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Theoretical Study of the Reactivity and Stereoselectivity of Heterodienophile Addition to 1,3,4-Oxadiazole

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Transition structures for Diels–Alder reactions of 1,3,4-oxadiazole with formaldehyde, formaldimine, diazenes, and nitrosyl hydride have been located by ab initio molecular orbital calculations using the RHF/3-21G level of theory. The activation energies were calculated with the MP2/6-31G*//RHF/3-21G theoretical model. Formaldehyde and exo hydrogen formaldimine have a higher activation energy than ethylene addition to 1,3,4-oxadiazole while the others have similar or lower activation energies. Transition structures that have an endo nitrogen or oxygen lone electron pair have higher energies than the corresponding structures with the exo lone pair. The opposite effect was obtained when a hydrogen was attached to nitrogen, the endo hydrogen decreases the energy of the transition structure. The exo-lone-pair preference for formaldimine is 7.0 kcal/mol, for *cis*-diazene 16.6 kcal/mol, and for nitrosyl hydride 9.0 kcal/mol estimated by MP2/6-31G*. These preferences are the result of the electrostatic repulsion between the nitrogen lone pair and the oxadiazole π-electrons and electrostatic attraction between the hydrogen bound to nitrogen and the oxadiazole π-electrons.

Introduction

The Diels–Alder reaction continues to be an important method for the preparation of a wide variety of products.[1] The hetero Diels–Alder reaction can be a powerful tool for the synthesis of natural heterocyclic compounds.[2] These reactions are generally assumed to be concerted, asynchronous cycloadditions, although the stepwise mechanism with charge separation or biradical intermediates has also been considered.[3] However, high level ab initio calculations prefer the concerted transition structure over the biradicaloid transition structure for the Diels–Alder reaction.[4] Although there is a large body of computational work on the all-carbon Diels–Alder reactions[5], the hetero Diels–Alder reactions[6] and particularly the heterodienophile additions to five-membered heterocycles[7] as dienes are underinvestigated. There is a recent Diels–Alder computational study on the addition of ethylene to two five-membered heterocycles (isoxazole and oxazole).[8] In view of the importance of the products, as well as from a theoretical point, it is interesting to study other heterocyclic dienes in Diels–Alder reactions. Here we are reporting the calculation on the transition structures in the addition of hetero dienophiles (formaldehyde, formaldimine, *trans*-diazene, *cis*-diazene, and nitrosyl hydride) to 1,3,4-oxadiazole. To the best of our knowledge there is no experimental evidence for the use of 1,3,4-oxadiazole or its derivatives as dienes in Diels–Alder reactions. Our preliminary results show that these reactions are feasible and an experimental study is underway.

Computational Methods

The structures of the compounds were built with Chem-X[9] and were saved as MOPAC[10] files for PM3[11] semiempirical calculations. The transition states were located with the SADDLE routine in MOPAC[12] and the obtained structures were refined with NLLSQ. These obtained structures were used as input files for ab initio calculations. The geometry optimizations were performed without restrictions at the RHF theory level using Gaussian 92.[13] Structures were fully optimized with the 3-21G basis set, followed by vibrational frequency calculations. All transition states were verified by having only one negative eigenvalue corresponding to one imaginary vibration whereas the ground states of the reactants and the products had no imaginary vibrations. Electron correlation energies were computed via restricted Hartree–Fock calculations and second-order

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Moller–Plesset perturbation theory with the 6-31G* basis set and frozen core orbitals.[14]

Results and Discussion

For all studied Diels–Alder reactions, a concerted, but potentially nonsynchronous mechanism was considered. For example, the experimentally determined reaction barrier for the 1,3-butadiene and ethylene cycloaddition is 27 kcal/mol.[15] Although the calculated barrier for the biradical transition state is only a few kcal/mol higher than for the concerted transition structure, nevertheless, it is broadly accepted that it follows a concerted pathway.[5]

The RHF/3-21G model chemistry has been used in the study of many Diels–Alder reactions. The obtained transition state geometries are in qualitative agreement compared to the MP2/6-31G* and MCSCF theoretical models, but since the electron correlation is not accounted for, this model is insufficient for energy calculations. On the other hand, although the second-order Moller–Plesset theory overestimates the effect of electron correlation in the transition structure, it has been shown that the relative energy values correctly estimate the effect of the substituents.[5,6]

In the work described herein, eight transition structures were located for the five dienophiles studied since some of the reactions have both endo and exo transition states. The concerted transition structures were found for all of the reactions and the geometries of the transition structures are presented in Figure 1. The structures of the heterodienophiles[7] and 1,3,4-oxadiazoles generated by the RHF/3-21G theoretical model were reported previously but the MP2/6-31G*//RHF/3-21G energies are reported herein.

Asymmetry and Geometries of the Transition Structures. It is not unexpected that the transition-state structures with the unsymmetrical dienophiles are asynchronous, i.e., have different lengths for the two new forming bonds. This difference has been explained in terms of the dienophile heteroatom lone pair interactions with the π-system of the diene.[6e] However, one must also first consider the differences in the overlap since two different bonds are being formed. The n–π interactions are absent in the structures of the products (Figure 2), so the bond length ratios in the transition states and the bond lengths in the products should indicate what effects are responsible for the asynchronicity (Table 1).

The transition structure for the formaldehyde addition to 1,3,4-oxadiazole (1) shows asynchronicity. By comparing the ratios of the new forming bonds in the products and the TS, it is apparent that it arises mostly from the differences in the overlap and the n–π interaction has a negligible effect.

The exo hydrogen transition structure 2 of formaldimine addition to oxadiazole shows a higher degree of asynchronicity ($\Delta r = 0.23$ Å), and the endo hydrogen transition structure 3 shows an even higher effect ($\Delta r = 0.36$ Å). Since the ratios of the bond lengths are different for the products and the TS (Table 1), it is obvious that the differences in overlap are not the only factors contributing to this effect. Endo lone pair repulsive interactions in 2, on the one hand, and endo hydrogen attractive interactions, on the other, are also responsible for the asynchronicity of these structures. The H_{exo}–N–C–H_{exo} dihedral in 2 and H_{endo}–N–C–H_{exo} in 3 is consistent with this proposed n–π repulsion and endo hydrogen attraction.

The addition of *trans*-diazene is an interesting case. In the transition structure 4, the lone pair repulsion and endo hydrogen attraction interactions with the π-system of the diene make the structure very asynchronous. In the product where the π-system is absent, these interactions do not exist, and the ratio of the lengths is actually reversed.

A very similar case is the endo nitrosyl hydride addition, where there are strong lone oxygen pair electron repulsion interactions and endo hydrogen repulsive interactions with the π-system of oxadiazole in the transition state which disappear in the final product. Again the ratio of the bond lengths is reversed.

Energetics of the Transition Structures. The calculated total energies for the reactants and the transition structures and the activation energies are given in Tables 2 and 3, respectively. The calculated activation energy for the reaction of oxadiazole with formaldehyde is 25.4 kcal/mol at the MP2/6-31G* level, a value much higher than that for the reaction with ethylene which is 15.9 kcal/mol.[16] The activation energy at the same theory level for the ethylene addition to butadiene is 17.6 kcal/mol,[6e] 1.6 kcal/mol higher than in the case of oxadiazole. On the other hand, when instead of ethylene, formaldehyde was used as dienophile in reaction with butadiene, the activation barrier increased by only 3.3 kcal/mol.[6e] In the present study in reaction with 1,3,4-oxadiazole, it shows an increase of 9.5 kcal/mol. Frontier molecular orbital (FMO) theory predicts that the incorporation of an electronegative atom into the dienophile will decrease its LUMO energy and lower the activation energy of the Diels–Alder reactions.[17] The rate accelerations have been calculated for other pericyclic reactions with oxo substitution.[18] Nevertheless, our calculation at the MP2/6-31G* level shows a 9.5 kcal/mol activation energy increase in respect to ethylene. This result is not so surprising if we compare the frontier orbital energies for the oxazole and heterodienophiles (Table 4). In terms of the FMO, the Diels–Alder reaction of 1,3,4-oxadiazole with ethylene appears to be controlled by the HOMO of the dienophile (Table 4), while in the case of the formaldehyde it is controlled by the LUMO of the dienophile. The energy difference is higher with formaldehyde as dienophile by 0.02402 eV than with ethylene and is reflected in the higher activation energy (by 9.5 kcal/mol, Table 2). Addition of formaldimine and *trans*- and *cis*-diazene to 1,3,4-oxadiazole is HOMO-dienophile controlled while the addition of the nitrosyl hydride is

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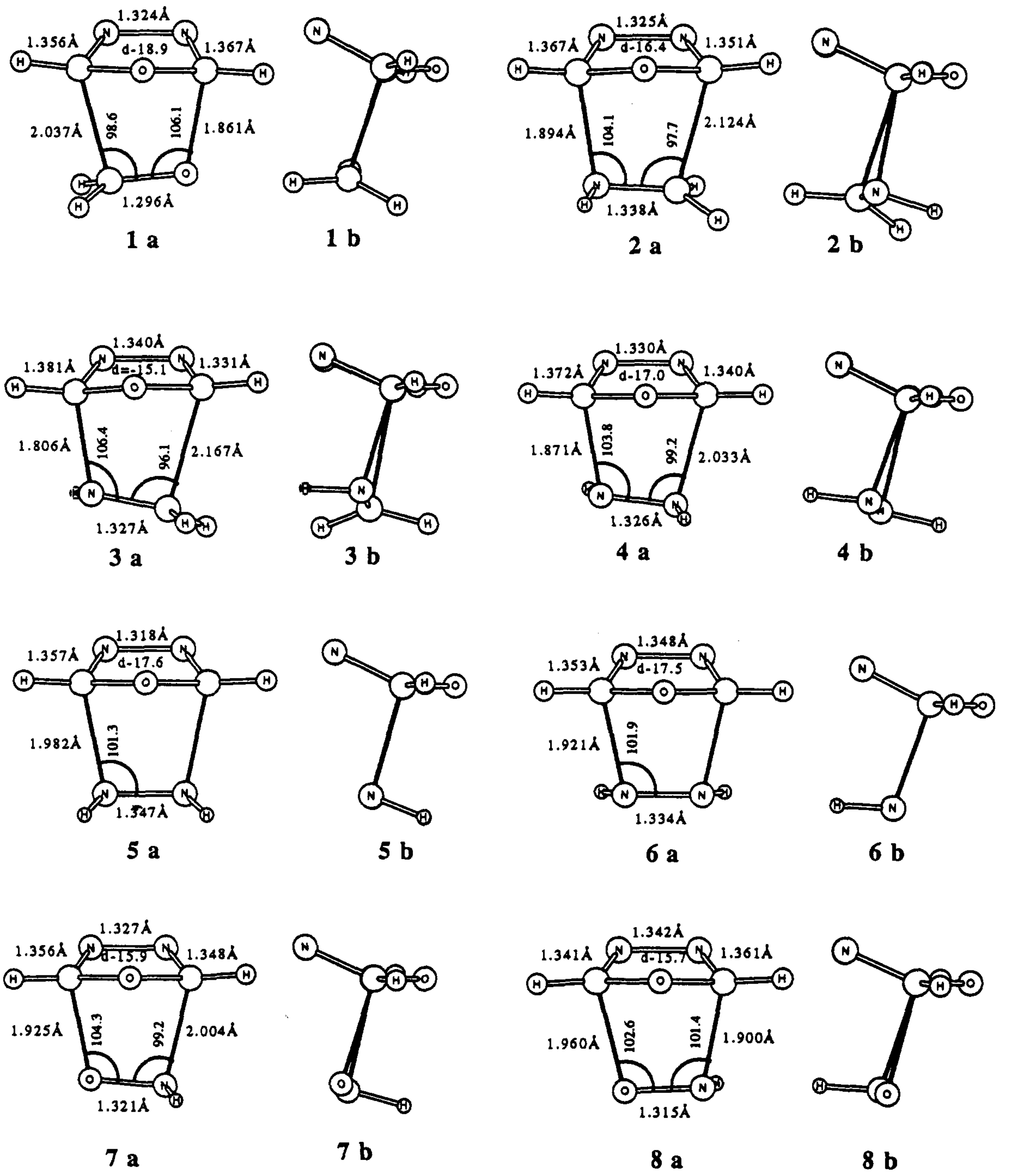

Figure 1. Front (a) and side (b) views of the transition-state structures for the Diels–Alder reaction of 1,3,4-oxadiazole with formaldehyde (1), formaldimine, exo (2), formaldimine, endo (3), *trans*-diazene (4), *cis*-diazene, exo (5), *cis*-diazene, endo (6), nitrosyl hydride, exo (7), and nitrosyl hydride, endo (8). (Angles in degrees, d = dihedral of ring O–C–N–N, clockwise.)

LUMO-dienophile controlled. The highest difference is present in the case of formaldimine, which should be the least reactive species in our study, and the nitrosyl hydride should have the lowest enerry barrier in the addition reaction. The prediction of the reactivity of the Diels–Alder reaction studied herein should include more than simple frontier orbital correlation because there are other factors that are also involved.

The predicted activation energies for the heterodienophile addition to 1,3,4-oxadiazole are presented in Figure 3. The reaction can be classified into three categories: additions that have higher, addition with similar, and additions with lower activation energies than the oxadiazole–ethylene addition. Interestingly, this energy barrier is the same for the ethylene addition to butadiene, performed at the same theory level.[5b]

In the first group are the transitions structures with formaldehyde (1) and the exo additions of formaldimine (2) and *cis*-diazene (5). The activation energies are quite higher than in the case of the ethylene addition at all studied ab initio levels of calculation (Figure 3). Besides the already mentioned higher gap in the HOMO–LUMO energies for these three dienophiles (Table 4), the bond distance and the lone pair–oxadiazole interactions are important for their higher activation energies. Formaldehydes has a C–O distance of 1.207 Å which is shorter than the C–C bond distance (1.315 Å) in ethylene.[19] 1,3,5-Oxadiazole must be strained to achieve simultaneous

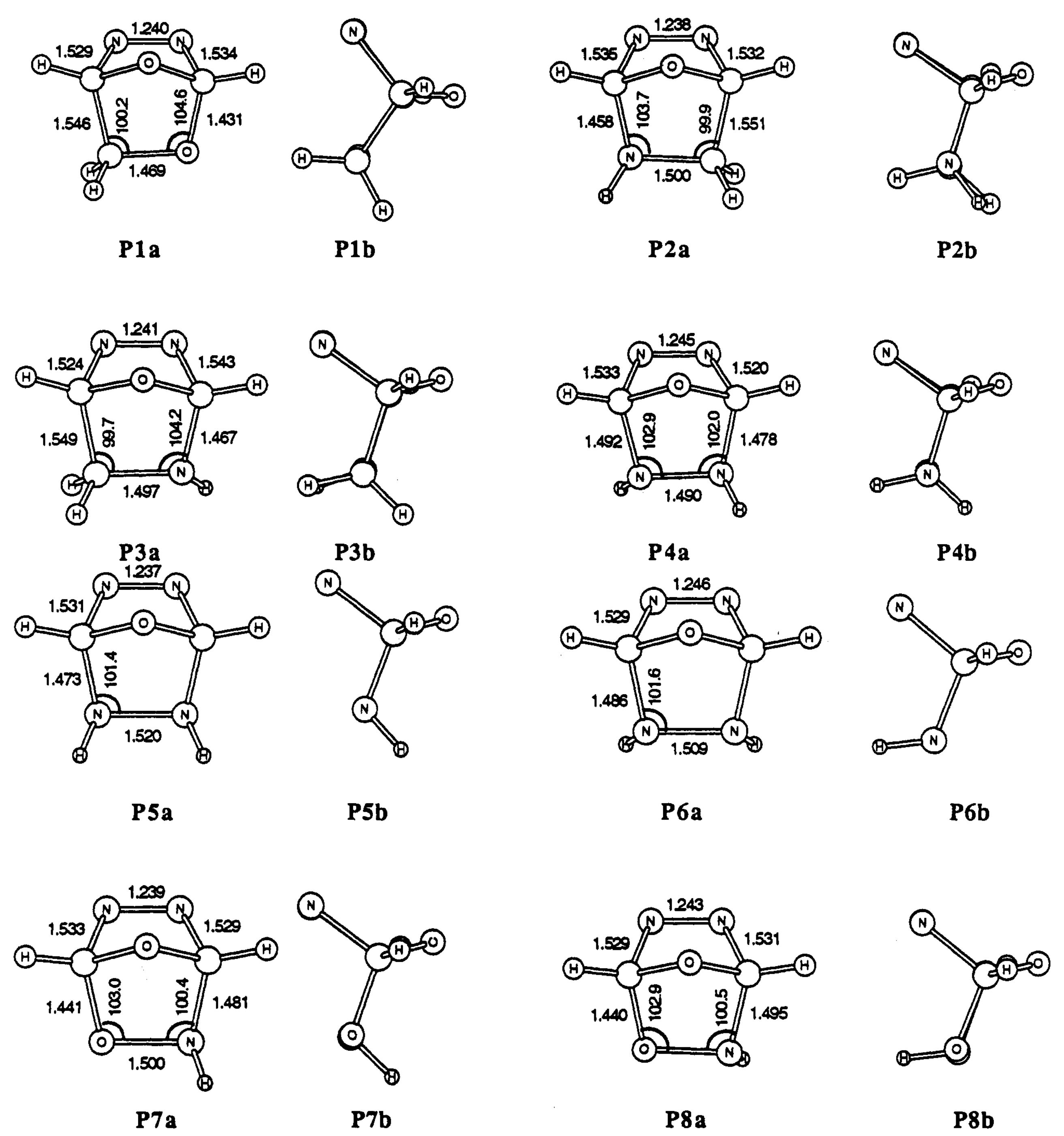

Figure 2. Front (a) and side (b) views of the product structures for the Diels–Alder reaction of 1,3,4-oxadiazole with formaldehyde (1), formaldimine, exo (2), formaldimine, endo (3), *trans*-diazene (4), *cis*-diazene, exo (5), *cis*-diazene, endo (6), nitrosyl hydride, exo (7), and nitrosyl hydride, endo (8). (Angles in degrees, d = dihedral of ring O–C–N–N, clockwise.)

Table 1. New Forming Bond Length Ratio in the Products and the Transition States for the Studied Reactions

	product	transition state		product	transition state
1	1.08	1.09	5	1.00	1.00
2	1.06	1.12	6	1.00	1.00
3	1.06	1.20	7	1.03	1.04
4	1.01	0.92	8	1.04	0.96

overlap at the two ends of the dienophile. Although the C–N bond in formaldimine is longer (1.256 Å), and can be partially explained by differences in the CN and CO overlap, as was pointed out, the lone pair-π interaction in the transition-state structure **2** is considerable. In the exo transition structure **5** there are two lone electron pairs that can interact with the π-system of the oxadiazole ring, thus raising the activation barrier.

In the second group are the reactions that have similar activation energies to the ethylene–oxadiazole reaction. In the endo hydrogen formaldimine–oxazole transition structure **3**, the lone pair nitrogen repulsion interaction with the oxadiazole ring is not present, and consequently, the activation energy is lower than that in the case of exo hydrogen transition structure **2**. Comparison of the HOMO–LUMO energies (Table 4) reveals that the energy of the transition structure should be more unfavorable than that calculated. This can be explained by the relatively polar N–H bond interactions with the π-system

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(19) The bond values were calculated at the RHF/3-21G theory level.

Table 2. Total Energies (au) of Reactants and Transition Structures for the Diels–Alder Reaction of 1,3,4-Oxadiazole with Heterodienophiles

species	RHF/3-21G	RHF/6-31G*// RHF/3-21G	MP2/6-31G*// RHF/3-21G
1,3,4-oxadiazole	−259.12387	−260.60463	−261.35775
formaldehyde	−113.22182	−113.86239	−114.16763
formaldimine	−93.49478	−94.025645	−94.31299
trans-diazene	−109.35477	−109.99247	−110.30837
cis-diazene	−109.34240	−109.97846	−110.29486
nitrosyl hydride	−129.03829	−129.78325	−130.12358
1	−372.28211	−374.38911	−375.48486
2	−352.55101	−354.55000	−355.63424
3	−352.56389	−354.55955	−355.64541
4	−368.42465	−370.51839	−371.65014
5	−368.39575	−370.49353	−371.62262
6	−368.41966	−370.51553	−371.64911
7	−388.10904	−390.30679	−391.45688
8	−388.12029	−390.31819	−391.47135

Table 3. Calculated Activation Energies (kcal/mol) for the Heterodienophile Addition to 1,3,4-Oxadiazole

dienophile	TS	RHF/3-21G	RHF/6-31G*// RHF/3-21G	MP2/6-31G*// RHF/3-2
ethylene[a]		38.1 (0.0)[b]	44.2 (0.0)	15.9 (0.0)
formaldehyde	1	39.9 (1.8)	48.9 (4.7)	25.4 (9.5)
formaldimine, exo H	2	42.4 (4.3)	50.4 (6.2)	22.9 (7.0)
formaldimine, endo H	3	34.3 (−3.8)	44.4 (0.2)	15.9 (0.0)
trans-diazene	4	33.9 (−4.2)	49.4 (5.2)	10.0 (−5.9)
cis-diazene, exo H	5	44.2 (6.1)	56.2 (12.0)	18.8 (2.9)
cis-diazene, endo H	6	29.2 (−8.9)	42.4 (−1.8)	2.2 (−13.7)
nitrosyl hydride, exo H	7	33.3 (−4.8)	50.9 (6.7)	15.3 (−0.6)
nitrosyl hydride, endo H	8	26.3 (−11.9)	43.7 (−0.5)	6.3 (−9.6)

[a] From ref 17. [b] Value in parentheses is the difference in activation energy (kcal/mol) from the ethylene addition to 1,3,4-oxadiazole.

Table 4. LUMO and HOMO Energies (eV) of 1,3,4-Oxadiazole and the Heterodienophiles Calculated by RHF/6-31G*[a]

compound	HOMO	LUMO	ΔE_{I}	ΔE_{II}
1,3,4-oxadiazole	−0.41559	0.14873		
ethylene[b]	−0.37480	0.18439	0.52353	0.59998
formaldehyde	−0.43982	0.13196	0.58855	0.54755
formaldimine	−0.41750	0.16317	0.56623	0.57876
trans-diazene	−0.38664	0.14689	0.53537	0.56248
cis-diazene	−0.38110	0.14771	0.52983	0.56330
nitrosyl hydride	−0.42710	0.09039	0.57583	0.50598

[a] $\Delta E_{\mathrm{I}} = E_{\mathrm{LUMO(1,3,4\text{-}oxadiazole)}} - E_{\mathrm{HOMO(dienophile)}}$. $\Delta E_{\mathrm{II}} = E_{\mathrm{LUMO(dienophile)}} - E_{\mathrm{HOMO(1,3,4\text{-}oxadiazole)}}$. [b] From ref 17.

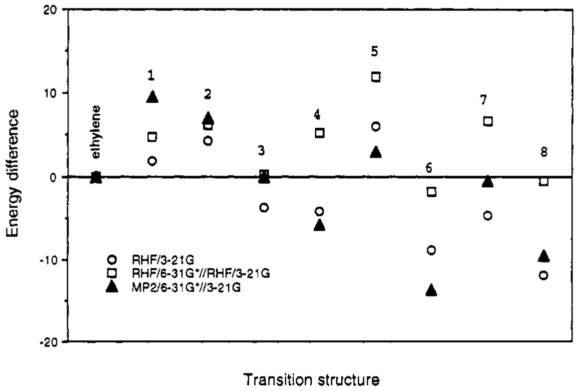

Figure 3. Activation energy for the heterodienophile addition to 1,3,4-oxadiazole correlated to the ethylene addition obtained by various theoretical models.

of the oxadiazole ring. Another reaction in this group is the exo hydrogen nitrosyl hydride–oxadiazole cycloaddition (7). Although FMO predicts (Table 4) a lower HOMO–LUMO energy gap, in the transition structure 7 there are two lone pair oxadiazole ring repulsion interactions that considerably increase the activation energy.

In the third group are the heterodienophile–oxadiazole reactions that have considerably lower activation energy than the ethylene–oxadiazole reaction. The transition structures 4, 6, and 8 have maximal possible interactions of the polar N–H bond with the oxadiazole ring and minimal repulsion interactions between the lone pairs and π-system of the oxadiazole ring. These interactions decrease the energy of the transition states and lower the barrier. Of all the studied species, the endo addition of *cis*-diazene to 1,3,4-oxadiazole is predicted to be the most energetically favored one.

These large endo preferences in the addition of *cis*-diazene (16.6 kcal/mol) and nitrosyl hydride (9.0 kcal/mol) should be useful in designing reagents for enantioselective Diels–Alder reactions. Werbitzky *et al.* and Sabuni *et al.* have experimentally demonstrated that some α-chloro nitroso compounds undergo Diels–Alder reactions with very high enantioselectivity, supporting this finding.[20]

Conclusion

This study shows that the reactions of 1,3,4-oxadiazole with formaldehyde, formaldimine, *cis*- and *trans*-diazene, and nitrosyl hydride are concerted and nearly synchronous. The MP2/6-31G* level of theory underestimates the activation energies but seems to reflect accurately the relative reactivity of the heterodienophiles. Stereoselectivity is determined by the interaction of the π-orbitals of the diene with the heterodienophiles. The lone pair orbitals on the heterodienophiles can exert a large destabilizing influence on the filled orbitals of 1,3,4-oxadiazole. On the other hand, the N–H bond interactions with the ring π-orbitals stabilize the corresponding transition structure. Both of these interactions can have a very large influence on stereoselectivity of the reaction.

When compared to the calculated energy barriers for the ethylene addition to butadiene performed at the same theory level,[5b] this study predicts that the reaction should be feasible under similar conditions with formaldimine, giving rise to the endo product. The reaction should be even easier to perform with *trans*-diazene, nitrosyl hydride, and *cis*-diazene, the last two again favoring the endo addition.

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