
Density Functional Study of the Relative Reactivity in the Concerted 1,3-Dipolar Cycloaddition of Nitrile Ylide to Disubstituted Ethylenes

HSIN-YI LIAO,¹ MING-DER SU,² WEN-SHENG CHUNG,³
SAN-YAN CHU¹

¹Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, ROC

²School of Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, ROC

³Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC

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ABSTRACT: Density functional theory was used to perform a theoretical evaluation of (*E*)-1,2-disubstituted ethylenes as dipolarophiles for the 1,3-dipolar cycloaddition reaction. The reactivities of electron-withdrawing and -donating substituted ethylenes were examined by estimating their activation energies. The calculated activation energies predicted that the most reactive species is (*E*)-1,2-C₂H₂(NO)₂, whereas the least reactive is (*E*)-2-butene. Namely, it was demonstrated that 16-electron 1,3-dipole reactants with more electropositive substituents in terminal positions and ethylenes that possess more strongly electron-withdrawing substituents facilitate 1,3-dipolar cycloaddition reactions. All of the theoretical results can be rationalized using the configuration mixing model.

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Key words: 1,3-dipolar cycloaddition reaction; configuration mixing model

Introduction

The 1,3-dipolar cycloaddition reaction is a powerful tool for synthesizing five-membered heterocyclic compounds. Many 1,3-dipoles are iso-electronic to an allyl anion, which has four π elec-

trons and at least one charge-separated resonance structure that has opposite charges in a 1,3 relationship. It is this structural feature that leads to the name 1,3-dipolar cycloaddition reaction. This reaction is generally assumed to be a concerted [$\pi 4_s + \pi 2_s$] cycloaddition [1, 2] like the Diels–Alder reaction [3]. This assumption is supported by their high regio- and stereoselectivity, although a stepwise radical mechanism has been proposed [4].

Correspondence to: M.-D. Su.

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Perhaps the most outstanding contribution to this field has come from the brilliant work of Hoisen [5]. His efforts have helped to transform 1,3-dipolar addition from an almost obscure phenomenon into a major reaction type. For comprehensive reviews of 1,3-dipolar cycloaddition, see Ref. [6]. Although there are excellent reviews [5, 6] in this field, several basic questions need to be solved for the sake of synthesis applications. One important question that arouses our interest is how to increase the reactivity of the dipolarophile and/or dipole. Our primary aim in this work is, therefore, to propose a theoretical model that can facilitate the 1,3-dipolar cycloaddition reaction.

It is generally acknowledged that substituents may influence reaction kinetics. In our previous study [7], we found that a 16-electron 1,3-dipole reactant with more electropositive substituents at the terminal positions may facilitate its cycloaddition with a dipolarophile. Nitrile ylide is thus a good example molecule for the 1,3-dipole. In addition to choosing a highly reactive dipole, increasing the potential reactivity of the dipolarophile by a proper choice of substituents is also expected to increase the reactivity. Indeed, it is of theoretical and experimental interest to determine the reactivity of different substituted dipolarophiles toward nitrile ylide. For this purpose, we choose ethylene, a classical dipolarophile whose reactivity can be changed by either electron-withdrawing or -donating substituents.

In this work, we report a density functional study of the effects of substituents on the 1,3-dipolar cycloaddition reaction. The systems we chose to investigate here are the addition of nitrile ylide to (*E*)-1,2-C₂H₂(NO)₂, (*E*)-1,2-C₂H₂(CN)₂, (*E*)-1,2-C₂H₂Cl₂, (*E*)-1,2-C₂H₂(OH)₂, and (*E*)-1,2-C₂H₂(CH₃)₂.

There are several ways to determine the reactivity of different compounds in a reaction. One very popular and mostly qualitative method is to determine the energy gap between the frontier molecular orbitals (FMO) of the reactants. According to this frontier orbital theory [8], the rate of the reaction is determined largely by the degree of highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) reactant interactions. These energy effects were explained by Sustmann [9] and Houk et al. [10] using perturbation theory [11]. The smaller the energy gap between the controlling orbitals, the faster the reaction. The reaction is controlled by both electron-donating and -withdrawing substituents on either component [7]. Nevertheless, we believe that a somewhat differ-

ent approach and emphasis on other aspects of the reaction analyzed here may supplement this approach. We will show that the reactivity of the 1,2-disubstituted ethylene is correlated strongly to its singlet–triplet splitting, which is important for understanding the origin of the substituent effects. We mention here that reports concerning the theoretical study of such substituent effects on the 1,3-dipolar cycloadditions are very rare [12], in marked contrast to the Diels–Alder reactions [5]. In particular, to our knowledge, to date no theoretical work has been devoted to the study of the reactivity of 1,2-disubstituted ethylenes with a 1,3-dipole.

Methodology

Gas phase geometry optimizations without any restraints were carried out with Gaussian 94 [13] at the B3LYP level using the 6-31G* basis set [5] (denoted as B3LYP/6-31G*). The reason for using the B3LYP/6-31G* method is that our previous study [7] indicated a good agreement between the B3LYP and CCSD(T) results for the 1,3-dipolar cycloaddition reactions. We have compared the B3LYP/6-31+G** and B3LYP/6-31G* results for the systems. The changes in ΔE^\ddagger and ΔH are +0.128 and -1.13 kcal/mol, respectively. All stationary points were identified by performing vibrational analysis with the same basis set used for the optimization. Additionally, we used these frequencies to evaluate the corresponding zero-point vibrational energy (ZPE) corrections to the relative energies.

Results and Discussion

The theoretical investigations [7, 16] suggest that the 1,3-dipolar cycloaddition reaction proceeds via initial formation of a precursor complex and subsequent rearrangement through a five-membered cyclic transition state to yield the eventual cycloaddition product. Thus, in this reaction the results for four regions on the potential energy surfaces will be presented: the reactants (R; nitrile ylide + 1,2-disubstituted ethylene), the orientation complex (C), the transition state (TS), and the cycloaddition product (P). The total energies and relative energies, including the ZPE corrections for the B3LYP/6-31G* level of theory used in the geometry determinations, are collected in Table I.

Basically, the kinetic stability of the initial orientation complex depends on the depth of this

TABLE I
Total energies^a and relative energies^b computed at the B3LYP/6-31G* levels of theory.

Systems	R	C	TS	P
C ₂ H ₂ (NO) ₂	-469.74258 (0.0) [0.0]	-469.74508 (-1.565) [-3.078]	-469.74485 (-1.422) [-2.810]	-469.83570 (-58.43)
C ₂ H ₂ (CN) ₂	-395.64641 (0.0)	-395.65128 (-3.057)	-395.64410 (+1.448)	-395.73741 (-57.10)
C ₂ H ₂ Cl ₂	-1130.37090 (0.0)	-1130.37175 (-0.5209)	-1130.35485 (+10.09)	-1130.47251 (-63.75)
C ₂ H ₂ (OH) ₂	-361.57418 (0.0)	-361.58212 (-4.981)	-361.55320 (+13.17)	-361.66825 (-59.03)
C ₂ H ₂ (CH ₃) ₂	-289.74496 (0.0)	-289.74293 (+1.271)	-289.72214 (+14.32)	-289.83862 (-58.77)

^a Values in atomic units.

^b Values in parentheses are the relative energies (in kcal/mol) that corresponding to its reactants. Values in brackets are the relative energies computed at the CCSD(T)/6-31G*//B3LYP/6-31G* levels of theory.

local minimum, i.e., on the complexation energy ΔE_c as well as on the height of the energy barrier for the transition state (ΔE^\ddagger). As can be seen in Table I, the orientation complexes for (*E*)-1,2-C₂H₂Cl₂, (*E*)-1,2-C₂H₂(OH)₂, and (*E*)-1,2-C₂H₂(CH₃)₂ reside in a fairly shallow minimum as shown by a complexation energy ΔE_c of -0.5–1.3 kcal/mol and an activation energy for the addition reaction of 10–14 kcal/mol. On the other hand, in the case of electron-withdrawing substituted ethylene, the energy of the transition state relative to its corresponding orientation complex is 4.5 [(*E*)-1,2-C₂H₂(CN)₂] and 0.14 [(*E*)-1,2-C₂H₂(NO)₂] kcal/mol, whereas the complexation energy of the orientation complex is -3.1 [(*E*)-1,2-C₂H₂(CN)₂] and -1.6 [(*E*)-1,2-C₂H₂(NO)₂] kcal/mol. It appears that the potential energy surfaces for the (*E*)-1,2-C₂H₂(CN)₂ and (*E*)-1,2-C₂H₂(NO)₂ orientation complexes are fairly flat. In addition, analytical force constant evaluations show that these complexes are indeed local minima. Accordingly, all of these theoretical results strongly indicate that the nitrile ylide forms a loose complex with the substituted ethylene and should not have a sufficient lifetime to be a spectroscopically observable species. Nevertheless, orientation complexes, due to van der Waals interactions, have recently have been found for ozone and ethylene in the gas phase and were confirmed by ab initio calculations; see [17].

The geometries of the B3LYP/6-31G* transition structures for each reaction are presented in Figure 1. The most interesting geometrical param-

eters for these species along with the transition vectors are also shown in Figure 1. All transition structures had only one imaginary vibrational frequency, corresponding to the motion for the newly forming C—C bonds in the concerted mechanism. In addition, all transition states represent the concerted, but not necessarily synchronous, mechanism of the reaction. The degree of synchronicity of the reactions can be determined by comparing the bond distances for the two newly forming bonds. As expected, all the transition structures are more or less asynchronous because the reactants are asymmetric. Indeed, the asynchronicity strongly depends on the polarity of both the 1,3-dipole and the dipolarophile, as well as the electronic and steric interaction between the constituents in the transition structures. The degree of asynchronicity for these transition structures is 0.309 Å [TS-C₂H₂(NO)₂], 0.198 Å [TS-C₂H₂(CN)₂], 0.107 Å [TS-C₂H₂Cl₂], 0.154 Å [TS-C₂H₂(OH)₂], and 0.025 Å [TS-C₂H₂(CH₃)₂]. Thus, by comparing the differences in the bond lengths for these cycloaddition reactions, the highest degree of asynchronicity is predicted for the transition structure TS-C₂H₂(NO)₂, whereas the transition structure TS-C₂H₂(CH₃)₂ is the most synchronous. In other words, from these theoretical results, it seems possible to conclude that the more electron-withdrawing substituted reactants should form products through more asynchronous transition states, and the more electron-donating substituted reactants will go through more synchronous transition structures as is the case with (*E*)-1,2-C₂H₂(CH₃)₂.

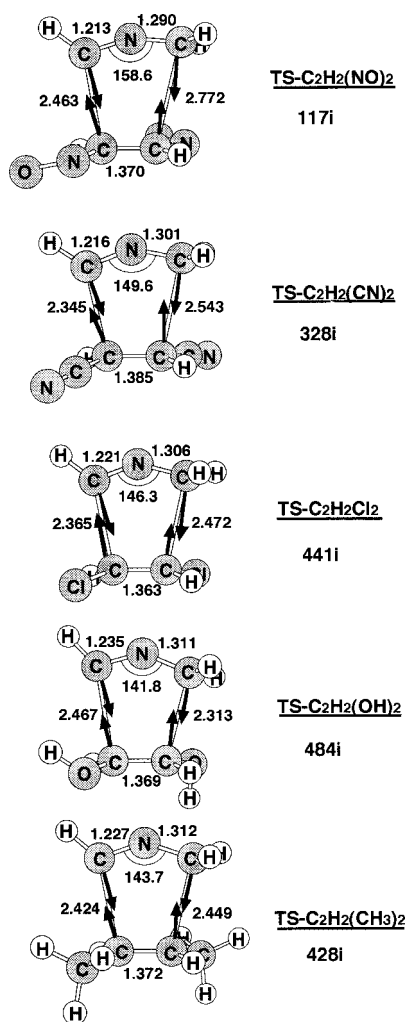


FIGURE 1. B3LYP/6-31G* optimized geometries (in angstroms) of the transition state of (*E*)-1,2-C₂H₂(NO)₂, (*E*)-1,2-C₂H₂(CN)₂, (*E*)-1,2-C₂H₂Cl₂, (*E*)-1,2-C₂H₂(OH)₂, and (*E*)-1,2-C₂H₂(CH₃)₂. The heavy arrows indicate the eigenvectors for the main atomic motion in the transition state. The corresponding imaginary frequencies are given.

We can understand the unsymmetrical structures of the transition state by the following consideration. We used the quantity $\Delta R = R_{CC}(\text{right}) - R_{CC}(\text{left})$ (see Fig. 1) to indicate the difference between the two newly forming C—C bonds. We found that ΔR for the transition state $\Delta R(\text{TS})$ correlate well with those for the product $\Delta R(\text{P})$, as is well expected for cycloaddition reaction with late transition states. For the products, the values of $\Delta R(\text{P})$ in decreasing order are NO (0.047) > CH₃ (0.042) > CN (0.034) > Cl (0.032) > OH (0.026), which agree qualitatively with $\Delta R(\text{TS})$ NO (0.31) > CN (0.20) >

Cl (0.11) > CH₃ (0.025) > OH (−0.15) with only CH₃ misplaced. We suspect that CH₃ has an important steric effect, but it is short ranged and therefore more sensitive for the product than the transition state.

Furthermore, considering the substituent effect, the density-functional theory (DFT) calculations suggest that the more strongly electron-withdrawing the substituent, the lower the activation energy of the cycloaddition reaction. For instance, because electron-withdrawing ability is ordered NO > CN > Cl ~ OH > CH₃ [18], the barrier height for the substituted ethylene addition to nitrile ylide increases in the order TS-C₂H₂(NO)₂ (−1.4 kcal/mol) < TS-C₂H₂(CN)₂ (1.4 kcal/mol) < TS-C₂H₂Cl₂ (10 kcal/mol) < TS-C₂H₂(OH)₂ (13 kcal/mol) < TS-C₂H₂(CH₃)₂ (14 kcal/mol) at the B3LYP/6-31G* level of theory (see Table I). That is to say, from a kinetic viewpoint, the most reactive dipolarophile is (*E*)-1,2-C₂H₂(NO)₂, followed by (*E*)-1,2-C₂H₂(CN)₂, (*E*)-1,2-C₂H₂Cl₂, (*E*)-1,2-C₂H₂(OH)₂, and (*E*)-1,2-C₂H₂(CH₃)₂.

As mentioned earlier, according to FMO theory [8], higher reactivity is predicted for the pair of reactants that have similar HOMO–LUMO energies or small energy gaps between the HOMO of one reactant, and the LUMO of the other [9, 10]. The differences in frontier orbital energies between the reactants are presented in Table II. We have thus examined the relationship between the Hartree–Fock orbital HOMO–LUMO energy gaps and the activation barriers for the aforementioned five systems as given in Table II. It is apparent that neither HOMO_{dipole}–LUMO_{ethylene} nor HOMO_{ethylene}–LUMO_{dipole} energy gaps correlate with the addition barriers. (Compounds with high-lying HOMOs are nucleophilic and those with low-energy LUMOs are electrophilic. According to FMO theory, highly nucleophilic 1,3-dipoles and potent electrophilic dipolarophiles are needed.) However, the sum of the two, which leads to a HOMO–LUMO energy gap for various ethylenes, has a better correlation with the barrier. [From Table II, the HOMO–LUMO energy gaps based on the Hartree–Fock orbitals are 0.04372, 0.4555, 0.5100, 0.5469, and 0.5418 au for *trans*-1,2-C₂H₂(NO)₂, *trans*-1,2-C₂H₂(CN)₂, *trans*-1,2-C₂H₂Cl₂, *trans*-1,2-C₂H₂(OH)₂, and *trans*-1,2-C₂H₂(CH₃)₂.] This is not surprising because FMO theory considers only the separated reactants without incorporating the possible extra interactions of the reactants in the transition state, which can play a crucial role in determining the reactivity. An alternative model for

TABLE II
HOMO and LUMO energies (au), singlet–triplet energy gaps (kcal/mol), barriers (kcal/mol), and enthalpies (kcal/mol) for 1,3-dipolar cycloadditions.^a

System	HOMO	LUMO	$\Delta E_{\text{HO-LU}}^b$	$\Delta E_{\text{LU-HO}}^c$	ΔE_{st}^d	ΔE_{\ddagger}^e	ΔH^f
$\text{C}_2\text{H}_2(\text{NO})_2$	-0.42298	+0.01422	0.3303	0.5727	+14.35	-1.4216	-58.43
$\text{C}_2\text{H}_2(\text{CN})_2$	-0.41716	+0.03834	0.3544	0.5669	+71.47	1.4480	-57.10
$\text{C}_2\text{H}_2\text{Cl}_2$	-0.37059	+0.13940	0.4555	0.5204	+91.92	+10.09	-63.75
$\text{C}_2\text{H}_2(\text{OH})_2$	-0.33247	+0.21443	0.5305	0.4822	+97.65	+13.17	-59.03
$\text{C}_2\text{H}_2(\text{CH}_3)_2$	-0.34130	+0.20053	0.5166	0.4911	+102.21	+14.32	-58.77

^a All at the B3LYP/6-31G* level. The HOMO and LUMO are based on the Hartree–Fock orbitals.

^b The energy difference between the HOMO of the 1,3-dipoles and the LUMO of the ethylene. The HOMO of reactant H_2CNCH is -0.3161 au.

^c The energy difference between the HOMO of ethylene and the LUMO of the 1,3-dipoles. The LUMO of reactant H_2CNCH is +0.1498 au.

^d A positive value indicates a singlet ground state.

^e The activation energy of the transition state, relative to its corresponding reactants.

^f The exothermicity of the products, relative to its corresponding reactants (also see Table I).

interpreting the reactivity of cycloaddition reactions is provided by the so-called configuration mixing (CM) model. The details of the CM model have been discussed in the literature [7, 19], and need not be reiterated here. According to this model, the energy barriers that govern processes with similar reaction energies should be proportional to the energy gap $\Delta E_{\text{st}} (= E_{\text{triplet}} - E_{\text{singlet}})$ between the singlet ground state and the first excited triplet state of the disubstituted ethylene. As can be seen in Table II, the trend for the singlet–triplet splitting ΔE_{st} of the disubstituted ethylene is in general agreement with the computed energy barriers, i.e., the smaller the ΔE_{st} of the disubstituted ethylene, the lower the barrier height. As a result, our theoretical findings suggest that if a disubstituted ethylene has a singlet ground state with a low-lying triplet state (leading to a smaller ΔE_{st} , also a smaller HOMO–LUMO gap), it may readily undergo a concerted reaction [7, 19]. The $\text{HOMO}_{\text{ethylene}}\text{--LUMO}_{\text{ethylene}}$ gap, which is closely related to ΔE_{st} , has a good correlation with the activation barriers.

Potential energy profiles based on the B3LYP data in Table I are summarized in Figure 2. Moreover, as discussed previously [7], our DFT results indicate that the stronger electron-withdrawing substituents should give a lower barrier for the 1,3-dipolar cycloaddition reaction. The reason for this can be simply understood in terms of the singlet–triplet splitting (ΔE_{st}). It is well known that a good electron withdrawer (or a good π acceptor, such as NO) will stabilize the π^* level of ethylene much more than the

π level of ethylene. This will decrease the HOMO–LUMO gap in the substituted ethylene [19, 20] and, in turn, lower its singlet–triplet splitting. Such an effect will facilitate the 1,3-dipolar cycloaddition reaction, as mentioned earlier.

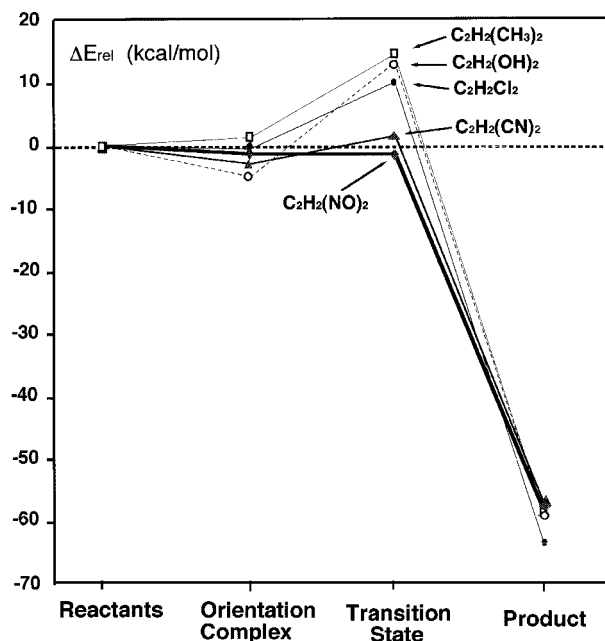


FIGURE 2. Potential energy surfaces for the cycloadditions of nitrile ylide with (*E*)-1,2-disubstituted ethylenes. The relative energies are taken from the B3LYP/6-31G* values as given in Table I. For optimized structures of the transition states, see Figure 1.

In summary, in the present work we have studied disubstituted ethylenes in reaction with nitrile ylide to determine the influence of electron-withdrawing and -donating substituents on the reactivity. Given the importance of substitution on both the 1,3-dipole [7] and the dipolarophile, it is, therefore, predicted that a 16-electron 1,3-dipole reactant with more electropositive substituents in terminal positions and an ethylene bearing more strongly electron-withdrawing substituents will facilitate 1,3-dipolar cycloaddition reactions.

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