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Theoretical Studies on Cycloaddition Reactions between Keteniminium Cations and Olefins

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The mechanisms of seven reactions between keteniminium cations and olefins have been theoretically explored at BHandHLYP/6-31G* level. It is found that these seven reactions always form a relatively stable hydrogen-bonded type of ion−molecule complex first except for reactions 1d+**2a** and 1e+**2a**, which have no hydrogen atom attached to nitrogen atom in keteniminium cations. Some reactions take place via a concerted but unsynchronous mechanism, and the others are stepwise processes. The substituent effects are also studied. The data reveal that the electron-pushing substituents on keteniminium cations disfavor the reaction, and the electron-attracting substituents on keteniminium cations favor the reactions. The substituent effects on ethene are contrary to the former case.

Introduction

The cycloaddition reactions between cumulenes and double bond compounds are very important routes for the synthesis of four-membered cycloadducts. They are of great value in organic synthesis and, in addition, the mechanism of these reactions has greatly interested chemists. In the past decades, [2 + 2] cycloaddition reactions of ketenes, ketenimines, and allenes have been extensively studied theoretically[1−3] and experimentally.[4] Morever, keteniminium cations (or salts), the analogues of ketenes, are also one kind of important intermediate in the organic synthesis. They open a new and potentially useful route to form four-membered ring compounds. Noteworthy are the facts that (a) keteniminium cations (or salts) are more electrophilic and more reactive;[4b,5−10] (b) keteniminium cations (or salts) do not dimerize or polymerize and can be stored in solution;[4b,11] and (c) they offer an easy access to homochiral cyclobutanones since chiral substituents can be readily introduced on the nitrogen atom.[4b,7−9,14] In addition, the starting material to keteniminium cations (or salts) is inexpensive and readily available.[4b,10−11]

Concerning the cycloadditions of keteniminium cations to olefins, including intramolecular[17−25] and intermolecular[5−16] cycloadditions, there have been many published reports. The intermolecular cycloaddition of keteniminium cation to the olefinic double bond was first reported by Ghosez[5] in 1972. In the same year, Marchand-Brynaert and Ghosez[10] reported a series of cycloaddtion

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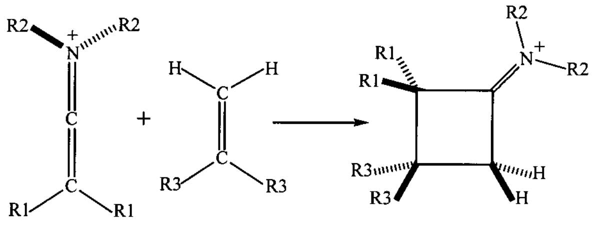
Chart 1. Reaction System



1 **2** **3**

1a: R1=R2=H
1b: R1=CH$_3$, R2=H
1c: R1=Cl, R2=H
1d: R1=H, R2=CH$_3$
1e: R1=H, R2=Cl

2a: R3=H
2b: R3=CH$_3$
2c: R3=Cl

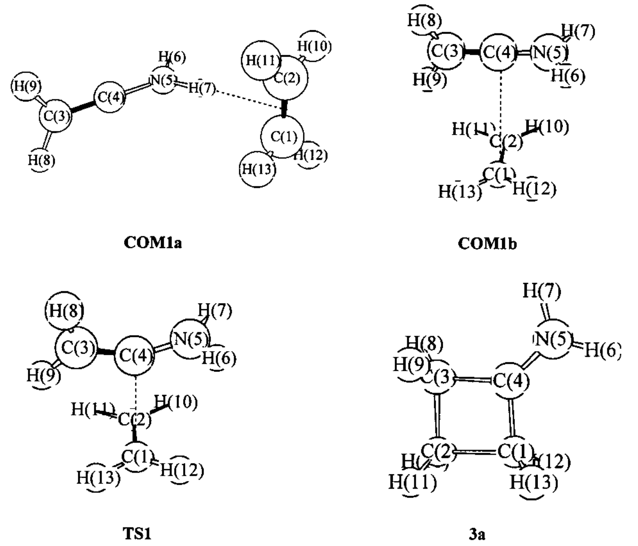
3a: R1=R2=R3=H
3b: R1=CH$_3$, R2=R3=H
3c: R1=Cl, R2=R3=H
3d: R1=R3=H, R2=CH$_3$
3e: R1=R3=H, R2=Cl
3f: R1=R2=H, R3=CH$_3$
3g: R1=R2=H, R3=Cl

reactions between keteniminium tetrafluoroborates and olefins and also proposed the mechanism according to the experimental results. They suggested that the cycloaddtion raections between keteniminium tetrafluoroborates and *cis*-cyclooctene or *trans*-cyclooctene were a $(\pi_{2s} + \pi_{2a})$ concerted mechanism. In 1982, Houge and Ghosez et al.[14] studied the intermolecular asymmetric [2 + 2] cycloaddition reaction between keteniminium salt and cyclopentene experimentally and put forward two possible perpendicular transition states. In 1983, Saimoto et al.[15] studied the cycloadditions of keteniminium salts to olefins and focused on the effect on the stereospecificity which is caused by the steric effect of the substituents on the nitrogen atom in keteniminium salts. They thought that the cycloaddition of a dialkyl-substituted keteniminium salt to *cis*-butene was a two-step mechanism via an intermediate.

Although the cycloaddition of keteniminium cations to olefins have been extensively studied by experiments, the theoretical study, to our knowledge, remains untouched. Therefore, the mechanism for $H_2C{=}C{=}NH_2^+ + CH_2{=}CH_2$ studied by DFT method is presented here. We have also investigated the substituent effects of these types of cycloaddition reactions. The reactions considered are shown in Chart 1.

Methods of Calculation

All the calculations included in this work have been performed with the Gaussian 98w program.[26] The geometries of reactants, products, complexes, intermediates, and transition states have been fully optimized. All stationary points and energies have been calculated at the BHandHLYP/6-31G* level. Transition states have been further confirmed by the computations of force constants analytically and characterized by the corresponding imaginary vibrational modes and frequencies. Bader's theory of AIM[27-29] has been used to study the bonding characters and charge distribution for stationary points in the reaction **1a** + **2a**.



COM1a **COM1b** **TS1** **3a**

Figure 1. The numbering system of some optimized stationary points in the model reaction.

AIM98PC package,[30] a PC version of AIMPAC,[31] has been employed for the electron density topological analysis using the electron densities obtained from the BHandHLYP/6-31G* calculation.

Results and Discussion

The Model Reaction: $H_2C{=}C{=}NH_2^+ + CH_2{=}CH_2$. The geometries of reactants (**1a** and **2a**), complexes (**COM1a** and **COM1b**), transition state (**TS1**), and product (**3a**) are optimized at BH and HLYP/6-31G* level. The numbering systems of the above stationary points are shown in Figure 1, and the optimized parameters are listed in Table S1 of the Supporting Information.

The structural parameters reveal that one of the reactants, keteniminium cation (**1a**), is a linear molecular with its skeleton atoms on the same plane. The plane including methylene is perpendicular to the plane of the imino group. The lengths of bonds are in reasonable agreement with those Arrieta et al.[3h] reported in 1999 at B3LYP/6-31G* level. In the product (see Figure 1 (**3a**) and Table S1), the ring-atom and the imino group are on the same plane, while the hydrogen atoms are distributed zygomorphically. The four-membered ring is almost on the same plane and stretched along C1−C3, with the angles C4−C1−C2 and C3−C2−C1 being 87.9 and 89.7°, respectively.

Because the interaction between reactants yields ion−molecule complexes first, two complexes, denoted as **COM1a** and **COM1b** in Figure 1, have been located. **COM1a** is a π-type of hydrogen-bonded complex. When the two reactants further approach, **COM1b** is formed, in which ethene and keteniminium cation approach in gauch mode (C4−C1−C2−C3 = −21.3°) and the complex

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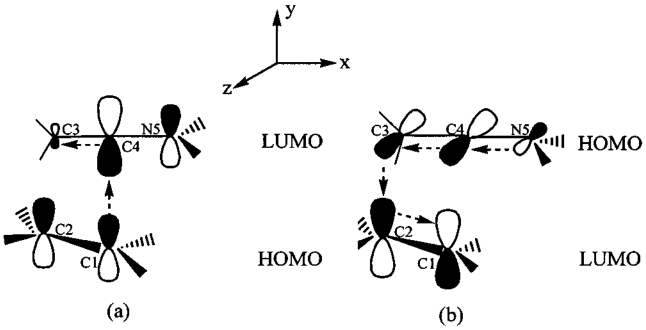
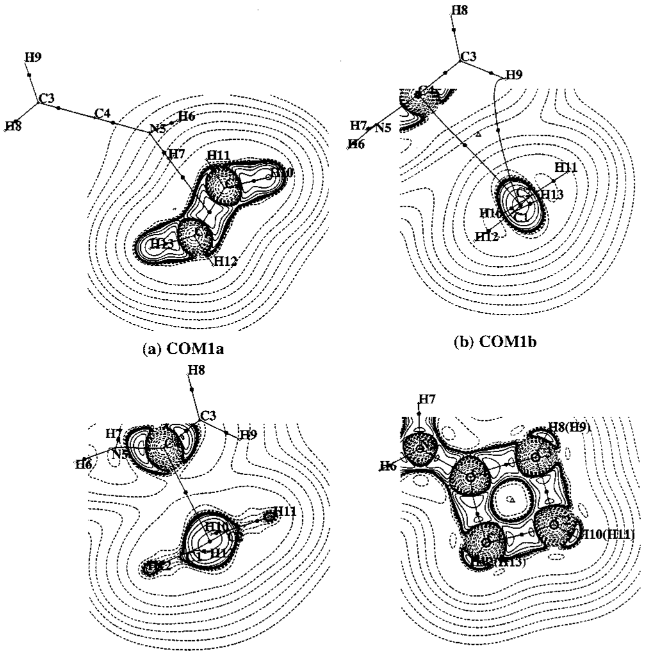


Figure 2. (a) The interaction between the HOMO of the keteniminium cation and the LUMO of ethene. (b) The interaction between the LUMO of the keteniminium cation and the HOMO of ethene.



(a) COM1a (b) COM1b (c) TS1 (d) 3a

Figure 3. The molecular graphs and Laplacian distribution of the stationary points in the model reaction. In these figures, positive values of $\nabla^2\rho_b$ are denoted by dashed lines and negative values by full lines. 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 ρ(r).

is quite loose (C2−C3 = 3.590 Å, C1−C4 = 3.411 Å). **COM1b** is less stable than **COM1a** by 26.1 kJ/mol.

The numbering system of **TS1** is shown in Figure 1. The geometry (for the optimized parameters, see Table S1 of the Supporting Information) of **TS1** is similar to **COM1b**, but the distances of C2−C3 and C1−C4 are much shorter (C2−C3 = 2.949 Å, C1−C4 = 2.400 Å), and the double bond lengths of C2−C1, C4−C3, and N5−C4 are somewhat lengthened (C2−C1 = 1.341 Å, C4−C3 = 1.299 Å, and N5−C4 = 1.287 Å) compared to those of **COM1b**. In addition, the angle of N5−C4−C3 changes from 177.5 to 149.5°. This geometry is in good agreement with the perpendicular transition state presumed by Houge et al.[14] in 1982. The bond length data reveal that these two bonds are formed unsynchronously. This situation can be explained by means of electrostatic and frontier orbital interactions. The net charges of carbons (C1, C2) in ethene are both −0.32, while the center carbon (C4) and terminal carbon (C3) in keteniminum cation are 0.57 and −0.35, respectively. Obviously, the approach of C1 to C4 is more favorable than that of C2 to C3. From the frontier orbitals of ethene and keteniminium cation, one can realize that four orbitals are involved in two types of interactions between the reactants, which are depicted in Figure 2 a and b. Two bonds (C2−C3 and C1−C4) with different ways of electron donation are formed, and a push−pull interaction is produced in the course of reaction. Because the energy difference between the LUMO of keteniminium cation and the HOMO of ethene is much smaller than that between the LUMO of ethene and the HOMO of keteniminium cation, the type Figure 2a interaction, a “head to head” overlap that favors the formation of C1−C4 bond, is much stronger than that of type Figure 2b, which favors C2−C3 bond formation. This reaction scheme reveals that these two bonds are formed basically “one by one”, so it is a “2 × [1 + 1]”-type cycloaddition, as stated in our earlier literature.[2d]

To study the bonding characters and charge distribution for stationary points in the reaction **1a** + **2a**, electron density analysis has been carried out. The electron densities ρ_b for C4−C1 bonds are 0.006 (**COM1b**), 0.039 (**TS1**), and 0.240 (**3a**), respectively, but no bond critical points between C3 and C2 can be found in **COM1b** and **TS1**, which indicates that these two bonds are formed unsynchronously. Laplacian distributions of the stationary points are illustrated in Figure 3, from which one can realize that there is a weak intermolecular interaction between C4 and the bond critical point of C2═C1 π bond in **COM1b** and **TS1** (See Figure 3 b and c). There is a critical point between H7 and the bond critical point of C2═C1 π bond in **COM1a**, which is a strong evidence of the π-type hydrogen bond's existence. Surprisingly, there are two types of interactions in **COM1b**. One is the interaction between C4 and the bond critical point of the C2═C1 π bond; the other is that of H9 with the same critical point of the C2═C1 π bond. In fact, the latter should be quite weak. Therefore, a ring critical point exists among H9, C3, C4 and the bond critical point of the C2═C1 π bond.

Only a transition state exists in this reaction, as confirmed by our IRC calculation. The **TS1** is further confirmed by vibrational analysis and characterized by the only imaginary frequency (−193i cm^{-1}). The imaginary vibration mode shows that it connects complex **COM1b** and product **3a**, which shows that **TS1** is on the right reaction path. Because **TS1** is a reactant-like one, the corresponding activation barrier is quite low, only 39.9 kJ/mol (see Figure 4). It is obvious that the reaction **1a** + **2a** is quite facile, which is consistent with Ghosez's experimental result[5] in 1972 that cycloaddition of keteniminium salt to ethene can take place at room temperature. The possible reaction path for this reaction is summarized in Scheme 1.

The solvent effect of the model reaction has also been investigated. We choose the PCM model[32] and CH_2Cl_2 as the solvent, which has been used in experimental investigations. It is found that the structures of all stationary points in solution phase (see Table S1 of the Supporting Information) are in excellent agreement with those in gas phase. The mechanism does not change as the CH_2Cl_2 solvent is introduced, but the barrier between the **TS1** and the **COM1a**-like complex is 30.6 kJ/mol, 9.3 kJ/mol

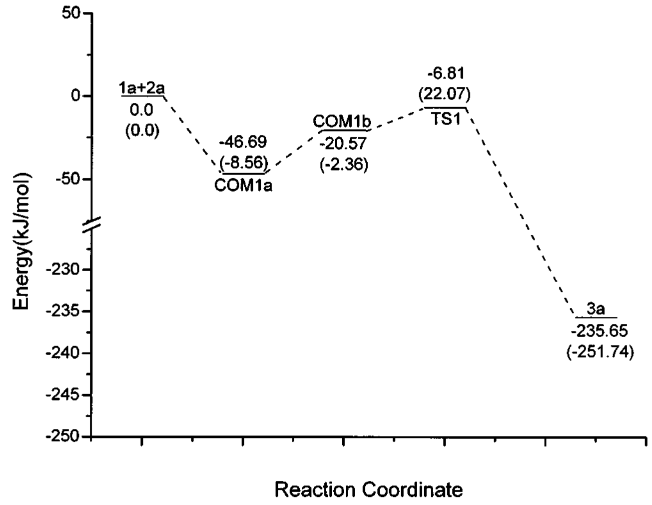
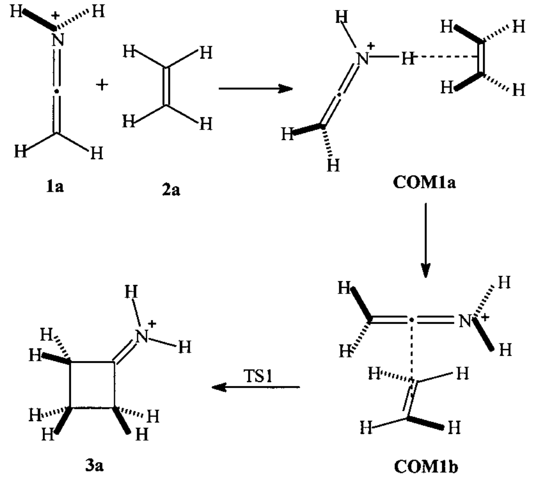


Figure 4. The schematic potential energy surface for the concerted mechanism of the model reaction (reaction 1) in gas phase. The data in paratheses are for solution phase.

Scheme 1



lower than that in gas phase (see Figure 4). This indicates that this reaction can take place in solution more easily.

Substituent Effect on the Terminal Carbon of Keteniminium Cation. The C=C bond of the keteniminium cation participates in the reaction directly, so the substituents on the terminal carbon atom might have notable electronic effect on the reaction activities. Therefore, we studied the substituent effect on the terminal carbon of the keteniminium cation first. To simplify the calculation we selected the symmetrically substituted keteniminium cation by CH_3 or Cl groups, namely, the reactions **1b** + **2a** and **1c** + **2a** (see Chart 1).

In Table S2 of the Supporting Information, the dihedral angles of C4−C1−C2−C3 of products in reactions **1b** + **2a** and **1c** + **2a** are much larger than those in other reactions. This is because the bulky substituents on the carbon atom neighboring the carbon attached to imino group have larger steric effect.

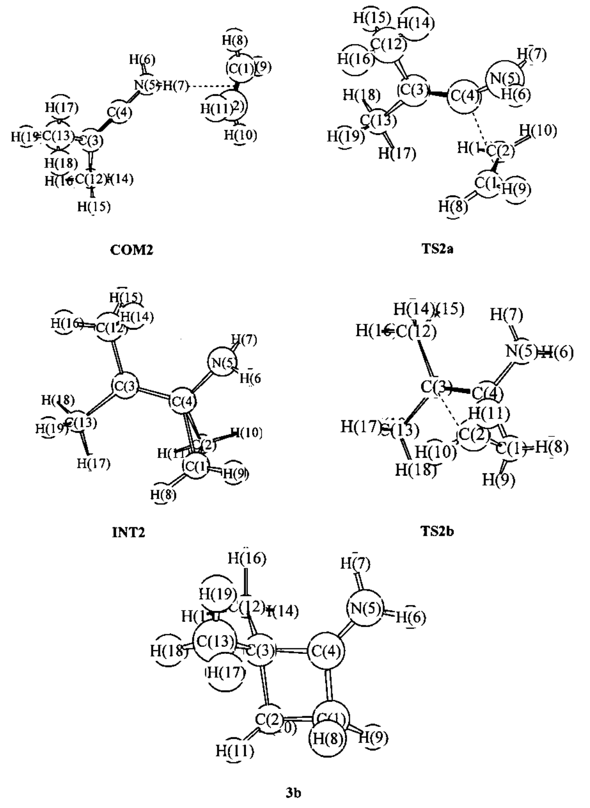


Figure 5. The numbering system of some optimized stationary points in reaction 2, in which both hydrogens on the terminal carbon of the keteniminium cation are substituted.

We have located two transition states and one intermediate for each reaction denoted as **TS2a**, **TS2b**, **INT2** (see Figure 5) and **TS3A**, **TS3b**, **INT3**, respectively (for the optimized parameters, see Table S2 of the Supporting Information). Only **COM1a**-like complexes for both reactions can be found, because the large substituents on the terminal carbon disfavor the **COM1b**-like complexes. With the approach of reactants, the hydrogen bonds in **COM1a**-like complexes are destroyed first and then the **TS1**-like transition states are formed. In this process, it is only C4−C1 and C3−C2 distances and the N5−C4−C3 angle that change greatly. When the ethene approaches closer to the center carbon C4 in the keteniminium cation, a three-membered ring intermediate is formed due to larger groups on the terminal carbon in the keteniminium cation. In this intermediate, C=N and C=C bonds in the keteniminium cation part become single bonds, the plus charge moving from N to the terminal C in the keteniminium cation. The distances between C4 and C1, C4 and C2 are almost equal (1.573 Å and 1.608 Å in **INT2**, 1.609 Å and 1.609 Å in **INT3**), and these bonds have been partly formed. The original three double bonds are lengthened considerably, whose bond length data are intermediate to those of typical single bonds and double bonds. As we know, three-membered ring intermediates are not stable, which can further proceed to form the final four-membered products via **TS2b** or **TS3b**. In **TS2b** or **TS3b**, the C4−C1 bond has been completely formed, and the distances between C2 and C3 are somewhat larger.

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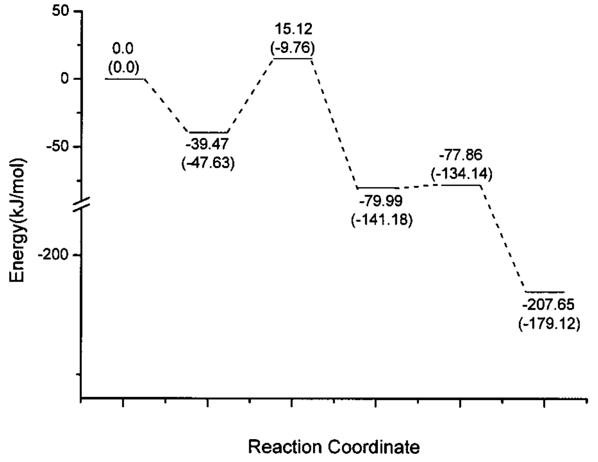
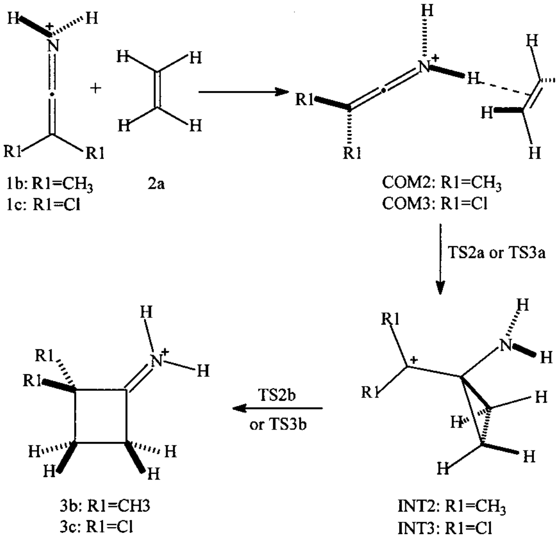


Figure 6. The schematic potential energy surface for stepwise mechanisms of reactions 2 and 3. The data in parentheses are for reaction 3.

Scheme 2



Scheme 2 shows the possible reaction path, and Figure 6 shows the schematic potential energy surface for these two reactions, which are both stepwise processes. The data reveal that the reaction is more facile when the substituents are Cl groups, the barrier being 37.9 kJ/mol, 2.0 kJ/mol lower than that of reaction **1a** + **2a**. While the hydrogen atoms in the keteniminium cation are both substituted by CH_3 groups, the reaction is energetically disadvantageous, the barrier being 54.6 kJ/mol, 14.7 kJ/mol higher than that of reaction **1a** + **2a**. This is due to the fact that the CH_3 group is an electron-pushing substituent, which decreases the net charge on C4 by 0.15 and so disfavors the reaction, while the Cl group is an electron-attracting substituent, which increases the net charge on C4 by 0.02 and then favors the reaction. This can also be explained by frontier orbital interaction. As we stated before, Figure 2a-type orbital interaction is the main one in these reactions. When an electron-attracting substituent, such as a Cl group, is attached to the terminal carbon in the keteniminium cation, the energy difference between the LUMO in keteniminium cation and the HOMO in ethene will be decreased, which can strengthen the Figure 2a-type orbital interaction and favor the formation of the C1–C4 bond. On the contrary, an electron-pushing substituent attached to the terminal carbon in the keteniminium cation, such as a CH_3 group, can increase the energy difference, which will weaken the interaction between C1 and C4 and will lead to higher energy barrier.

Substituents on Nitrogen in Keteniminium Cation. Although the C=N bond of the keteniminium cation did not participate in the reaction directly, we still tried to study the effect of the substituents on the nitrogen atom. We selected the symmetrically substituted keteniminium cation with two CH_3 or two Cl groups, respectively, as shown in reactions **1d** + **2a** and **1e** + **2a** of Chart 1.

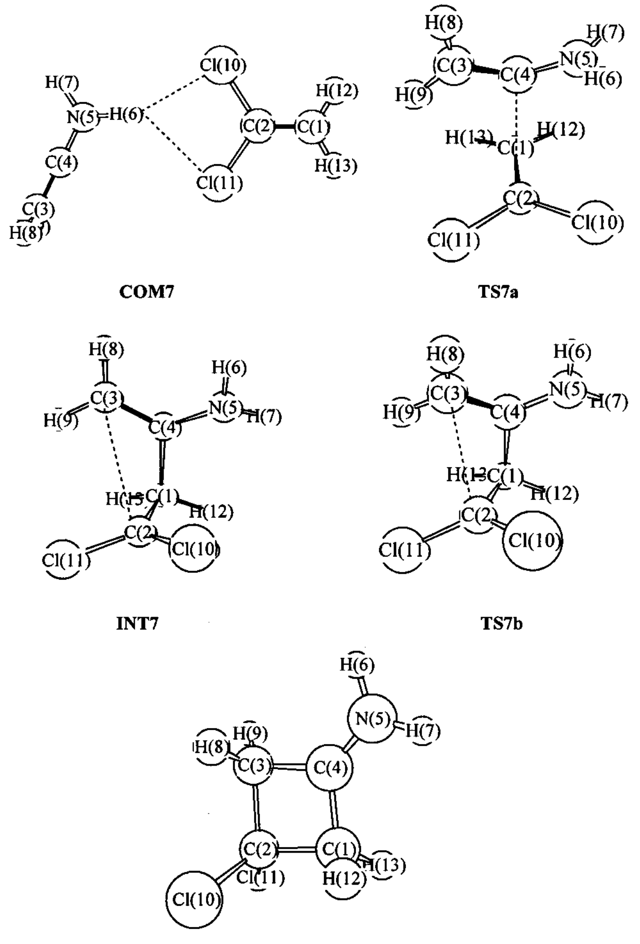
For reactions **1d** + **2a** and **1e** + **2a**, only a **COM1b**-like complex has been located for each reaction since both hydrogen atoms on nitrogen are substituted. We also locate only one transition state for each reaction, which are all **TS1**-like. These transition states are also further confirmed by vibrational analysis and characterized by the only imaginary frequency. The imaginary vibration modes show that these transition states are on the proper reaction paths.

Just like the model reaction, these two reactions both take place in a concerted but unsynchronous reaction scheme. The energies for these two reactions are listed in Table S5. From the data we can see that the Cl group, which is an electron-attracting substitutent and increases the net charge on C4 to 0.66, favors the reaction, the energy barrier being only 2.9 kJ/mol. On the contrary, the CH_3 group, which is an electron-pushing substituent, disfavors the reaction, the energy barrier being 44.8kJ/mol. It is obvious that electron-attracting substitutents on nitrogen atom notably increase the reactivity of the reactants.

Substituents on Carbon in Ethene. In this section, we tried to investigate the substitutent effect on the carbon atom in ethene (see Chart 1). There are two possibilities when the substituted ethane adds to the keteniminium cation, forming the ortho- or para-product. Because the ortho-product is sterically unfavorable, only the para-product is considered here.

For reaction **1a** + **2b**, both **COM1a**-like and **COM1b**-like complexes are located. The former is more stable than the latter by 29.1 kJ/mol, owing to the existence of the hydrogen bond. In the **COM1b**-like complex, the lengths of the C4–C1 and C4–C2 bonds are different because of the bulky substituents, while they are equal in the **COM1b** of reaction **1a** + **2a**. The length of the former (3.071 Å) is shorter than that of the latter (3.234 Å) by 0.163 Å. With the approach of the reactants to each other, this type of steric effect is more remarkable and the difference extends to 0.225 Å in **TS6**. Taking account of the electronic effect, these two electron-pushing CH_3 groups in ethene make the net charge on C2 positive, which can also explain why the lengths of the two bonds mentioned above are different. For reaction **1a** + **2c**, we can only locate one complex denoted as **COM7** in Figure 7 and Scheme 3, which is formed between a hydrogen atom connected with nitrogen and the two chlorine atoms connected with a carbon in ethene.

The system of substituents on ethene is somewhat different from that of substituents on the keteniminium cation. These two reactions take place via a different mechanism. Reaction **1a** + **2**c is stepwise (see Scheme 3) with two transition states (see **TS7a** and **TS7b** in Figure 7) while reaction **1a** + **2b** is a concerted but



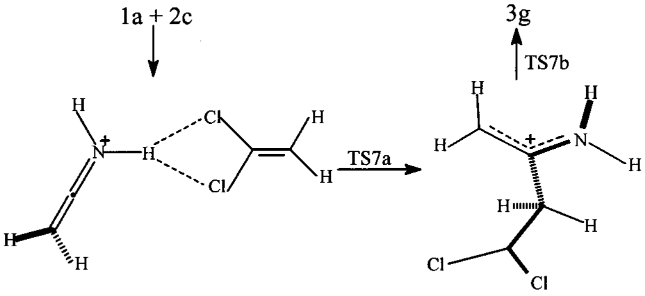
COM7 TS7a

INT7 TS7b

3g

Figure 7. The numbering system of some optimized stationary points in reaction 7, in which both hydrogens on one of the carbons of ethene are substituted.

Scheme 3



unsynchronous one, which is similar to but more facile than the reaction **1a** + **2a** (see Scheme 1). The geometries of transition state **TS6** and **TS7a** are quite similar except the angle of N5−C4−C3. In reaction **1a** + **2b**, the **COM6b** can change into product **3f** directly via **TS6,** while an intermediate **INT7** can be located in reaction **1a** + **2c**.

As far as the energy barrier is concerned, the barriers of these two steps for reaction **1a** + **2c** are 52.3 and 2.8 kJ/mol, respectively. Compared with the reaction **1a** + **2a**, the first barrier of this reaction is 12.4 kJ/mol higher than that of reaction **1a** + **2a** because of the introduction of the electron-attracting substituents Cl. While the barrier of reaction **1a** + **2b** is 9.8 kJ/mol lower than that of the reaction **1a** + **2a** as a result of electron-pushing effect of substituents CH$_3$ on ethene. Thus, we can draw a conclusion that the electron-attracting substituents disfavor the reaction while the electron-pushing substituents favor the reaction, which is different from the case of substituted keteniminium cation. This conclusion can also be inferred from the frontier orbital interaction, because the electron-pushing groups make the HOMO of ethene higher, which favors the Figure 2a-type interaction and lowers the reaction barrier. Obviously, the electron-attracting groups have the opposite effects.

Summary

The reaction **1a** + **2a**, namely the model reaction, takes place via a concerted but unsynchronous mechanism denoted as “2 × [1 + 1]”.

Substituents on the carbon or nitrogen atom in the keteniminium cation and the carbon of ethene have notable electronic effects on the reactivity of reactions. The electron-attracting substituents on keteniminium cations disfavor the reaction but the electron-pushing substituents favor the reaction. When substituents are on ethene, the cases are opposite.

Substituents on the terminal carbon atom in the keteniminium cation have a notable steric effect on the reaction activities, which is a stepwise process.

The activation barriers of these reactions are quite low, which is in good agreement with the experimental conclusion that reactions between keteniminium cations (or salts) and olefins can occur at room temperature.

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Supporting Information Available: The Z-matrixes and energetics of all the stationary points are listed in Table S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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