Theoretical Study of the Mechanism of the Addition of Diazomethane to Ethylene and Formaldehyde. Comparison of Conventional ab Initio and Density Functional Methods

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The 1,3-dipolar cycloaddition reactions of diazomethane with ethylene and formaldehyde as well as the nitrogen elimination reactions from the cycloadducts have been studied using density functional and conventional ab initio methods. The exothermicity of the reactions is underestimated by DFT methods with respect to CCSD(T) due to an overestimation of the C−N dissociation energy of diazomethane. For the cycloaddition reactions all methods lead to similar transition state geometries, and the potential energy barriers computed using DFT methods are similar to the CCSD(T) ones. On the other hand, for the nitrogen elimination reactions transition state geometries and energy barriers are more dependent on the level of calculation. The results obtained show that for the reaction between diazomethane and ethylene the pyrazoline intermediate is more stable than the reactants and that the Gibbs energy barrier for nitrogen elimination is larger than the barrier corresponding to its formation. On the contrary, for formaldehyde the kinetically most favorable cycloadduct, 1,2,3-oxadiazoline, is less stable than the reactants and has a lower barrier for nitrogen elimination.

Introduction

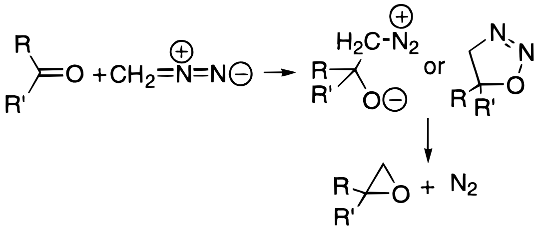
The 1,3-dipolar cycloaddition of diazomethane to electron-poor olefins is a useful synthetic tool in obtaining of cyclopropane derivatives through photoinduced or thermal decomposition of the corresponding pyrazolines.[1] The reaction of diazomethane with carbonyls leading to the direct formation of oxiranes has also been reported by our group.[2] Ortuño et al. have recently observed that in the reaction between diazomethane and chiral cyclohexenones catalyzed by palladium diacetate the methylenation can take place both at the C═C double bond and at the carbonyl group, the site-selectivity of the process being related to the nature of the substituents.[3] More recently, Saladino et al.[4] have reported the unexpected 1,3-dipolar cycloaddition of diazomethane to a carbonyl group in uracil and uridine derivatives leading to the formation of oxadiazolines.

The formation of epoxides from the thermal reaction between diazomethane and carbonyl compounds is generally explained through a two-step mechanism that involves the formation of betaines or 1,2,3-oxadiazolines as intermediates[5] (Scheme 1). The formation of oxadiazolines as intermediates was discarded for a long time in favor of betaines, but Huisgen awakened a new interest in oxadiazolines with his fundamental studies on 1,3-dipolar cycloadditions.[6] However, the formation of such intermediates is rarely detected.

The cycloaddition of diazomethane to olefins has been theoretically studied by several authors.[7−11] Annunziata et al.[10] have located the transition state of the addition of diazomethane to ethylene at the HF/3-21G level of calculation. The transition states corresponding to reactions with other olefins have also been reported.[9,11]

The addition of diazomethane to thioformaldehyde to yield thiadiazoline has been studied by Sustmann et al.[12] at the HF and CASSCF levels obtaining a concerted mechanism in all cases. CASSCF calculations have also been performed on the reaction between diazomethane and phosphacetylene.[13]

SCHEME 1



Kroeger-Koepke et al.[14] have studied the decomposition of 1,2,3-oxadiazoline to yield diazomethane and formaldehyde at the HF and MP2 levels of calculation. Finally, Sorensen and Sun[15] have reported a study of the reaction between diazoethane and methyl ketene to form cyclopropanones through a two-step process involving the formation of an oxadiazoline intermediate.

In recent years the application of methods based on the density functional theory[16] (DFT) to the study of chemical reactions has experienced a spectacular increase.[17−19] Several authors have shown that DFT methods using gradient-corrected functionals and hybrid functionals provide results in excellent agreement with conventional ab initio methods in cycloaddition reactions.[18,19] The application of DFT methods in the study of 1,3-dipolar reactions has been considered by Sosa et al.[19] These authors have studied the reactions of fulminic acid and nitrone with ethylene and acetylene using several functionals. They predict concerted mechanisms, in excellent agreement with CASSCF calculations.[20] The potential energy barriers computed with functionals that include gradient corrections are in reasonable agreement with those obtained at the MP4SDTQ level of calculation.[19]

In this paper we report a theoretical study on the mechanism of the reactions of diazomethane with ethylene and formaldehyde using several theoretical methods. For the reaction of

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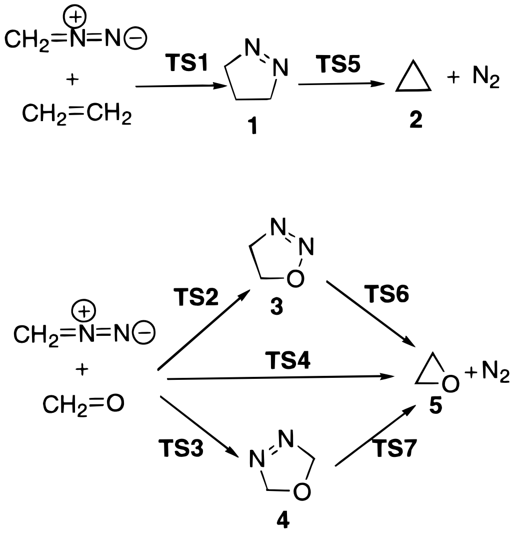
SCHEME 2



formaldehyde we have considered several mechanisms: a direct mechanism leading to the formation of oxirane and nitrogen and two mechanisms involving the formation of oxadiazolines as intermediates (see Scheme 2). We have used both conventional ab initio and density functional methods, so that the results obtained at different levels of calculation will be compared.

Computational Details

All calculations have been done using the Gaussian-94 program.[21] In the DFT calculations several gradient-corrected functionals have been used. The first one, denoted BLYP, consists of the Becke[22] exchange functional with the correlation functional of Lee, Yang, and Parr.[23] In the second one, the hybrid Becke[24] exchange functional has been used with the LYP correlation functional (B3LYP). Finally, the Becke exchange functional has also been used with the correlation functional of Perdew and Wang[25] (BPW91). Conventional ab initio calculations have been performed using the quadratic configuration interaction with single and double excitations (QCISD)[26] and the complete active space self-consistent field (CASSCF)[27] methods. In the QCISD calculations the 1s orbitals of C, N, and O have been kept frozen. In the CASSCF calculations for the transtition states of the reactions of diazomethane with ethylene and formaldehyde the active space consists of 8 electrons in 7 orbitals. This space would be consistent with an active space of 6 electrons in 5 orbitals for diazomethane, the active orbitals being $1b_1$, $7a_1$, $2b_1$, $3b_1$, and $8a_1$, that describe the π system and the σ_{C-N} bond, and an active space consisting of the π orbitals of ethylene and formaldehyde. For the transition states of the N_2-elimination reactions from pyrazolines and oxadiazolines, the active space consists of 4 electrons in 4 orbitals. This space would be consistent with active spaces of 2 electrons in 2 orbitals for each one of the resulting fragments.

Molecular geometries have been fully optimized at these levels of calculation. Transition states have been located with no geometry restriction on the full potential energy surfaces. All calculations have been done using the standard 6-31G* basis set.[28] Harmonic vibrational frequencies have been computed for all stationary points to verify that for energy minima all frequencies are real, while for transition states there is one and only one imaginary frequency.

Potential energy barriers have also been calculated through single-point calculations at the coupled cluster with single and double excitations and a perturbative estimate of the triples (CCSD(T)) level.[29] Finally, to check the effect of the basis set, single-point calculations have been done using the 6-311G** basis set.[28] In some cases the larger cc-pVTZ basis set has also been used.[30]

TABLE 1: Selected Geometry Parameters[a] Obtained at Several Levels of Calculation for Diazomethane, Ethylene, Formaldehyde, 2, 5, and Nitrogen

	CH_2N_2		C_2H_4	H_2CO	**2**	**5**		N_2
	C−N	N−N	C−C	C−O	C−C	C−C	C−O	N−N
QCISD	1.299	1.155	1.338	1.217	1.507	1.468	1.435	1.115
BLYP	1.304	1.160	1.341	1.218	1.5215	1.481	1.450	1.118
B3LYP	1.293	1.146	1.331	1.2065	1.5085	1.469	1.430	1.1055
BPW91	1.299	1.158	1.339	1.215	1.513	1.475	1.439	1.116
expt	1.300[b]	1.139[b]	1.339[c]	1.208[d]	1.510[e]	1.513[f]	1.435[f]	1.094[g]

[a] See Scheme 2; bond lengths in Å. [b] ref 31. [c] Reference 32. [d] Reference 33. [e] Reference 34. [f] Reference 35. [g] Reference 36.

Results and Discussion

We have first studied the 1,3-dipolar cycloaddition reactions of diazomethane to ethylene and formaldehyde leading to the formation of pyrazoline **1** and oxadiazolines **3** and **4** (Scheme 2). For formaldehyde we have also considered a direct mechanism that would yield oxirane **5** in a single step. The possible formation of a betaine intermediate has also been considered, but all attempts lead to oxadiazoline **3** or to oxirane and nitrogen.

Tables 1 and 2 present the geometries of the reactants and products of the studied reactions obtained at different levels of calculation. Table 1 shows that all theoretical methods yield similar bond lengths, in excellent agreement with experiment. Regarding the geometries of the products of the 1,3-dipolar cycloadditions (Table 2), one can observe that all theoretical methods also yield very similar results. The maximum difference is obtained for the N−O bond length in **3**, where the value computed at the BLYP level of calculation is 0.048 Å larger than the B3LYP result.

Table 3 presents the values of the cycloaddition reaction energies computed at different levels of calculation. We have also computed CCSD(T) reaction energies using all DFT optimized geometries, and the values obtained are very similar to the values based on QCISD geometries. We can observe that DFT methods underestimate the exothermicity of the reactions with respect to QCISD and CCSD(T). Moreover, we can observe an important dispersion between the values obtained with the different functionals. In all cases, the maximum discrepancy with the CCSD(T) value is obtained in the BLYP calculations, while the minimum discrepancy corresponds to B3LYP in the formation of **1** and **4**, and to BPW91 in the formation of **3**. The values obtained for the formation energy of **3** can be compared with the value of -16.0 kcal mol^{-1} reported by Kroeger-Koepke et al. at the MP2 level.[14]

We have examined the basis set dependence of the reaction energies at the B3LYP and CCSD(T) levels of calculation using the 6-311G** basis set. For the formation of **1** the computed reaction energies are, respectively, -30.0 and -39.5 kcal mol^{-1}. If we compare these values to the ones presented in Table 3, we can observe that there is an important basis set effect in the B3LYP calculation, while the CCSD(T) value only slightly changes. On the other hand, for the formation of **3** the computed reactions energies are -13.8 kcal mol^{-1} at the CCSD(T)/6-311G** level and -8.9 kcal mol^{-1} at the B3LYP/6-311G** level. In this case, the CCSD(T) value is also sensitive to the basis set (see Table 3). Finally, for the formation of **4** the reaction energies are -25.8 kcal mol $^{-1}$ (CCSD(T)) and -19.9

TABLE 2: Selected Geometry Parameters[a] Obtained at Several Levels of Calculation for the Products of the 1,3-Dipolar Cycloadditions of Diazomethane with Ethylene and Formaldehyde

	1				3						4			
	C−C	C−N	N−N	C−N−N	C−O	C−C	C−N	N−N	N−O	C−N−N	C−O	C−N	N−N	C−N−N
QCISD	1.537	1.494	1.247	112.6	1.446	1.532	1.483	1.234	1.421	111.6	1.415	1.481	1.247	110.2
BLYP	1.553	1.515	1.253	113.2	1.461	1.549	1.500	1.238	1.466	112.1	1.429	1.499	1.255	110.1
B3LYP	1.542	1.494	1.239	112.8	1.444	1.536	1.482	1.227	1.418	111.8	1.413	1.480	1.240	110.2
BPW91	1.546	1.501	1.249	112.5	1.456	1.540	1.488	1.238	1.432	111.7	1.421	1.486	1.252	110.0

[a] See Scheme 2; bond lengths in Å, bond angles in degrees.

TABLE 3: Reaction Energies[a] for the 1,3-Dipolar Cycloadditions of Diazomethane with Ethylene and Formaldehyde Leading to the Formation of 1, 3, and 4 Obtained at Different Levels of Calculation

	1	3	4
QCISD	−42.3	−17.3	−29.2
CCSD(T)[b]	−41.6	−17.9	−28.7
BLYP	−29.6	−11.8	−18.2
B3LYP	−37.0	−15.7	−25.9
BPW91	−36.1	−17.3	−23.4

[a] In kcal mol^{-1}. [b] QCISD/6-31G* geometries.

TABLE 4: Decomposition of the Diazomethane + Ethylene Reaction Energy Computed at Different Levels of Calculation[a]

	ΔE	ΔE_{dist}	ΔE_{int}
CCSD(T)[b]	−41.6 (0.0)	104.7 (0.0)	−146.3 (0.0)
BLYP	−29.6 (+12.0)	116.4 (+11.3)	−146.0 (+0.3)
B3LYP	−37.0 (+4.6)	126.0 (+21.3)	−163.0 (−16.7)
BPW91	−36.1 (+5.5)	118.7 (+14.0)	−154.8 (−8.5)

[a] In kcal mol^{-1}. In parentheses, values relative to CCSD(T). [b] QCISD/6-31G* geometries.

TABLE 5: Reaction Energies[a] for the Reaction of Formation of 5 from Diazomethane and Formaldehyde and for the Decomposition of 1

	5	1→2
QCISD	−56.9	−30.2
CCSD(T)[b]	−55.0	−28.5
BLYP	−37.9	−20.6
B3LYP	−44.3	−20.9
BPW91	−40.5	−18.4

[a] In kcal mol^{-1}. [b] QCISD/6-31G* geometry.

TABLE 6: Dissociation Energy[a] of Diazomethane into $^1A_1$ CH_2 and N_2

	ΔE
CCSD(T)[b]	40.4 (0.0)
BLYP	58.3 (+17.9)
B3LYP	54.5 (+14.7)
BPW91	64.8 (+24.4)

[a] In kcal mol^{-1}; in parentheses, values relative to CCSD(T). [b] QCISD/6-31G* geometries.

kcal mol $^{-1}$ (B3LYP). From these results we can conclude that there is an important basis set effect in the reaction energies computed using DFT methods. The use of a larger basis set increases the difference between DFT and CCSD(T) reaction energies, so that the underestimation of reaction energies by DFT calculations with respect to CCSD(T) is an intrinsic feature of these methods.

To analyze the dependence on the level of calculation of the reaction energies, we have decomposed the formation energy of **2** from diazomethane and ethylene into two contributions: the distortion energy of both reactant molecules from their equilibrium geometries to the geometries that the corresponding fragments have in the reaction product (ΔE_{dist}) and the interaction energy between the distorted reactant fragments (ΔE_{int}). The results obtained in this analysis are presented in Table 4. We can observe that all DFT methods overestimate the distortion energy with respect to CCSD(T). The main contribution to this term comes from the diazomethane fragment.

Table 5 presents the values computed for the reaction energies corresponding to the direct formation of **5** from diazomethane and formaldehyde and to the nitrogen elimination from **1** leading to **2**. We can observe again that DFT methods underestimate the reaction energies with respect to QCISD and CCSD(T).

The underestimation of these reaction energies as well as those presented in Table 3 by DFT methods can be related to the values of the dissociation energy of diazomethane into CH_2 (ã $^1A_1$) and N_2 shown in Table 6. We can observe that all DFT methods overestimate this dissociation energy with respect to CCSD(T). This discrepancy decreases when a larger basis set is used, but it is still important: using the cc-pVTZ basis set, the computed values are 39.8 kcal mol^{-1} at the CCSD(T) level and 50.7 kcal mol^{-1} at the B3LYP level. These values can be compared with those reported in the literature at the MP4SDTQ/6-31G* level (43.6[37] and 42.6[31] kcal mol^{-1}) and at the CASSCF level (22.2 kcal mol^{-1}).[38] The experimental values reported for the dissociation enthalpy range between 51 and 62 kcal mol^{-1}, depending on the value taken for the enthalpy of formation of diazomethane.[31] From these results we can conclude that the underestimation of the exothermicity of the reactions of diazomethane with ethylene and formaldehyde in DFT calculations with respect to CCSD(T) is due to the overestimation of the dissociation energy of diazomethane.

Figure 1 presents the structures of the transition states for the reactions of diazomethane with ethylene and formaldehyde. Tables 7 and 8 present the values of the most relevant geometry parameters obtained for these transition states at different levels of calculation. The values of the corresponding potential energy barriers are presented in Table 9.

Table 7 shows that for the reaction between diazomethane and ethylene, all levels of calculation provide similar geometries for the transition state. These values are also similar to those obtained by Annunziata et al.[10] at the HF/3-21G level of calculation. Regarding the computed potential energy barriers for this reaction, Table 9 shows that the values obtained in the DFT calculations are in reasonable agreement with CCSD(T), while the barrier is overestimated at the QCISD level.

For the reactions of formaldehyde, Table 9 shows that the formation of **3** is kinetically the most favorable process, while oxadiazoline **4** is thermodynamically more stable (see Table 3). On the other hand, the direct formation of **5** involves the highest energy barrier, so that this mechanism would not be operative.

Table 8 shows that all levels of calculation lead to similar geometries for the transition states corresponding to the formation of oxadiazolines **3** and **4**. On the other hand, for the direct mechanism the transition state geometries vary within a broader range. From the values of the C−N (the breaking bond) and

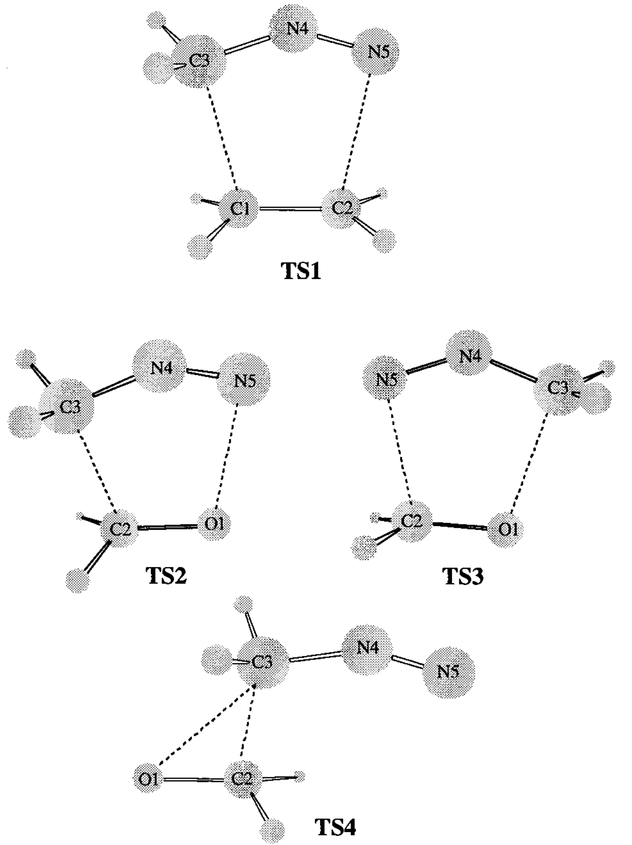


Figure 1. Geometries of the transition states of the reactions of diazomethane with ethylene (**TS1**) and formaldehyde (**TS2**, **TS3**, and **TS4**).

TABLE 7: Selected Geometry Parameters[a] Corresponding to the Transition State of the Reaction between Diazomethane and Ethylene (TS1) Obtained at Different Levels of Calculation

	QCISD	CASSCF	BLYP	B3LYP	BPW91
C2−C1	1.378	1.384	1.384	1.374	1.378
C3−C1	2.210	2.171	2.278	2.255	2.301
N4−C3	1.357	1.388	1.360	1.347	1.345
N5−N4	1.168	1.140	1.174	1.159	1.168
N5−C2	2.303	2.352	2.394	2.350	2.406
N5−N4−C3	142.4	139.0	144.0	144.4	145.2

[a] See Figure 1; bond lengths in Å and bond angles in degrees.

C−C (one of the forming bonds) distances, we can observe that all the DFT calculations predict a transition state that appears later along the reaction coordinate than the conventional ab initio methods.

Regarding the potential energy barriers, Table 9 shows that for the reactions involving formaldehyde the BLYP and BPW91 energy barriers are somewhat lower than the CCSD(T) values, while the B3LYP calculations lead to a closer agreement with CCSD(T). On the other hand, the energy barrier for the formation of **3** has been reported to be only 3 kcal mol^{-1} with the MP2 method.[14] The comparison of the CCSD(T) barriers computed at different geometries shows that for the formation of **3** and **4** the dispersion is less than 1 kcal mol^{-1}. On the other hand, for the direct formation of **5**, the CCSD(T) energy barriers vary within a range of 3.4 kcal mol^{-1}. These results can be related to the differences in transition state geometries mentioned above.

TABLE 8: Selected Geometry Parameters[a] Corresponding to the Transition States of the Reaction between Diazomethane and Formaldehyde Obtained at Different Levels of Calculation

	QCISD	CASSCF	BLYP	B3LYP	BPW91
TS2					
C2−O1	1.275	1.296	1.276	1.265	1.267
C3−C2	1.961	1.937	2.024	1.986	2.029
N4−C3	1.390	1.394	1.381	1.374	1.365
N5−N4	1.142	1.123	1.158	1.140	1.153
N5−O1	2.235	2.160	2.289	2.258	2.323
N5−N4−C3	143.2	137.7	143.3	143.6	146.0
TS3					
C2−O1	1.273	1.290	1.282	1.266	1.274
C3−O1	2.052	1.975	2.074	2.074	2.116
N5−C2	2.008	2.045	2.016	2.007	1.988
N5−N4	1.189	1.157	1.195	1.179	1.189
N4−C3	1.333	1.347	1.342	1.325	1.329
N5−N4−C3	138.6	135.0	138.4	139.7	140.7
TS4					
C2−O1	1.280	1.266	1.298	1.293	1.315
C3−C2	1.761	1.810	1.695	1.636	1.600
N4−C3	1.422	1.469	1.450	1.491	1.510
N5−N4	1.137	1.1245	1.155	1.134	1.150
C3−O1	2.386	2.395	2.328	2.239	2.200
C3−C2−O1	102.3	100.8	101.3	99.0	97.6
N5−N4−C3	154.2	143.5	147.4	144.3	141.1

[a] See Figure 1; bond lengths in Å and bond angles in degrees.

TABLE 9: Energy Barriers[a] for the Reactions[b] of Diazomethane with Ethylene and Formaldehyde Leading to the Formation of 1, 3, 4, and 5

	TS1	TS2	TS3	TS4
QCISD	18.0 (13.8)	14.3 (11.0)	19.7 (15.9)	21.6 (18.9)
BLYP	12.5 (13.7)	8.6 (10.5)	13.6 (16.1)	11.8 (18.1)
B3LYP	14.3 (13.6)	10.5 (10.7)	15.5 (15.8)	16.8 (16.9)
BPW91	11.4 (13.3)	7.4 (10.8)	12.5 (16.0)	9.7 (15.5)

[a] In kcal mol^{-1}; in parentheses values computed at the CCSD(T)/6-31G* level for each geometry. [b] See Scheme 2.

The results obtained up to now predict the same kind of mechanism for the reactions of diazomethane both with an olefin and with a carbonyl compound. However, while pyrazolines are generally the observed products in reactions with olefins, the formation of oxadiazolines as a result of diazoalkane addition to carbonyl compounds is rarely observed. In fact, 1,3,4-oxadiazolines **4** have been synthesized[39] using methods other than 1,3-dipolar cycloadditions and have been used as starting materials for carbenes[39a] and diazoalkanes.[39b]

To obtain a more complete description of the whole process, we have also studied the decomposition of pyrazoline **1** to yield cyclopropane **2** and N_2 and the elimination of N_2 from oxadiazolines **3** and **4**. First, we have carried out the transition state location at the CASSCF/6-31G* level of calculation with an active space of 4 electrons in 4 orbitals. The obtained structures have been used as starting points for the transition state location at the other levels of calculation. The obtained transition state structures are represented in Figure 2 and the corresponding geometry parameters are presented in Table 10. As we can observe, for **TS5** and **TS7** both C−N distances have the same value. However, the transition state searches have been done without imposing any symmetry restriction, and all the transition states for nitrogen elimination have C_1 symmetry. Table 11 presents the values of the energy barriers computed for these structures. The values of the natural orbital occupation numbers in the CASSCF calculations indicate that these transition states have a certain biradical character. For this reason, we have done the DFT calculations within a spin-unrestricted formalism, by breaking the symmetry between α and β spin densities. For **TS6** and **TS7** the calculation lead to

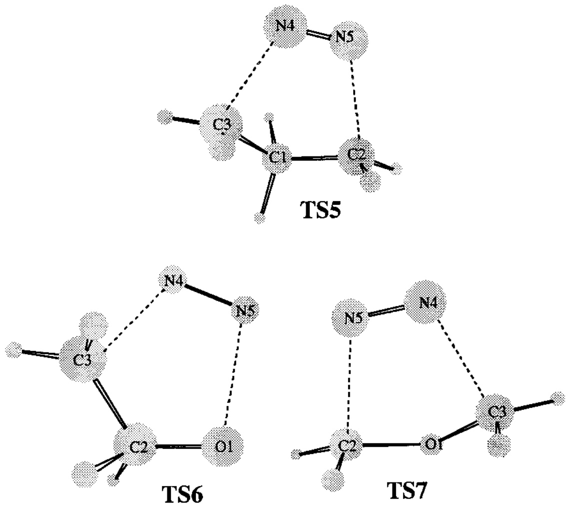


Figure 2. Geometries of the transition states of the reactions of elimination of N_2 from pyrazoline (**TS5**), 1,2,3-oxadiazoline (**TS6**), and 1,2,4-oxadiazoline (**TS7**).

TABLE 10: Selected Geometry Parameters[a] for the Transition States Corresponding to the Nitrogen Elimination from Pyrazoline 1, 1,2,3-Oxadiazoline 3, and 1,2,4-Oxadiazoline 4

	QCISD	CASSCF	BLYP	B3LYP	BPW91
TS5					
C2−C1	1.473	1.496	1.486	1.485	1.482
N5−C2	2.291	2.083	2.459	2.237	2.466
N5−N4	1.136	1.128	1.137	1.134	1.134
C3−C1−C2	120.7	113.7	121.4	117.8	121.0
TS6					
C2−O1	1.352	1.368	1.300	1.297	1.312
C3−C2	1.503	1.496	1.499	1.479	1.4825
N4−C3	1.839	1.864	2.002	1.940	1.951
N5−N4	1.1385	1.127	1.144	1.132	1.143
N5−O1	2.206	2.159	2.290	2.242	2.289
C3−C2−O1	113.7	112.5	118.4	117.4	118.3
TS7					
C2−O1	1.334	1.330	1.344	1.324	1.330
N4−C3	2.095	2.026	2.116	2.136	2.224
N5−N4	1.154	1.133	1.162	1.145	1.149
C3−O1−C2	118.7	117.3	119.4	120.7	121.9

[a] See Figure 2; bond lengths in Å and bond angles in degrees.

TABLE 11: Energy Barriers[a] for the Reactions[b] of Elimination of Nitrogen

	TS5	TS6	TS7
QCISD	53.5 (44.3)	27.8 (26.6)	34.1 (28.6)
BLYP	37.5 (41.5)	22.5 (26.8)	18.9 (28.3)
B3LYP	41.7 (44.6)	29.3 (28.0)	28.1 (28.5)
BPW91	43.0 (41.5)	27.4 (27.7)	24.1 (27.1)

[a] In kcal mol^{-1}; in parentheses values computed at the CCSD(T)/6-31G* level for each geometry. [b] See Scheme 2.

the spin-restricted solution, but for **TS5** the unrestricted solution was more stable. In this case, we have obtained the energy of the singlet state by using spin projection.[18b,40]

N_2-elimination from pyrazoline **1** through **TS5** leads to the trimethylene biradical. Several theoretical studies have been devoted to the potential energy surface of this biradical and its role in cyclopropane isomerizations.[41] According to these studies the conversion from trimethylene to cyclopropane involves a very small energy barrier, so that it is not a kinetically relevant intermediate. N_2-elimination from oxadiazoline **3** through **TS6** leads to the ethylenoxy biradical, which is isoelectronic with trimethylene. This intermediate would also rapidly undergo cyclization to yield oxirane, since the computed energy barrier at the CASSCF level with an active space of 2 electrons in 2 orbitals is only 0.6 kcal mol^{-1}. Finally, N_2-elimination from oxadiazoline **4** through **TS7** leads to the carbonyl ylide biradical. The potential energy surface of this system has been recently studied by Yamaguchi et al.[42] We have obtained that the barrier for the conrotatory evolution to oxirane is 9.0 kcal mol^{-1} at the CASSCF(2,2) level of calculation, in very good agreement with the results reported by Yamaguchi et al.[42] So, this intermediate would have a longer lifetime than either trimethylene or ethylenoxy biradicals.

TABLE 12: Computed Energy Barriers[a] for the Reactions of Diazomethane with Ethylene and Formaldehyde Computed at Different Levels of Calculation Using the 6-311G Basis Set**

	TS1	TS5	TS2	TS6
CCSD(T)[b]	13.0	41.7	11.6	23.5
BLYP	14.1	31.6	10.8	16.9
B3LYP	16.0	37.0	12.7	23.8
BPW91	12.7	37.8	9.1	21.9

[a] In kcal mol^{-1} [b] QCISD/6-31G* geometries.

Table 10 shows that the DFT calculation has a tendency to give later transition states than QCISD and CASSCF methods for the nitrogen elimination reactions. The maximum discrepancy is observed for **TS5**, where BLYP and BPW91 predict C−N bonds 0.4 Å longer than CASSCF. Regarding the potential energy barriers, Table 11 shows that the BLYP functional leads to barriers that seem too low. On the contrary, BPW91 and B3LYP barriers are in a good agreement with the CCSD(T) results. Finally, we can observe that the QCISD energy barriers computed for **TS6** and **TS7** are too high.

We have also examined the effect of the basis set on the computed potential energy barriers of the reactions of diazomethane with ethylene and formaldehyde. The results obtained using the 6-311G** basis set are presented in Table 12. For formaldehyde we have considered only the mechanism involving **3** as intermediate. For the transition states corresponding to the 1,3-dipolar cycloadditions of diazomethane to ethylene(**TS1**) and formaldehyde (**TS2**) the DFT barriers increase with respect to the values obtained with the smaller basis set (Table 9) by more than 1 kcal mol^{-1}, while CCSD(T) values slightly decrease. For ethylene the BPW91 functional is the one that yields the closest result to CCSD(T), while for formaldehyde the B3LYP result is closer to CCSD(T). The use of a larger basis set in the CCSD(T) calculations has not been possible with our computational resources. However we have examined the effect of extending the basis set on the potential energy barriers at the MP2 level of calculation.[28] When going from the 6-311G** to the cc-pVTZ basis sets the barrier corresponding to **TS1** increases by 0.1 kcal mol^{-1}, while the barrier corresponding to the formation of **3** decreases by 1.2 kcal mol^{-1}.

Regarding nitrogen elimination reactions, the energy barriers obtained using the 6-311G** basis set are lower than those reported in Table 11 at all levels of calculation. For the CCSD(T) calculations the same effect has already been observed for **TS1** and **TS2**. On the other hand, the lowering of the energy barriers corresponding to **TS5** and **TS6** in the DFT calculations is mainly due to the fact that formation energies of **1** and **3** decrease when a larger basis set is used (see above).

From the energies computed at the CCSD(T)/6-311G** level of calculation and the B3LYP/6-31G* vibrational frequencies we have computed the Gibbs energies of the most relevant structures involved in the reactions of diazomethane with

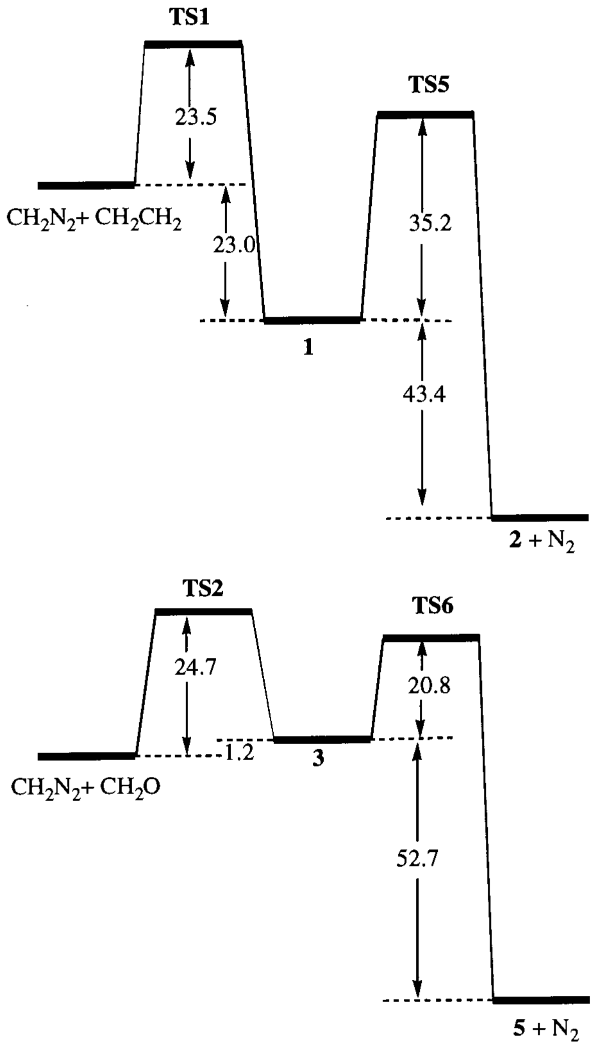


Figure 3. Gibbs energy diagrams for the reactions of diazomethane with ethylene and formaldehyde. All values are in kcal mol^{-1}.

ethylene and formaldehyde. The results obtained are schematically represented in Figure 3. For the reaction between diazomethane and ethylene we can observe that pyrazoline **1** is thermodynamically more stable than the reactants and that the Gibbs energy barrier corresponding to its decomposition is larger than the one corresponding to its formation. This result is in agreement with the formation of **1** as a stable product in the reaction between diazomethane and olefins. On the other hand, for the reaction of formaldehyde the 1,2,3-oxadiazoline intermediate has a similar Gibbs energy than the reactants and its barrier for decomposition is lower than the barrier corresponding to its formation. This result is in agreement with the difficulty in isolating **3** in reactions between diazomethane and carbonyl compounds.

Concluding Remarks

The reactions of diazomethane with ethylene and formaldehyde have been studied using density functional and conventional ab initio methods. In both cases, the DFT calculations underestimate the reaction energies with respect to CCSD(T) due to an overestimation of the strength of the C−N bond of diazomethane. Regarding the transition states geometries and the potential energy barriers, the comparison between DFT and conventional ab initio methods leads to different results depending on the reaction.

For the 1,3-dipolar cycloadditions all methods lead to similar geometries for the transition states and all DFT calculations yield energy barriers in reasonable agreement with CCSD(T) values. Using the 6-311G** basis set, the BPW91 functional is the one that yields the closest result to CCSD(T) for ethylene, while for formaldehyde the B3LYP result is closer to CCSD(T). On the other hand, for nitrogen elimination reactions, transition state geometries and potential energy barriers are more dependent on the level of calculation.

The results obtained show that for the reaction of formaldehyde the most favorable mechanism is the one involving the formation of 1,2,3-oxadiazoline as intermediate. This product is thermodynamically less stable than the reactants and easily decomposes into oxirane and nitrogen. On the contrary, for the reaction of ethylene, the pyrazoline intermediate is more stable than the reactants and its decomposition would not be kinetically favorable.

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