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Solvent Effects on the Stereoselectivity of Reaction of Methyl Acrylate, Methyl Methacrylate and Methyl *trans*-Crotonate with Cyclopentadiene: A Computational Study*

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Abstract. The stereoselectivity of reaction of methyl acrylate, methyl methacrylate and methyl *trans*-crotonate with cyclopentadiene was studied with *ab initio* RHF/6-31G* and B3LYP/6-31G* levels of theory. The stereoselectivities predicted for methyl acrylate and methyl methacrylate with cyclopentadiene in the gas phase were found to be in good agreement with experimental results. The preference of *endo* selectivity in solvents was more pronounced for methyl acrylate, however, the preference for the *exo*-addition for methyl methacrylate was predicted to be reduced in solvents. The solvent calculations predicted the *endo*- preference for methyl *trans*-crotonate in agreement with the experimental observations. The lower *endo* selectivity for methyl *trans*-crotonate with cyclopentadiene seems to be governed by the degree of asynchronicity of *endo*- and *exo*-transition states in water. B3LYP/6-31G* calculated activation enthalpy was found to be in good agreement with the observed activation enthalpy for methyl acrylate and cyclopentadiene, however, this method does not predict the stereoselectivities correctly in all cases. The hydrogen bonding between water and polarized transition states seems to be important for rate acceleration in water

Keywords: DFT, Diels-Alder, stereoselectivity, solvent, global electrophilicity

INTRODUCTION

The Diels-Alder reaction is one of the most powerful carbon-carbon bond formation processes and continues to be an important subject for both computational[1–7] and experimental studies.[8,9] Solvent effects on the reactions have received much attention due to rate accelerations and selectivities that have been observed in different media.[10–28] Recently, rate accelerations of traditionally Diels-Alder reactions have been studied computationally in aqueous media.[1] The role of hydrophobic association of reactants and hydrogen bonding between the water molecules and the polarized transition states have been indicated. The stereoselectivity of Diels-Alder reactions have been examined experimentally in different solvents and the observed selectivities were rationalized *via* Alder rule of "maximum accumulation of unsaturation",[29] dipole moment of transition states,[17] hydrophobic and hydrogen bonding interactions[16,30] and strong intermolecular attractive forces of alkyl groups overcoming secondary attractive forces of carbonyl or nitrile groups.[31] Domingo and co-workers have carried out studies to explain the stereoselectivity and role of water/organic solvents in Diels-Alder reactions with different dienes and dienophiles[32,33] and demonstrated the usefulness of global electrophilicity power, ω, to show the polarity of transition states in Diels-Alder reactions.[34] However, computational reports to evaluate the importance of some of these factors toward the stereoselectivity of Diels-Alder reactions with similar dienophiles are limited in the literature.

To explore the stereoselectivities observed for Diels-Alder reactions in gas, aqueous and non-aqueous solvents, cyclopentadiene and three dienophiles namely, methyl acrylate, methyl methacrylate and methyl *trans*-crotonate (Scheme 1) has been investigated using *ab initio* RHF/6-31G* and hybrid-DFT B3LYP/6-31G* calculations. Solvent calculations were performed in water and methanol. The calculated results were compared with the available experimental stereoselectivities for these Diels-Alder reactions. This study has focused on the relative importance of solvent polarity and dipole moment on the stereoselectivities observed in these cases.[17] Further, the global electrophilicity index used to examine the electrophilicity power of diene and dieno-

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

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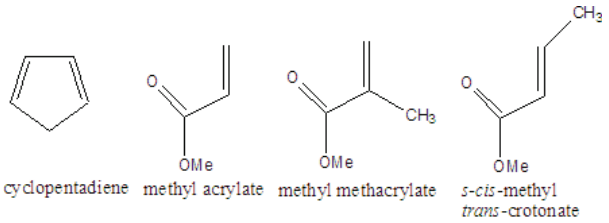


Scheme 1.

philes in these DA reactions.[34] This analysis will help to determine the polar nature of the transition states studied here.

COMPUTATIONAL METHODOLOGY

All calculations were performed with Gaussian 03 program[35] at RHF/6-31G* level and single point calculations with B3LYP/6-31G* using RHF/6-31G* optimized geometries. The choice of the method and basis set in the present study was based on similar Diels-Alder reactions reported in the literature.[31,36] The stationary points were characterized by frequency calculations in order to verify that the transition structures had one, and only one, imaginary frequency. To verify that each saddle point connects two putative minima, intrinsic reaction coordinate (IRC) calculations of gas phase geometries were performed in the forward and backward directions, *i.e.*, by following the eigenvectors associated to the unique negative eigen value of the Hessian matrix, using the González and Schlegel integration method.[37,38] Full geometry optimization was performed in water and methanol with Conducter-like Polarizable Continuum Model (CPCM).[39–41] This approach describes the solvent reaction field by means of apparent polarization charge distributed on the cavity surface, which are determined by imposing that the total electrostatic potential cancels out on the surface.[40]

In CPCM approaches, the solute interacts with the solvent represented by a dielectric continuum model. The solute molecule is embedded into a cavity surrounded by a dielectric continuum of dielectric coefficient ε. The cavity surface is partitioned into small domains called tesserae. Each tessera is characterized by the position of its center, its area and the electrostatic vector normal to the surface passing through its centre. The CPCM solvation model also provides the nonelectrostatic contribution to the solute free energy.[40,42]

The global electrophilicity index, ω, was calculated for cyclopentadiene and all three dienophiles using the expression, $\omega = (\mu^2/2\eta)$.[43,44] The electronic chemical potential μ and the chemical hardness η were evaluated in terms of one electron energies of the frontier molecular orbitals (FMO) HOMO and LUMO, ε_H and ε_L, using the expression, $\mu \approx (\varepsilon_H + \varepsilon_L)/2$ and $\eta \approx (\varepsilon_H - \varepsilon_L)$, respectively, at the ground state (GS) of the molecules using B3LYP/6-31G*//RHF/6-31G* level of theory.

RESULTS AND DISCUSSION

The transition state geometries of cyclopentadiene with methyl acrylate, methyl methacrylate and methyl *trans*-crotonate were located at RHF/6-31G* level of theory (Scheme 2 and Figure 1). These geometries were further located in water ($\varepsilon = 78.4$) and methanol ($\varepsilon = 32.6$). We have discussed the difference in geometries and energies in vaccum and in solvents and their influence on the observed *endo*/*exo* stereoselectivities. Methyl *trans*-crotonate can exist in *s-cis* and *s-trans*-forms. The *s-cis* conformation was used in most of the studies due to stereoselective preferences.[45] We have also examined the *s-cis* conformation in our study for comparison in the gas and solvent phase. The predicted geometries for the transition states correspond to a concerted although asynchronous in agreement with the earlier reports.[46] The newly forming bond carries the $-CO_2Me$ group is larger than the other C···C forming bond in all the computed transition state geometries (Figure 1). The asynchronicity was found to be larger for methyl methacrylate than methyl acrylate and methyl *trans*-crotonate. Further, the computed intrinsic reaction coordinates (IRCs) starting from the TSs demonstrated that such points connect nicely the reactants and cycloadduct products. These points are located in a smooth drop in energy after the barrier height, explaining the unfeasibility of finding any molecular complex or intermediates as a stationary point. IRC calculated results revealed that these cycloadditions follow a concerted mechanism.

The transition state geometries in water also show that the newly forming C···C bonds are asynchronous in nature (Figure 1). However, the bonds carrying the $-CO_2Me$ groups are longer in water than the gas phase calculated geometries. Similar observation was also made for methanol calculations (Figure 1). The change of TS location in solutions, as compared to the gas phase suggests that the reaction path in solution cannot be deduced from the reaction path in a vacuum by simply adding the solvation energy and that a full geometry (and electronic) relaxation of the solvated TS structures is required. The calculated RHF/6-31G* energies suggests that the *endo*-transition state for methyl acrylate is 0.5 kcal mol^{-1} stable than the corresponding *exo*-transition state in the gas phase (Table 1). This result was found to be in good agreement with the observed results.[17] The preferential formation of *endo*- transition state support the rule of "maximum accumulation of unsaturation".[29] Moving from methyl acrylate to methyl methacrylate, the transition state calculations show that

Table 1. RHF/6-31G* calculated relative electronic energies (kcal mol^{-1}) between *endo* and *exo* TS in the gas phase, water and methanol[(a)]

	Cyclopentadiene + Methyl acrylate		Cyclopentadiene + Methyl methacrylate		Cyclopentadiene + *s-cis*-Methyl *trans*-crotonate	
Medium	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
Gas phase	0.0	0.43	0.75	0.0	0.49	0.0
	(0.0)	(0.49)	(0.69)	(0.0)	(0.39)	(0.0)
	[2.28]	[2.00]	[1.98]	[1.81]	[2.17]	[1.95]
Water	0.0	1.32	0.18	0.0	0.0	0.17
	(0.0)	(1.30)	(0.25)	(0.0)	(0.0)	(0.11)
	[3.62]	[3.46]	[3.15]	[3.11]	[3.36]	[3.33]
Methanol	0.0	1.10	0.18	0.0	0.0	0.22
	(0.0)	(1.07)	(0.28)	(0.0)	(0.0)	(0.22)
	[3.53]	[3.39]	[3.10]	[3.06]	[3.39]	[3.28]

[(a)] Relative free energies (kcal mol^{-1}) calculated at 298 K are in ( ) and dipole moments (debye) in [ ].

the *exo*- TS is stable by 0.7 kcal mol^{-1} compared to *endo*-TS (Table 1). The calculated *exo*-selectivity was found to be in agreement with experimental observations.[17] To explain the failure of Alder's rule of the stereoselectivity for metyl methacrylate, Furukawa attempted to rationalize the stereoselectivity on the basis of the strong intermolecular attractive forces of methyl groups.[30] To examine this hypothesis, we have performed the charge analysis to verify the attractive force

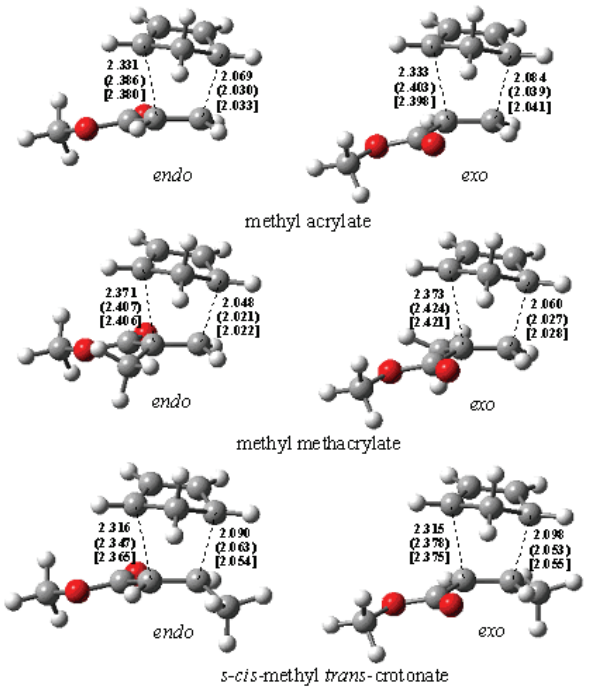
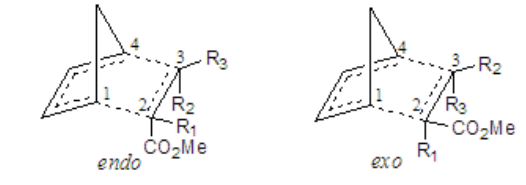


Figure 1. RHF/6-31G* calculated geometrical parameters (Å) of TS for various systems in gas phase, aqueous phase ( ) and in methanol [ ] [Gray = Carbon, Red = Oxygen and White = Hydrogen].

with the methyl group of the dienophile and diene in the transition state geometries of methyl methacrylate and cyclopentadiene. The mulliken charge analysis suggests that the charge distribution was similar in both *exo*- and *endo*-transition structures (Figure 2) and any unusual attractive interaction was not observed for the *exo*-transition state geometry. However, it is to note that the mulliken population analysis is significantly dependent on the choice of basis set.[47,48] The natural population analyses (NPA),[49] however, is less sensitive with the choice of basis set, and hence we have also computed natural charges for those *exo*- and *endo*- transition structures (Figure 2). The NPA charge distributions were found to be similar to that of the calculated mulliken charges. The inadequacies of the Alder rule were also revealed in the case of methyl *trans*-crotonate. The experimental results show that the ratios of products is close to the statistical 1:1 distribution in all solvents.[17] Recently, the product ratios determined in different solvents show that the *endo*- addition is preferred over the *exo*- addition and supports the Alder rule.[13,29] The calculated results with RHF/6-31G* level show that *exo*-TS is favored over *endo*-TS for methyl *trans*-crotonate (Table 1). The gas phase predicted *exo*-



$R_1 = R_2 = R_3 = H$ Cyclopentadiene + methyl acrylate
$R_1 = CH_3, R_2 = R_3 = H$ Cyclopentadiene + methyl methacrylate
$R_1 = R_2 = H, R_3 = CH_3$ Cyclopentadiene + *s-cis*-methyl-*trans*-crotonate

Scheme 2.

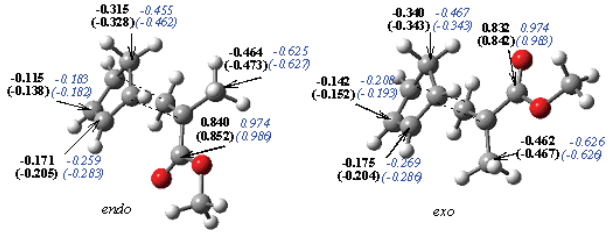


Figure 2. RHF/6-31G* calculated mulliken charges and natural charges (in blue) on *endo*- and *exo*-transition states of methyl methacrylate in the gas and aqueous phase ( ).

preference for methyl *trans*-crotonate with cyclopentadiene was not in agreement with experimentally observed results.[13,17]

The effect of solvents on the transition state energies was also examined at RHF/6-31G* level of theory. The calculated results show that the *endo* preference seen in the gas phase for methyl acrylate is more pronounced in water. The electrostatic effect of the solvent favors the *endo* with respect to *exo* isomers, in agreement with the experimentally observed results *i.e.*, increase of the *endo*/*exo* selectivity as a function of solvent polarity for the reaction of cyclopentadiene with methyl acrylate.[50] The less polar solvent, methanol also shows the pronounced *endo* preference compared to the calculated gas phase results, however, the transition state energy difference is smaller than water (Table 1). Experimentally, the *endo*/*exo* stereoselectivity was not observed in pure water, however, the organic solvent-aqueous mixture showed the enhanced selectivity for *endo*-addition with higher percentage of water.[50] The effect of solvent polarity was also observed on stereoselectivities in other Diels-Alder reactions.[51] The degree of asynchoronicity of $C_1\cdots C_2$ *vs*. $C_3\cdots C_4$ bond formations in the *exo*- and *endo*- transition states for methyl acrylate with cyclopentadiene is similar in both water and methanol solvents (Scheme 2 and Figure 1). Therefore, the influence of hydrophobic interaction towards the association of transition states in water does not seem to be important in this case.[10–13,16] The enhancement in the *endo*-selectivity presumably arises between the electrostatic effect of the water and polarized transition states more compared to methanol.

The effect of solvent seems to be more pronounced on the *endo*/*exo* selectivity of methyl methacrylate. The computed gas phase transition state energy difference is reduced in water and methanol solvents. The *exo*-addition is preferred over *endo*-addition by 0.2 kcal mol^{-1} (Table 1). This is in agreement with the previously observed result for methyl acrylate that the *endo*-addition gets stabilized more in solvents compared to *exo*-addition. Consequently, the transition state energy difference is smaller in solvents than the gas phase calculated results. The experimentally observed *endo*/*exo* ratio in methanol for methyl methacrylate with cyclopentadiene was 40:60.[17] In one of the recent studies, the *endo*/*exo* ratio reported in water was 29:71.[13] These experimental results suggest that the transition state energy difference should be larger in water compared to methanol and that was not observed with CPCM solvation model. It is to note that the ratios were determined in different experimental conditions. Therefore, the quantification of computed results seems to be not possible. Comparing the transition state geometries obtained in water and methanol, it appears that the hydrophobic interaction towards the association of transition state geometries is less important (Figure 1). The degree of asyncronicity of newly formed bonds in the transition states is similar in both *endo*- and *exo*- case. Moving to methyl *trans*-crotonate, the transition state calculations predicts *endo* preference in water and methanol, which is in agreement with the experimental observations (Table 1).[13] The *exo*-selectivity predicted in the gas phase for methyl *trans*-crotonate with cyclopentadiene and the change to *endo*-preference in the solvents further verifies that solvents stabilizes the *endo*-transition state more compared to *exo*-transition state. Comparing the *endo*/*exo* selectivities observed in water and methanol, it appears that the *endo* preference is less in water compared to organic solvents.[13] The calculated results show that the energy difference between the *endo*- and *exo*- transition states is higher by 0.1 kcal mol^{-1} in methanol than water, which qualitatively supports the observed selectivities (Table 1). Recently, the lower *endo*-selectivity in water than organic solvents was explained with the hydrophobic packing of the methyl group in the transition states.[13] The methyl group is more hydrophobic than the carboxylate group, so the hydrophobic packing of the methyl group in the transition state would lead to more $endo_{methyl}$ (*exo*-transition state) corresponding to more exo_{methyl} (*endo*-transition state). However, our calculated *endo*- and *exo*- transition state geometries suggest that the association of diene and dienophile do not support the tight association of the former transition state than the later in water (Figure 1). The degree of asynchronicity obtained is more in the *exo*-transition state of methyl *trans*-crotonate with cyclopentadiene than the corresponding *endo*-transition state in water. However, in methanol the asyncronicities are similar for both the transition states. This analysis suggests that the asynchronicity of the reaction is favored by the interactions with solvent. The *exo*-TS for methyl *trans*-crotonate with cyclopentadiene seem to be stabilized more in water than methanol compared to their corresponding *endo*-transition states and hence the *endo*/*exo* selectivity would expected to be lower in water than methanol.[13]

To gain further insights concerning the polar nature of the transition states of these DA reactions, global

electrophilicity index[43] was examined within the context of the conceptual density functional theory.[52] In Table 2, the electronic chemical potential, μ, chemical hardness, η, and the global electrophilicity, ω, are shown. The large electrophilicity difference, $\Delta\omega$, between cyclopentadiene and the dienophiles used in this study indicates that these DA reactions would be polar in nature. To examine the reliability of the method used to calculate the global electrophilicity, we have also chosen 1,3-butadiene and ethylene as a reference for a non-polar DA reaction.[34] The electrophilicity difference for non-polar DA reaction between 1,3-butadiene and ethylene showed comparable ω values at the same level of theory (Table 2). The electronic chemical potential, μ, of the dienophiles are less than cyclopentadiene, indicating that the charge transfer will take place from cyclopentadiene to the dienophiles, whereas, the electronic chemical potential, μ, values are comparable for 1,3-butadiene and ethylene (Table 2). Therefore, neither of them tend to provide charge to the other, in agreement with a non-polar pattern.

The higher level DFT B3LYP/6-31G* calculated results predict the *exo*-selectivity for methyl acrylate with cyclopentadiene in the gas phase. However, the selectivities predicted in water and methanol is *endo*-preferred (Table 3). Methyl methacrylate with cyclopentadiene is *exo*-selective in all cases as predicted in the RHF level of theory and in agreement with the observed selectivities.[17] The trend of *endo*/*exo* selectivity for methyl *trans*-crotonate with cyclopentadiene predicted at B3LYP was found to be *exo*-selective in all cases, which is opposite to the observed selectivity ratios. These results suggest that the hybrid-DFT B3LYP calculations do not predict the stereoselectivity correctly in all cases. To verify the B3LYP/6-31G* calculated single point results, the transition structures were optimized in the gas phase and water at this level of theory as well. The computed relative energies upon optimization at B3LYP/6-31G* level was found to be similar to that obtained with B3LYP/6-31G*//RHF/6-31G* single point calculations (Table 3).

Table 2. B3LYP/6-31G*//RHF/6-31G* calculated global properties for diene and dienophiles in gas phase

Molecule	Global properties		
	ω/eV	μ/*a.u.*	η/*a.u.*
Methyl acrylate	5.49	−0.30827	0.23523
Methyl methacrylate	4.99	−0.29487	0.23693
s-cis-Methyl *trans*-crotonate	4.89	−0.29331	0.23901
Cyclopentadiene	3.12	−0.21943	0.20993
Ethylene	0.71	−0.12330	0.29064
Butadiene	0.95	−0.12503	0.22319

The activation barrier calculated for methyl acrylate in gas phase, water and methanol with CPCM model was found to be higher at RHF/6-31G* level of theory (Table 4). It is known that the HF calculations overestimate the activation barriers for Diels-Alder reactions.[36] The experimental activation enthalpy measured for methyl acrylate and cyclopentadiene in Toluene is 15.1 kcal mol^{-1}.[31] The B3LYP/6-31G* calculated activation enthaply for methyl acrylate and cyclopentadiene in methanol and water was predicted to be 15.2 kcal mol^{-1} in good agreement with the experimental result. Comparing the computed activation enthalpy in the gas and water, it appears that the barrier is marginally lower in water with CPCM solvation model (Table 4). Recently, the QM/MM study performed for Diels-Alder reactions suggest that the increase in the rate in water are primarily due to enhanced hydrogen bonding between the solvent and the polarized transition states. The contribution from enforced hydrophobic association is of minor importance.[1] In our study, the calculations with CPCM solvation model lacks the hydrogen bonding interaction between the solvent and the transition states, and hence the reaction rate predicted to be marginally preferred in water. To examine further, the importance of hydrogen bonding in rate acceleration in water, we have used the semi-empirical AM1-SM5.4

Table 3. B3LYP/6-31G*//RHF/6-31G* calculated relative electronic energies (kcal mol^{-1}) between *endo* and *exo* TS in the gas phase, water and methanol[(a)]

	Cyclopentadiene + Methyl acrylate		Cyclopentadiene + Methyl methacrylate		Cyclopentadiene + *s-cis*-Methyl *trans*-crotonate	
Medium	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
Gas phase	0.43	0.0	1.19	0.0	1.07	0.0
	(0.45)	(0.0)	(1.10)	(0.0)	(1.04)	(0.0)
Water	0.0	0.32	0.87	0.0	0.56	0.0
	(0.0)	(0.26)	(0.90)	(0.0)	(0.35)	(0.0)
Methanol	0.0	0.13	0.85	0.0	0.47	0.0

[(a)] B3LYP/6-31G* optimized relative electronic energies (kcal mol^{-1}) are in ( ).

Table 4. RHF/6-31G* calculated activation enthalpies in kcal mol^{-1} for TSs in the gas phase, water and methanol[(a)]

	Cyclopentadiene + Methyl acrylate		Cyclopentadiene + Methyl methacrylate		Cyclopentadiene + *s-cis*-Methyl *trans*-crotonate	
Medium	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
Gas phase	35.36	35.79	39.96	39.21	40.68	40.19
	(15.48)	(15.04)	(19.12)	(17.92)	(20.45)	(19.38)
Water	35.20	36.53	40.26	40.07	41.19	41.37
	(15.11)	(15.43)	(19.28)	(18.41)	(20.88)	(20.32)
	[34.14]	[35.77]	[38.94]	[39.20]	[40.09]	[41.70]
Methanol	35.44	36.54	40.28	40.09	41.17	41.40
	(15.33)	(15.46)	(19.30)	(18.45)	(20.82)	(20.35)

[(a)] B3LYP/6-31G*//RHF/6-31G* calculated activation enthalpies in kcal mol^{-1} ( ) and SM5.4 calculated activation enthalpies in [ ].

solvation model,[53−55] which accounts well for hydrogen-bond formation. The RHF/6-31G* optimized geometry was taken for the calculation of activation enthalpy in SM5.4 solvation model. The SM5.4 calculated results show that the activation enthalpy for methyl acrylate with cyclopentadiene in *endo*- attack is lower by 1.22 kcal mol^{-1} compared to the gas phase result in agreement with the recent study.[1] This trend was also observed for methyl methacrylate and methyl *trans*-crotonate in water as well (Table 4).

The importance of electric dipole moment of transition state geometries was also discussed in terms of influence of solvent polarity and selectivity.[17,56] We have examined the role of dipole moment towards the selectivity ratios for these dienophiles with cyclopentadiene. The calculated dipole moments with RHF/6-31G* and B3LYP/6-31G* suggest that the *endo*-transition states have higher dipole moments than their corresponding *exo*-transition states in the gas and solvent phase (Table 1). The stereoselectivity trend observed for methyl acrylate, methyl methacrylate and methyl *trans*-crotonate cannot be explained on the basis of dipole moment results. There is apparently no connection between the dipole moments and ratios of *exo*- and *endo*- products for these Diels-Alder reactions.

CONCLUSION

In the present work, we have investigated the stereoselectivities of methyl acrylate, methyl methacrylate and methyl *trans*-crotonate with cyclopentadiene in gas and solvent phase. The stereoselectivities predicted for methyl acrylate were found to be in good agreement with the observed results. The higher *endo* selectivity in water compared to methanol was also borne out from this computational study. The degree of asynchronicity of transition states seems to be important in solvents to determine the observed stereoselectivity. Hydrogen bonding between the solvent and the polarized transition states is more important for rate enhancement in water than the hydrophobic association of diene and dienophile. The computed activation enthalpy with B3LYP/6-31G* level is in good agreement with the experimental activation enthalpies, however, this method does not predict the stereoselectivity correctly in all cases. The global electrophilicity index calculations showed the polar nature of the transition states for these DA reactions.

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SAŽETAK

Utjecaj otapala na stereoselektivnost metil akrilata, metil metakrilata i metil *trans*-krotonata s ciklopentadienom: računska studija

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Proučavana je stereoselektivnost metil akrilata, metil metakrilata i metil *trans*-krotonata s ciklopentadienom primjenom *ab initio* RHF/6-31G* i B3LYP/6-31G* nivoa teorije. Predviđena stereoselektivnost za metil akrilat i metil metakrilat s ciklopentadienom u plinskoj fazi je u dobrom slaganju s eksperimentalnim rezultatima. Prioritetnost *endo*-selektivnosti u otopini je izraženija za metil akrilat, dok je prioritetnost *egzo*-adicije metil metakrilata u otopini smanjena. Računi u otopini predviđaju *endo*-prioritetnost za metil *trans*-krotonat u skladu s eksperimentalnim opažanjima. Smanjena *endo*-selektivnost metil *trans*-krotonata s ciklopentadienom čini se da je utvrđena stupnjem asinhroniteta *endo*- i *egzo*-prijelaznih stanja u vodi. Aktivacijske entalpije izračunate na B3LYP/6-31G* razini teorije su u dobrom slaganju sa opaženim aktivacijskim entalpijama metil akrilata i ciklopentadiena, no ova metoda ne predviđa stereoselektivnost na ispravan način u svim slučajevima. Stvaranje vodikove veze između molekula vode i polariziranih prijelaznih stanja ima važnu ulogu za ubrzavanje reakcija u vodi.