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Theoretical Studies on Cycloaddition Reactions between the 2-Aza-1,3-butadiene Cation and Olefins

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Density functional (B3LYP) calculations, using the 6-31G** basis set, have been employed to study the title reactions. For the model reaction ($H_2C{=}C{-}NH^+{=}CH_2 + H_2C{=}CH_2$), a complex has been formed with 6.2 kcal/mol of stabilization energy and the transition state is 4.0 kcal/mol above this complex, but 2.1 kcal/mol below the reactants. However, the substituent effects are quite remarkable. When ethene is substituted by electron-withdrawing group CN, the reaction could also yield six-membered-ring products, but the energy barriers are all more than 7 kcal/mol, which shows that CN group unfavors the reaction. The other substituents, such as CH_3O and CH_3 groups, have also been considered in the present work, and the results show that they are favorable for the formation of six-membered-ring adducts. The calculated results have been rationalized with frontier orbital interaction and topological analysis.

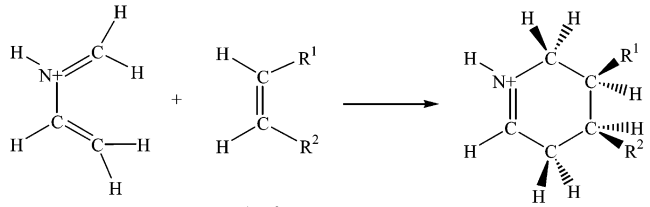
Introduction

The Diels−Alder reaction is the most general method employed for the synthesis of six-membered rings.[1] The hetero [4+2] reaction is also becoming a very useful method for the preparation of six-membered-ring heterocycles.[2] Polar cycloadditions,[2,3] i.e., those in which ionic reactions such as even-electron negatively (M^-) and positively charged (M^+) species are employed, are used with success in many synthetic strategies in solution chemistry. Odd-electron cations (M^+) generated in solution participate in "hole" catalyzed polar cycloaddition reactions,[4] which often display extremely low activation barriers.[4e]

Neutral azabutadienes and analogues, often under acid catalysis, or cationic azabutadienes react promptly in solution with several dienophiles by [4+2] or polar [4^++2] Diels−Alder cycloadditions, respectively, and these reactions have been used as key steps in important routes to heterocyclic systems.[2−5]

Although there are many reports on theoretical studies of the Diels−Alder cycloaddition reaction, the hetero-Diels−Alder reactions have been by far less studied from a theoretical point of view. However, there is an increase in the number of ab initio studies of several types of hetero-Diels−Alder reactions,[6] which confines the neutral−neutral cycloaddition reactions.

CHART 1



The N-protonated form of 2-aza-1,3-butadiene, as a cation, is easily accessible and kinetically and thermodynamically stable in the gas phase. Experimentally the cycloadditions of the 2-aza-1,3-butadiene cation to ethene and its analogues already have been studied,[7] but theoretical studies, to our knowledge, still remain incomplete. Therefore, we have employed a model reaction

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(1) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: New York, 1990.

(2) Boger, D. L.; Weinreb, S. N. *Hetero Diels−Alder Methodology in Organic Synthesis*; Academic Press: San Diego, CA, 1987.

(3) (a) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 212. (b) Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. *J. Am. Chem. Soc.* **1987**, *109*, 2182.

(4) (a) Kim, T.; Pye, R. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 6285. (b) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. (c) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825. (d) Bauld, N. L. *Adv. Electron-Transfer Chem.* **1992**, *2*, 1. (e) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550.

(5) (a) Barluenga, J.; Aznar, F.; Fustero, S.; Tomás, M. *Pure Appl. Chem.* **1990**, *62*, 1957. (b) Knoelker, H.-J.; Baum, G.; Gonser, P. *Tetrahedron Lett.* **1995**, *36*, 8194. (c) Beifuss, U.; Ledderhose, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2137.

(6) (a) McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499. (b) Gonzalez, J.; Houk, K. N. *J. Org. Chem.*, **1992**, *57*, 3031. (c) Bachrach, S. M.; Liu, M. J. *J. Org. Chem.* **1992**, *57*, 6736. (d) Gonzalaz, J.; Taylor, E. C.; Houk, K. N. *J. Org. Chem.*, **1992**, *57*, 3753. (e) McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1993**, *58*, 3330. (f) Suarez, D.; Sordo, T. L.; Sordo, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 763. (g) Suarez, D.; Gonzalez, J.; Sordo, T. L.; Sordo, J. A. *J. Org. Chem.* **1994**, *59*, 8058. (h) Jursic, B. S.; Zdravkovski, Z. *J. Org. Chem.* **1995**, *60*, 3163. (i)Tietze, L. F.; Fennen, J.; Geissler, H.; Schulz, G.; Anders, E. *Liebigs Ann* **1995**, 1681. (j) Venturini, A.; Joglar, J.; Fustero, S.; Gonzalez, J. *J. Org. Chem.* **1997**, *62*, 3919.

(7) Augusti, R.; Gozzo, F. C.; Moraes, L.A. B.; Sparrapan, R.; Eberlin, M. N. *J. Org. Chem.* **1998**, *63*, 4889.

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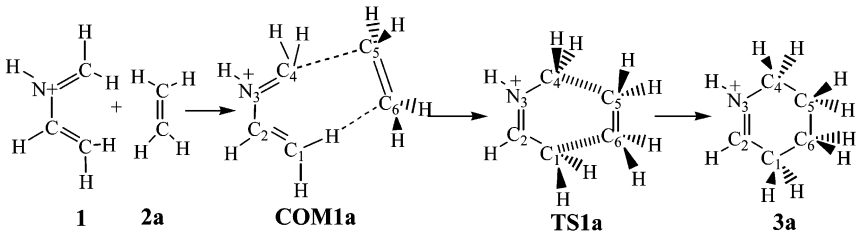
SCHEME 1



($H_2C{=}^{+}NH{-}CH{=}CH_2$ + $CH_2{=}CH_2$) to investigate the mechanism with use of density functional theory (DFT). Moreover, substitutent effects on the carbon in olefin are also investigated for comparison. The reactions considered are shown in Chart 1.

This work is one part of our research program devoted to the study of the cycloaddition reactions of some comulene cations, including keteniminium[8] and azonniaallene[9] cations.

Methods of Calculations

Density functional calculations are carried out for [4⁺+2] cycloaddition reactions between the 2-aza-1,3-butadiene cation (**1**) and olefins. All calculations included in this work have been performed with the Gaussian98 program package.[10] The geometries of reactants, products, complexes, intermediates, and transition states have been fully optimized. All the geometric parameters of the possible stationary points have been located at the B3LYP/6-31G** level and characterized by the number of imaginary frequencies. The B3LYP method has been confirmed to be good at describing the structures and energetics for pericyclic reactions.[11] For most of the reaction paths, the Intrinsic Reaction Coordinate (IRC)[12] has been traced to confirm the **TS** connecting with the corresponding two minima. The solvent effect has been performed for the model reaction with use of the PCM method[13] and CH_2Cl_2 as solvent (dielectric constant $\epsilon = 8.93$) at a temperature of 298 K, and geometric parameters have been optimized at the B3LYP-SCRF/6-31G** level; however, for other reactions, only single-point SCRF calculations have been performed with B3LYP/6-31G** geometries. The relative energies of all stationary points are corrected with a 0.95 scaling factor of zero-point vibrational energies.

Bader's theory of AIM[14] has also been used to study the bonding character and charge distribution for some stationary points in our studied reactions. Topological analysis locates bond critical points (BCPs). It is very suitable for studying the properties of the weak bonds, such as hydrogen bonds, and also to see whether cyclization has occurred. The topological properties of the electron density distribution of a molecule are based on the gradient vector field of the electron density $\nabla\rho(\boldsymbol{r})$, and on the Laplacian of the electron density $\nabla^2\rho(\boldsymbol{r})$, where $\boldsymbol{r}$ is the positional vector of an electron in three-dimensional space. Several excellent reviews have been published[15,16] on this project.

The AIM98PC package,[17] a PC version of AIMPAC,[18] has been employed for the electron density topological analysis, using the electron densities obtained with the B3LYP/6-31G** calculation.

Results and Discussion

The Model Reaction: $H_2C{=}NH^{+}{-}CH{=}CH_2$ + $CH_2{=}CH_2$. The geometries of reactants (**1** and **2a**), complex (**COM1a**), transition state (**TS1a**), and product (**3a**) are optimized at the B3LYP/6-31G** level and all the stationary points are characterized by vibrational frequencies. The atomic numbering systems of the above stationary points are shown in Scheme 1.

A weak complex **COM1a** is formed when **1** approaches **2a**, in which the C4−C5, C1−C6, and C4−C6 bond distances are 2.90, 3.87, and 2.97 Å, respectively. From the geometric parameters of **TS1a**, one can realize that the C4−C5 and C1−C6 bond distances are 2.17 and 2.84 Å, respectively, which shows that the reaction proceeds in an asynchronous way. The bond lengths of C1−C2 and N3−C4 are 0.02 and 0.03 Å longer than those in **COM1a**, respectively, but the bond length of N3−C2 is 0.04 Å shorter than that in **COM1a**, which is on the right way of the reaction path. Vibrational analysis and IRC calculation confirm that **TS1a** connects **COM1a** and six-membered-ring product **3a**, which indicates that the model reaction is concerted but asynchronous. To check the possibility of diradical character of **TS1a**, a single-point CAS(6,6)/6-31G** calculation, based on the B3LYP/6-31G** geometry, has been performed. The configura-

(8) Ding, W. J.; Fang, D. C. *J. Org. Chem.* **2001**, *66*, 6673.
(9) (a) Yang, S. Y.; Sun, C. K.; Fang, D. C. *J. Org. Chem.* **2002**, *67*, 3841. (b) Wei, M. J.; Fang, D. C.; Liu, R. Z. *J. Org. Chem.* **2002**, *67*, 7432.
(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(11) (a)Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378. (b) Houk K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*, 169.
(12) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.
(13) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *J. Chem. Phys. Lett.* **1996**, *255*, 32. (d) Cances, M. T.; Mennucci, V.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (e) Barone, V.; Cossi, M.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210. (f) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, 286, 253. (g) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404. (h) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (i) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1998**, *109*, 249.
(14) (a) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 983. (b) Bader, R. F. W. *Atoms in molecules, a Quantum Theory*; Clarendon Press: Oxford, UK, 1990.
(15) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.
(16) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-K'nig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946.
(17) Fang, D.-C.; Tang, T.-H. *AIM98PC*, the PC version of AIMPAC; Beijing Normal University: Beijing, China, 1998.
(18) Available from Professor R. F. W. Bader's Laboratory, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

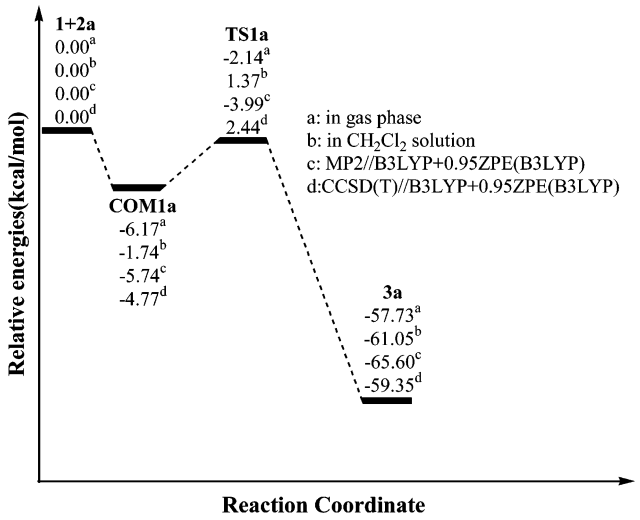


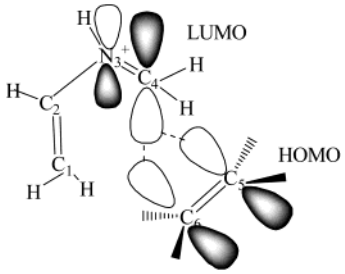
FIGURE 1. The schematic potential energy surface for the mechanism of the reaction **1** + **2a**.

tion coefficient of the ground state is 0.96 and all others are less than 0.15, which shows that **TS1a** is of some zwitterion but not of diradical character. In fact, the singlet open-shell UB3LYP/6-31G** calculation shows the same result with closed-shell B3LYP/6-31G**.

The schematic potential energy surface for the model reaction is shown in Figure 1, from which one can see that the stationary points along this reaction scheme are well below the reactant's asymptote due to the formation of **COM1a** (with a stabilization energy of 6.2 kcal/mol). Transition state **TS1a** is only about 4.0 kcal/mol above **COM1a**, but 2.1 kcal/mol below the reactants. If the basis set superposition error (BSSE) correction, at the B3LYP/6-31G** level, is considered, the stabilization energy of **COM1a** becomes 5 kcal/mol, while the energy of **TS1a** is about 2 kcal/mol higher than the original energy. Product **3a** is of a stable structure with a binding energy of 57.7 kcal/mol. The single-point energy correction, at the level of CCSD(T)/6-31G**//B3LYP/6-31G**, does not change the relative energy very much, for example, the difference for **3a** is only 1.6 kcal/mol, but that for **TS1a** is slightly larger (about 4 kcal/mol), therefore, B3LYP/6-31G** gives a promising result. In general, hetero-[4+2] reactions are more easily accessible when they are catalyzed with Lewis acid or H^+. As reported in ref 6b, the energy barrier of the model reaction is only 1.4 kcal/mol at the MP2/6-31G*//HF/3-21G level, which is quite close to our present result. Our best estimation for **TS1a** (the highest one) is only 2.44 kcal/mol (with ZPE correction) over **1** + **2a** at CCSD(T)/6-31G**//B3LYP/6-31G**, i.e., the reaction should take place; however, Augusti et al.[7] did not observe the reaction between the 2-aza-1,3-butadiene cation and ethene. Therefore, more work needs to be done.

Analysis of the frontier orbital interaction (from the calculation of B3LYP/6-31G**) shows that the main interaction should be between LUMO of **1** and HOMO of ethene. As shown in Chart 2, the lobes of LUMO of **1** are mainly the C4−N3 antibonding orbital and the lobe of C4 is especially large, therefore, P−π interaction is involved in the formation of **COM1a**. Topological analysis, shown in Figure 2, indicates that there are two

CHART 2



interactions between two portions of reactants in **COM1a**, i.e., P−π interaction and C−H···C interaction, the latter of which is very weak. The interaction between the lobe of the P orbital in C_4 and the π orbital of ethene leads to the bond path between C_4 and C_5 in **COM1a** approaching the middle of C_5−C_6 first and then C_5 last. The almost superposition between the bond critical and ring critical points indicates a very weak interaction of C−H···C. Mulliken population and Bader's AIM analysis show that there are 0.14 and 0.13 e transferred from a portion of **2a** to **1**, respectively, which leads to the stability of **COM1a**. **TS1a** is a ring system and the interactions for C4−C5 and C_1−C_6 are quite weak (the electron densities for those two bonds are 0.057 and 0.016, respectively). Because the C_4 in isolated **1** has more positive charge, therefore it could accept the electron from ethene and disperse the overplus positive charge in **1**. Mulliken population (B3LYP/6-31G**) shows that the **1** and **2a** portions in **TS1a** have 0.73 and 0.27 e positive charges, respectively, while Bader net charges for the **1** and **2a** portions are 0.74 and 0.26 e, which makes it more stable than the reactants.

We have also considered the solvent effect with CH_2Cl_2 as solvent. The geometric parameters obtained for the possible stationary points are similar to those in the gas phase, but **COM1a** becomes only 1.7 kcal/mol below the reactants, 4.4 kcal/mol less stable than in the gas phase (see Figure 1). Meanwhile, **TS1a** is about 1.4 kcal/mol above the reactants, which is also slightly different than in gas phase.

Substituent Effect on Ethene with the Electron-Withdrawing Group CN. In this porting of the study, we tried to investigate the substituent effect on the carbon atom in ethene with the electron-withdrawing group CN (see Scheme 2), i.e., the reaction of **1** with acrylonitrile **2b**. Here we have considered four possibilities: (a) the carbon with the CN group in the olefin attacking C4 in **1** (exo and endo forms)and (b) the carbon with the CN group in the olefin attacking C1 in **1** (exo and endo isomers). The geometric parameters of the corresponding transition states (**TS1b-1**,**TS1b-2**,**TS1b-3**, and **TS1b-4**) and adducts (**3b-1, 3b-2, 3b-3**, and **3b-4**) have been optimized with B3LYP/6-31G**, with the numbering systems given in Scheme 2.

From the geometric parameters for these transition states, one can realize that they are similar to those of **TS1a**, with two bonds being formed asynchronously and the carbon site (C4) adjacent to the N atom being easier to attack. The C4−C5 distances in **TS1b-1** and **TS1b-2** are 2.04 and 2.24 Å, 0.9 and 0.2 Å shorter than the corresponding values of C1−C6, and similar to the results for 2-azabutadiene and acrylonitrile (but more

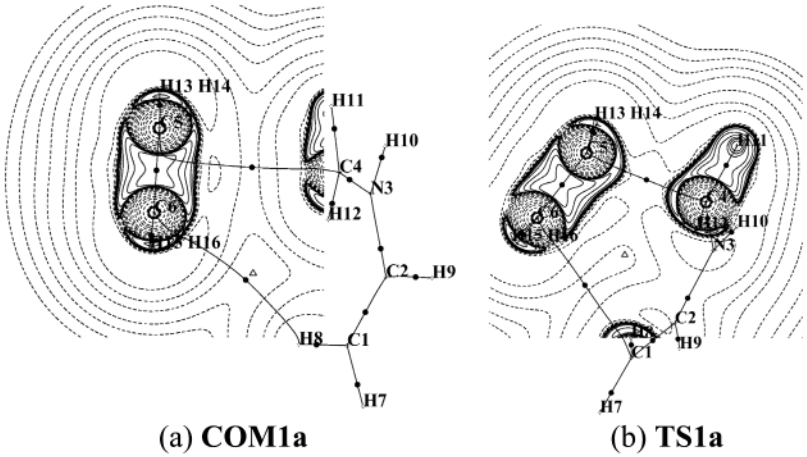
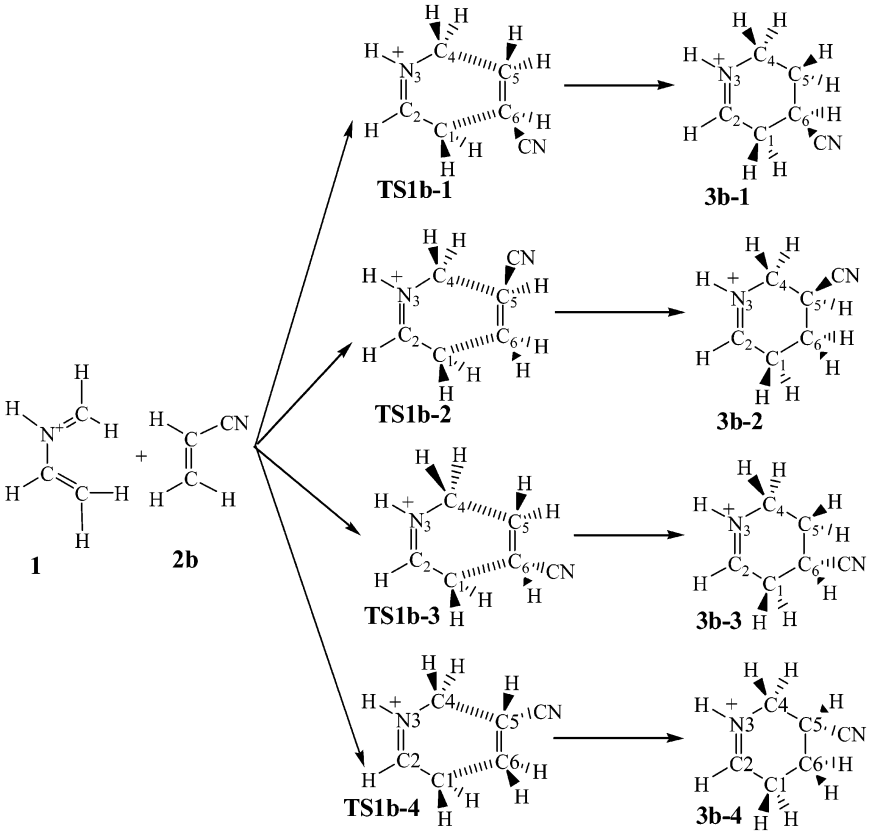


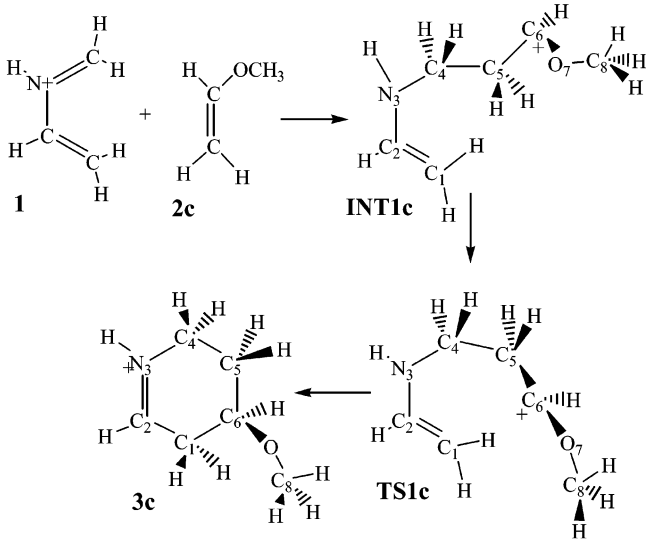
FIGURE 2. The molecular graphs and Laplacian distribution of some stationary points. In these figures, dashed lines denote positive values of $\nabla^2\rho_b$ and solid lines stand for negative values of $\nabla^2\rho_b$. The bonded charge concentrations are indicated by solid squares. In addition, bond paths (heavy solid lines), bond critical points (solid circle), and ring critical points (triangle) are shown for $\rho(\boldsymbol{r})$.

SCHEME 2

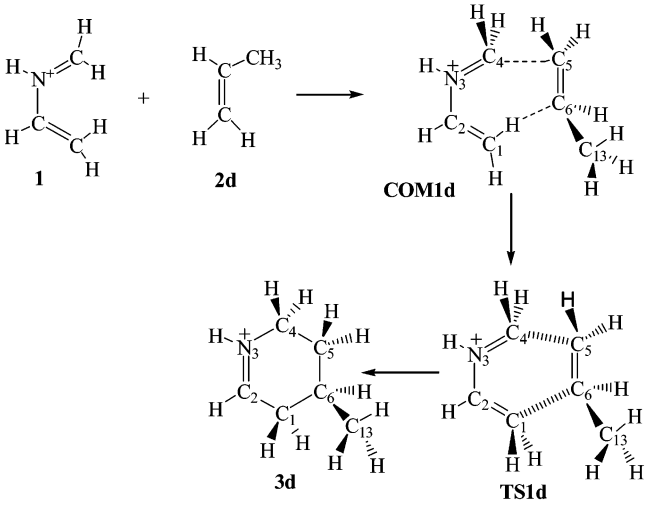


asynchronous).[6b] **TS1b-1** and **TS1b-2** are exo structures with different attacking sites, while **TS1b-3** and **TS1b-4** are endo structures. As shown in Figure 2, the cycloaddition products from **3b-1** to **3b-4** are stable for their relative energies are about 44 kcal/mol below the reactants **1** + **2b**. The different product isomers have quite similar stabilities (the biggest energy difference is only 2 kcal/mol), and **TS1b-1** and **TS1b-3** are about 2 kcal/mol more stable than the respective **TS1b-2** and **TS1b-4**. Therefore, the reactions could proceed in attacking both C6 and C5 sites, but the former is 2−3 kcal/mol more favorable than the latter, so the reaction is of some regioselectivity. Among these TSs, exo **TS1b-1** is the most stable form with an energy 0.4 kcal/mol lower than endo **TS1b-3,** but endo **TS1b-4** has an energy about 1 kcal/mol lower than exo **TS1b-2**, therefore, we cannot predict the endo−exo stereoselectivity. The BSSE corrections for **TS1b-1**, **TS1b-2**, **TS1b-3**, and **TS1b-4** are calculated to be 1.8, 2.0, 1.9, and 2.1 kcal/mol, respectively. HF/6-31G** gives a much higher energy barrier (27−29 kcal/mol) and the AM1 method provides a 11−16 kcal/mol energy barrier, while CCSD(T)/6-31G**//B3LYP/6-31G**

SCHEME 3



SCHEME 4



calculations indicate that these four transition states are much closer in energy than B3LYP/6-31G** calculations (about 9−11 kcal/mol). As we know, there is no stereochemical information about the [4⁺+2] reactions of the 2-aza-butadiene cation with olefins. Anyway, these transition states are 7 kcal/mol in energy above the reactants, namely, less favorable than the model reaction, which is in good agreement with chemical intuition and frontier orbital interaction.

Substituent Effect on Ethene with the Electron-Releasing Groups OCH_3 and CH_3. In this portion of the study, we chose two different substituent groups, such as methoxyl and methyl groups, and the corresponding reactions are denoted as **1** + **2c** and **1** + **2d** reactions. We have tried all possible reaction schemes to form the six-membered products, but for the reaction **1** + **2c**, we could only locate the stationary points for the methoxyl group on C_6, and exo one which is more favorable as reported here. As for the **1** + **2d** reaction, four reaction paths could be located, but the most favorable one is reported here. The numbering systems of the stationary points for reactions **1** + **2c** and **1** + **2d** are given in Schemes 3 and 4, respectively.

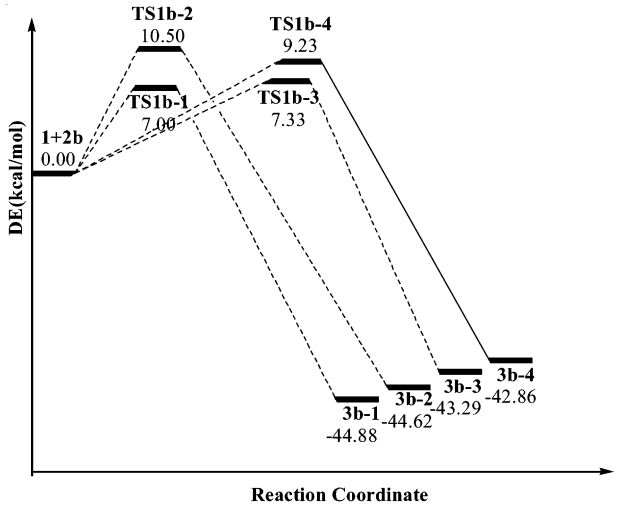


FIGURE 3. The schematic description of the potential energy surface for the reaction **1** + **2b** (including a 0.95 scaling factor of ZPE).

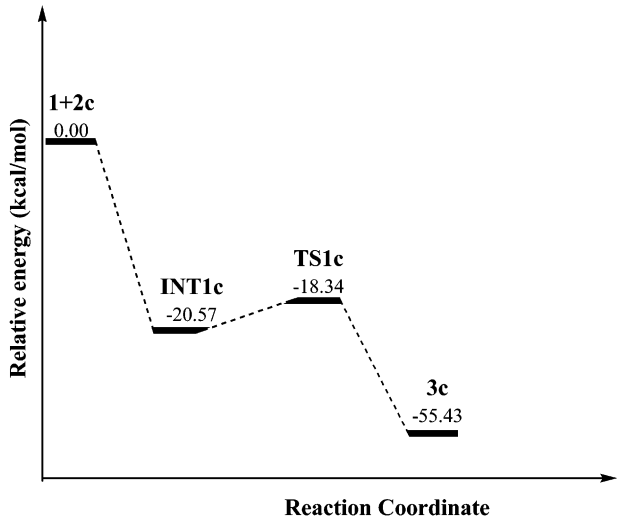


FIGURE 4. The schematic potential energy surface for the mechanism of the reaction **1** + **2c** (with a 0.95 ZPE correction).

Methoxylethene (**2c**, CH_2═$CHOCH_3$) is a rich π system, which is easier to react with electron-deficient **1**. The methoxyl group is such a strongly electron-donating group that when **2c** approaches **1**, an intermediate (**INT1c)** is formed without climbing up any energy barrier. **INT1c** is a nearly trans structure, with the bond length of C4−C5 being 1.63 Å and the dihedral angle of N3−C4−C5−C6 being −175°, i.e., one bond is almost formed. We tried to locate the transition state between **INT1c** and **1** + **2c**, but it always failed. Such a situation has been confirmed in other reaction systems, such as ClHC═N^+═CHCl + $(CH_3)_2$C═CH_2[9a] and H_2C═N^+═NH + $(CH_3)_2$C═CH_2.[9b] The formation of the cycloaddition product **3c** is via a transition state (**TS1c)**, which is a rotation transition state along the C4−C5 bond. The torsional angle N3−C4−C5−C6 in **TS1c** becomes −133°, and our IRC calculation predicts that the second bond is mainly formed after **TS1c**. The energy potential surface is depicted in Figure 4, from which one can see that this reaction is exothermic and all of the stationary points

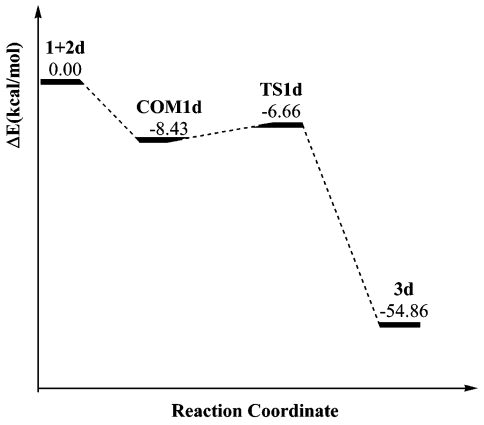


FIGURE 5. The schematic potential energy surface for the reaction **1** + **2d** (with a 0.95 ZPE correction).

are well bellow the reactant's asymptote; therefore, the reaction should proceed in very low temperature.

For the **1** + **2d** reaction, we have found a complex **COM1d** first when propene (**2d**) approaches the reactant of the 2-aza-1,3-butadiene cation (**1**). Because the electron-donating effect of the methyl group is not as strong as that of the methoxyl group, the present reaction scheme is different from the reaction of **1** + **2c**, but the same as the model reaction. The bond lengths of C4−C5, C4−C6, and C1−C6 in this complex are 2.63, 2.96, and 3.78 Å, respectively, but the positive charge in **1** is partially transferred to the fragment of the olefin (+0.20 e), which leads to about 8.4 kcal/mol stabilization energy of **COM1d** over the reactants. Only **TS1d** has been located between **COM1d** and **3d**, which is 1.8 kcal/mol in energy over **COM1d**, but 6.7 kcal/mol below the reactants. Comparing with the model reaction, **COM1d** and **TS1d** are about 2 and 4 kcal/mol stable than **COM1a** and **TS1d**, respectively, and thus the methyl group favors the reaction. The bond lengths of C4−C5 and C1−C6 in **TS1d** are calculated to be 2.10 and 3.22 Å, respectively, at the B3LYP/6-31G** level, which is close to **COM1d**, and thus is a low energy barrier. Our IRC calculations verify that **TS1d** connects **COM1d** and **3d**, so the potential energy surface of this reaction can be depicted as in Figure 5.

Summary

In the gas phase, the reaction of the 2-aza-1,3-butadiene cation (**1**) with ethene takes place with one complex and one transition state, where all the stationary points are well below the reactants. In the CH_2Cl_2 solution, the basic reaction scheme is the same as that in the gas phase. The calculations at the CCSD(T)/6-31G**//B3LYP/6-31G** level show that the higher correlation effect is not crucial for the present system.

When the electron-withdrawing group (such as CN) is on the olefin (e.g. acrylonitrile), the reaction seems to proceed with more difficulty than the model reaction because **1** is a electron-deficient system and the π electron in acrylonitrile is not rich.

Electron-donating groups favor the reaction. The reaction of methoxyethene (**2c**) with **1** yields a stable intermediate directly and then a rotation transition state connects the intermediate and final product with an energy barrier of only 2.2 kcal/mol. However, the reaction of propene with **1** is similar to the model reaction, but with more stable **COM1d** and **TS1d**, and thus a low energy barrier.

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Supporting Information Available: The *Z*-matrixes, frequencies, and energies of all the stationary points are listed in Tables S1−S12 and the numbering systems are given in Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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