp	52.2	57.0	45.7	65.5	56.0
MRMP2(12,12) sp	52.2	55.7	40.7	62.9	54.0
DFT/PBE ^(a)	40.6	47.7	32.3	48.3	33.4
DFT/BP86 ^(a)	40.7	47.7	33.3	46.2	34.9
DFT/B3LYP	49.2	51.5	31.9	54.1	40.6
MP2	73.4	84.0	55.0	78.9	52.0

^(a) Geometries (i) and (ii) in Table S-2 (Supp. Inf.) have virtually the same energy, therefore only one entry is shown. All figures are expressed in kcal/mol, relative to the single state reactant (Table 2); 'sp' means the single point energy MRMP2 calculation at the CASSCF-optimized geometry

calculated here, we have applied MRMP2 method implemented in GAMESS. Single point MRMP2 calculations on the geometry optimized at the CASSCF(6,6) level resulted in the energy barrier of 20.5 kcal/mol for the concerted mechanism (a decrease by about 20 kcal/mol corresponding to the CASSCF result is observed). Single point calculations in the largest active space gave a similar result. Clearly, this decrease is not due to the geometry changes —

we have optimized the reactant, TS and product at the MRMP2 level using 6 electrons/6 orbitals active space and the barrier is only about 1 kcal/mol higher than calculated in the single point MRMP2 computation using CASSCF(6,6) geometries. Barriers of the two stepwise TS's are decreased by 11 and 6 kcal/mol, respectively, if the single point MRMP2 calculations are performed on the CASSCF optimized geometry (similar results are obtained for 6 electrons/6 orbitals and 8 electrons/8 orbitals active space). The energy of the singlet state intermediate increases slightly in the single point MRMP2 computation (about 1 kcal/mol), resulting in the intermediate lying above the transition states. This is because there is no stable singlet state intermediate at the MRMP2 level — the optimization of its geometry at the MRMP2 level, using 6 electrons/6 orbitals active space leads to the product geometry (Table 2). In contrary, the triplet state intermediate is stable at the MRMP2 level and has energy of 47.1 kcal/mol — similar to the value obtained at the CASSCF(12,12) level. This observations are consistent, as both, increasing the active space and applying the MRMP2 methods, adds dynamical electron correlation and leads to a proper separation of the singlet and triplet potential energy surfaces.

All single-reference methods applied here, have failed in calculations of the singlet stepwise mechanism. The reason — as stated above — is that the contribution of the ground state configuration is small in singlet state. On the other hand, using

Fig. 3 Geometry of the singlet state structures. Details of the geometry can be found in the Supporting Information. The values of the C2–C3 and O–C6 bonds are given, as well as the values of the dihedral angles: C1–C2–C3–C4 and C2–C3–C4–C5. The bond lengths are in Å, the angles are in degrees. The values correspond to the level of theory indicated in the box

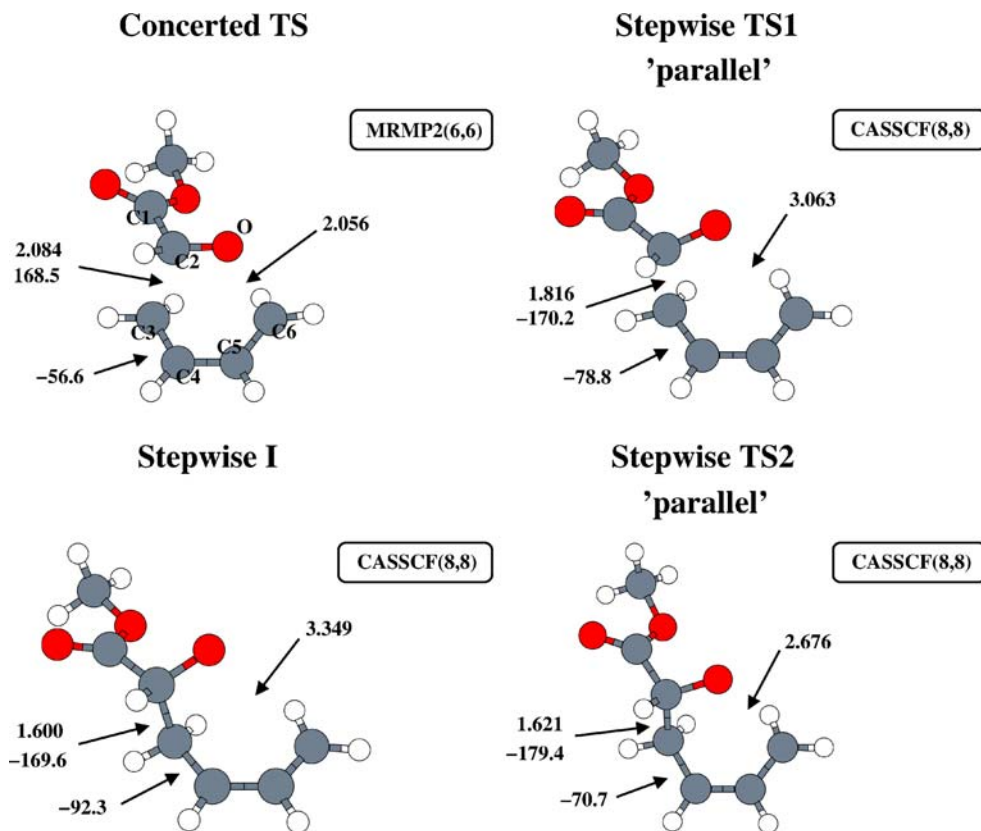
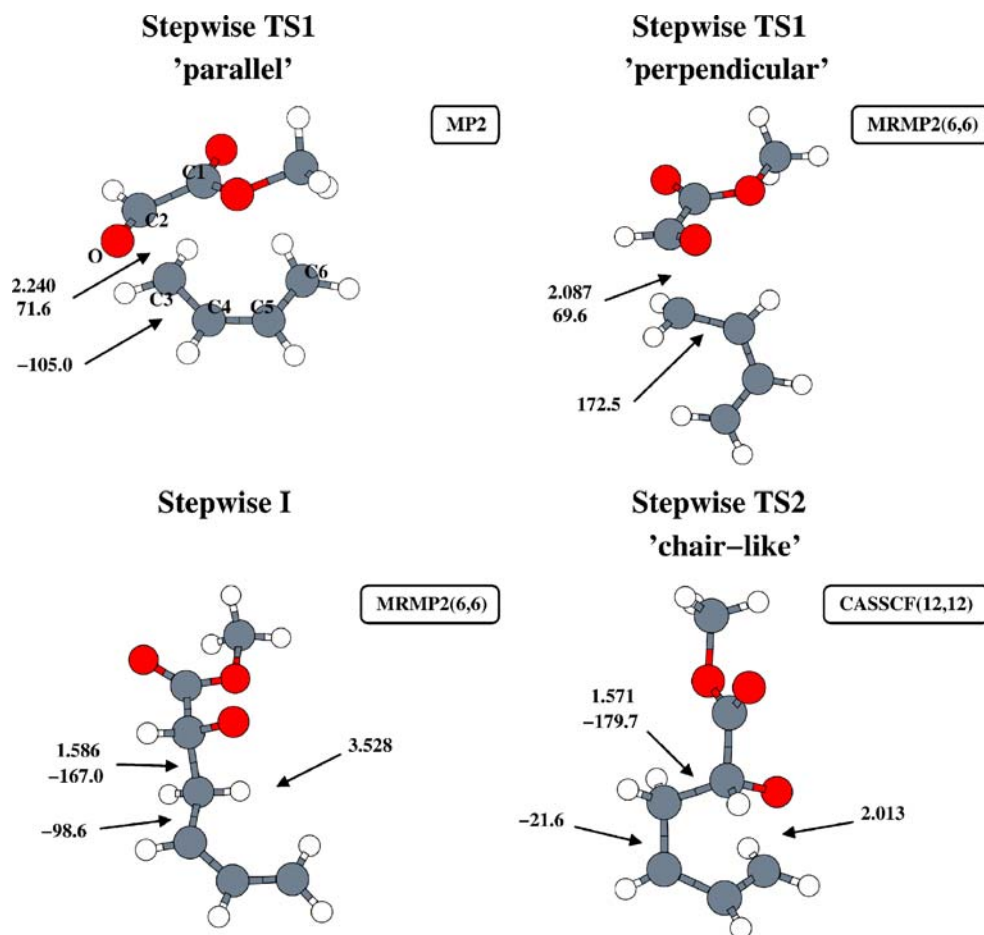


Fig. 4 Geometry of the triplet state structures. Details of the geometry can be found in the Supporting Information. The values of the C2–C3 and O–C6 bonds are given, as well as the values of the dihedral angles: C1–C2–C3–C4 and C2–C3–C4–C5. The bond lengths are in Å, the angles are in degrees. The values correspond to the level of theory indicated in the box



DFT and MP2, the triplet state stepwise mechanism can be calculated, but the energies are much above the singlet state. In the concerted mechanism, the DFT methods underestimate the barriers in both, singlet and triplet state (Fig. 2). The barrier obtained at the MP2 level for the singlet state (concerted mechanism) is in perfect agreement with the MRMP2 result. All DFT methods resulted in similar energetics of the reaction, oscillating about -30 kcal/mol, which is about 20 kcal/mol below the value calculated at the MRMP2 level, whereas the MP2 method gave results consistent with the MRMP2. This is a likely result because the reactant, product and concerted TS are well described by the ground state configuration and the perturbation scheme used in the MRMP2 method is the same as in the MP2 method. It is often considered, that triple-zeta basis sets are needed to obtain fully converged reaction energy. Indeed, the barrier height and value of the reaction energy can be altered if a bigger basis set is applied (Table 4), however it is remarkable, that application of a large double-zeta basis set (aug-cc-pVDZ) and coupled clusters level of theory (CCSD(T)), results in exactly the same value of the activation barrier energy as MP2/lanl2dz, due to the cancellation of errors. The barrier of the reverse reaction is changed by about 15%, when CCSD(T)/aug-cc-pVDZ level of theory is used.

Geometry of the transition states and intermediates The best estimates of the geometry of concerted TS presented here, have been obtained at the MRMP2 level of theory. These results indicate, that two bonds created during reaction have approximately the same length in the TS: C2–C3 distance is 2.08 Å and O–C6 distance is 2.06 Å (Table S-1 in Supp. Inf. and Fig. 3). CASSCF(6,6) calculations slightly underestimate the first distance (2.03 Å) and overestimate the second one (2.16 Å). However, increasing the active space to 12 electrons/12 orbitals, results in bond distances being more consistent with the MRMP2 ones. Single-reference methods significantly overestimate the C2–C3 distance, for example using PBE functional the value of 2.24 Å is obtained.

Table 4 Activation barrier (ΔE^\ddagger) and reaction energy (ΔE) calculated using various basis sets at MP2 and CCSD(T) level. All values are in [kcal/mol]

	ΔE^\ddagger	ΔE
MP2/lanl2dz	19.79	-15.76
CCSD(T)/lanl2dz	22.51	-17.37
MP2/aug-cc-Pvdz	13.42	-21.81
CCSD(T)/aug-cc-pVDZ	19.93	-20.96

Geometries of stepwise transition states have been calculated in the singlet and triplet state. The singlet state geometries could be found only at the CASSCF level, using 6 electrons/6 orbitals and 8 electrons/8 orbitals active spaces. These geometries form ‘parallel’ conformation, similar to the conformation of the concerted TS (Table S-1 in Supp. Inf. and Fig. 3). The triplet state geometries of the stepwise mechanism, except the intermediate, differ significantly from its singlet state counterparts. TS1 may have a ‘perpendicular’ or a ‘parallel’ conformation, whereas TS2 has a ‘chair-like’ conformation (Table S-2 in Supp. Inf. and Fig. 4). The first TS1 conformation, in which the buta-1,3-diene plane is perpendicular to the glyoxylate plane, has been found using CASSCF and MRMP2 methods. The second one (the ‘parallel’ conformation), was found using all single-reference methods. In Table S-2 in Supp. Inf. the DFT/PBE and DFT/BP86 geometries (i and ii) are listed; having almost the same energy but differing in the mutual orientation of buta-1,3-diene and glyoxylate. One of them could be described as preoriented for the *S* enantiomer and the other as preoriented for the *R* enantiomer. The difference in energy between the (i) and (ii) conformation is about 0.6 kcal/mol for DFT/PBE and below 0.1 kcal/mol for DFT/BP86; values in Table 3 correspond to the lower-lying conformer. The geometry of the triplet state intermediate is similar to the geometry of the singlet state intermediate. TS2 in the triplet state forms conformation similar to the chair conformation of cyclohexane with glyoxylate substituent approximately in equatorial position. This geometry is consistent throughout all the methods except DFT/BP86, where the glyoxylate sidechain is in axial position. The effect of including dynamical correlation on the reaction energetics is not significant — barrier calculated at the single point MRMP2(6,6) is almost the same as calculated for the MRMP2(6,6) optimized geometries. However, in the triplet state, the geometry changes after including dynamical correlation: for example, the dihedral angle C2–C3–C4–C5 of the intermediate changes its value from –112.3 to –98.6 degrees (Table S-2 in Supp. Inf.). Once again, it must be noted, that the triplet state stepwise mechanism energies are too high and only the singlet state concerted mechanism is valid.

Conclusions

In this paper, one of the first multireference analysis of the HDA reaction is presented. To the best of our knowledge, this is the first investigation where large active space is applied in CASSCF calculations and triplet state is considered. Two possible mechanisms are investigated for Diels-Alder and hetero-Diels-Alder reaction in the literature [15, 24, 25]. Calculations presented here, show that application of the high-level CASSCF and MRMP2 methodology excludes the

stepwise mechanism, provided that a well-balanced (12 orbitals/12 electrons) active space is used. The reason behind it is that, if an unbalanced active space is applied, the singlet and triplet states are not properly separated in the intermediate geometry. When sufficiently large active space is used, the energy of the triplet state increases and singlet state intermediate disappears. In such a case, the stepwise mechanism is no longer valid. The single reference methods provide a proper qualitative description of the mechanism, owing to the fact that the wave functions of the reactant (R), product (P) and concerted transition state (TS) are well described by the ground state configuration. Our best estimates of the barrier (MRMP2 calculations at the CASSCF(12,12) optimized geometry) is 19.8 kcal/mol — this value is preserved at the MP2 level but underestimated at DFT level. The reaction is exothermic: the best estimate of the reaction energy is –13.1 kcal/mol (MRMP2 calculations at the CASSCF(12,12) optimized geometry).

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