Chinese Journal of Chemistry, **2004**, *22*, 594—598 **Article**

Density Functional Study on the Mechanism of Collision Reaction among Protons, N_2 and Water Vapor

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The mechanism of collision reaction among protons, N_2 and water vapor was theoretically studied using Density Functional Theory. The geometries of reactants, transition states, intermediates and products were optimized at the B3LYP/6-311＋G** level by the BERNY gradient analysis method. Transition states and intermediates have been identified by vibrational frequency analysis. The relationship among reactants, intermediates, transition states and products was affirmed by IRC calculation. The variations of energy and geometry along the IRC-determined reaction paths were described. The possible reaction pathways were represented and the optimal one was decided from the viewpoint of energy.

Keywords density functional theory, reaction mechanism, transition state, proton, N_2, water vapor

Introduction

Nitrogen gas, the main component of atmosphere, is always the hotspot in scientific studies, such as nitrogen fixation, to find feasible ways to dissociate its tri-bond and so on. In recent years, interstellar nitrides have attracted extensive attention in experimental and theoretical areas.[1,2] In addition, there exist a great deal of water vapor and protons as well, the major components of cosmic rays, and therefore their reactions play a significant role in chemistry and biochemistry.[3] There is also some indication that the reaction of those three by collision can generate hydrides and oxides of nitrogen and contribute to the destruction of ozone.[4-6] The products, such as $NNOH^+$ ions, can react with CH_4 and NO, and cause the atmospheric pollution.[7] So a detailed study on the mechanism of this reaction is of great value and importance.

Computational methods

Full optimizations by means of Schlegel's algorithm[8] at the B3LYP DFT level[9] with the 6-311＋＋G** basis set were performed using the Gaussian 98W program. The nature of the stationary points was further checked, and zero point vibrational energies (ZPVE) were evaluated by analytical computations of harmonic vibrational frequencies at the same theory level. Intrinsic reaction coordinate (IRC) calculations with the same method and level were also carried out to check the connection between all the critical structures located, using the Gonzalez and Schlegel method[10] implemented in Gaussian 98W.

Results and discussion

Verification of intermediates and transition states

The results derived from our calculations confirm that there are five intermediates, eight transition sates and two products on the potential energy surface (PES). The geometries and structural parameters of all stationary points are depicted in Figure 1.

In order to affirm the intermediates and transition states along the reaction pathways, we analyzed the vibrational frequencies of all the stationary points. All of them have twelve vibration fundamentals, but only TS1, TS2, TS3, TS4, TS5, TS6, TS7 and TS8 have merely one vibration fundamental which has an imaginary frequency, and consequently are proved to be really transition states. Their imaginary frequencies are 1854.4312i cm^{-1} (TS1), 816.6063i cm^{-1} (TS2), 1601.1969i cm^{-1} (TS3), 1292.9153i cm^{-1} (TS4), 718.7362i cm^{-1} (TS5), 392.6493i cm^{-1} (TS6), 98.4653i cm^{-1} (TS7), 356.3885i cm^{-1} (TS8), respectively. The cartesian displacement vectors associated with the imaginary vibration frequencies of the transition states are listed in Table 1. While the vibrational frequencies of IM1, IM2, IM3, IM4 and IM5 are all real and positive, which implies that they are all minima on the PES. The connections of reactants, intermediates, transition states and products

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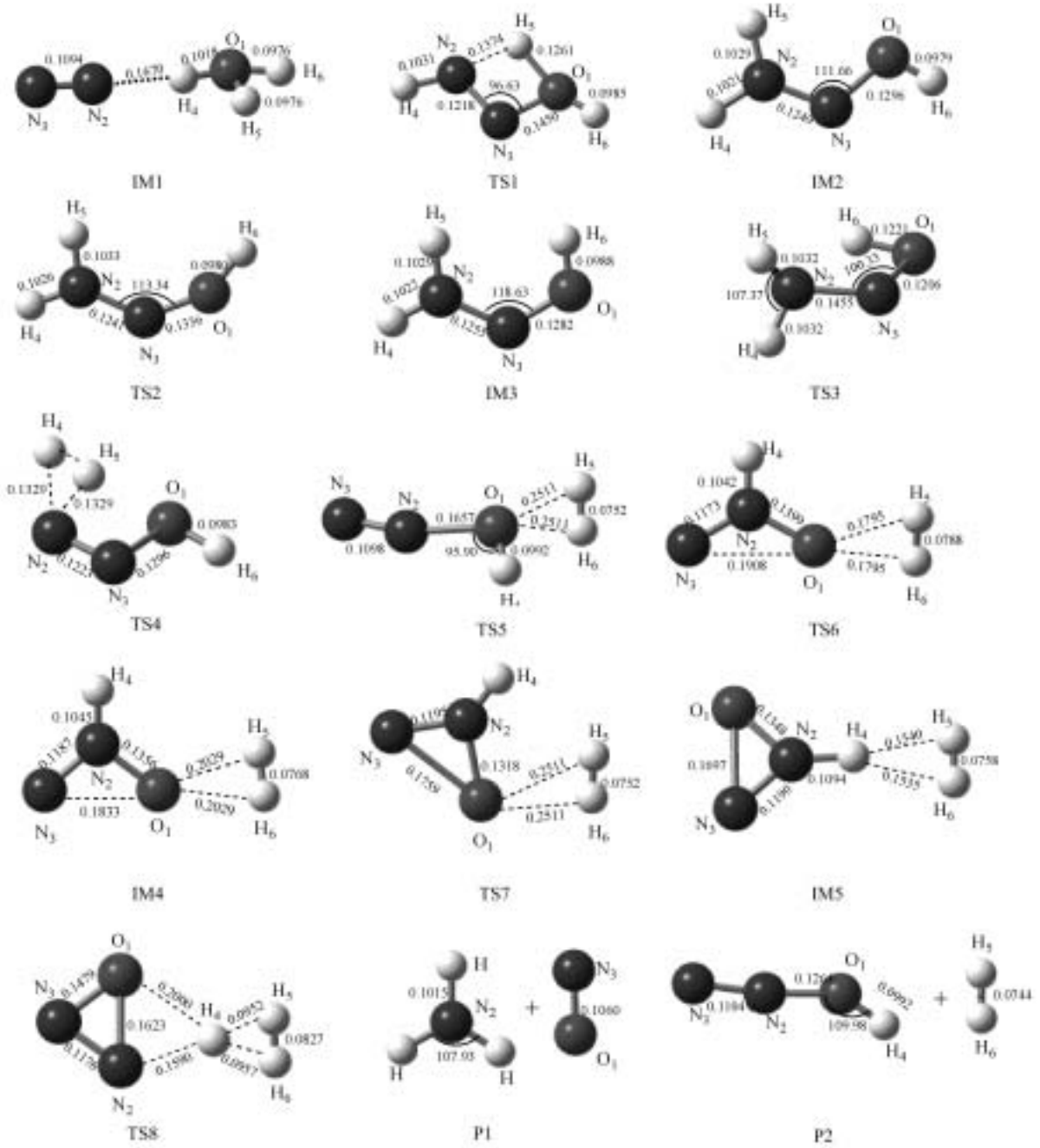

Figure 1 Geometries of all the species at the pathways (unit: bond length in nm, bond angle in degree).

are further affirmed by IRC calculation, indicating that they are located on the correct pathways.

Analysis of reaction mechanism

It was reported that the rate constant for the reaction $N_2H^+ + H_2O \rightarrow H_3O^+ + N_2$ is $(2.5 \pm 0.7) \times 10^{-9}$ $cm^3 \cdot sec^{-1}$ at 300 K,[11] and our study has also shown that the system of the above products is much more stable. So we begin the reaction of N_2, water vapor and a proton with H_3O^+ and N_2 (IM1). Heat (726.26 kJ/mol) released in this step is sufficient for the next steps. The energies of all species are listed in Table 2 and potential energy surface is depicted in Figure 2.

According to our computational results, the title reaction is a dual-channel process. The reaction can be represented as the following steps:

(1) $N_2 + H^+ + H_2O \rightarrow NH_3 + NO^+$

(2) $N_2 + H^+ + H_2O \rightarrow NNOH^+ + H_2$

The products NH_3 and NO^+ from channel (1) can be generated via the route R→IM1→TS1→IM2→TS2→IM3→TS3→P1. Hydrogen transference (TS1→IM2) and single bond rotation (IM2→TS2→IM3) go through successively, and whereafter another hydrogen transference and concomitant chemical bond break (IM3→TS3→P1) result in the product 1 (NH_3 and NO^+). The barrier height for such process is 438.29 kJ/mol and

Table 1 Vibration models of imaginary frequencies of all transition states

Transition states	TS1			TS2			TS3			TS4		
Imaginary frequencies/cm^{-1}	1854.4312i			816.6063i			1601.1969i			1292.9153i		
Coordinates	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
O(1)	0.00	0.03	0.00	−0.04	0.08	−0.04	−0.01	0.03	0.00	−0.01	0.01	0.00
N(2)	0.03	−0.02	0.00	0.01	−0.01	−0.04	−0.02	−0.03	0.00	−0.04	0.13	0.00
N(3)	0.04	0.00	0.00	−0.01	−0.00	0.07	−0.04	0.01	0.00	0.06	−0.05	0.00
H(4)	0.00	−0.12	−0.02	0.00	0.01	−0.03	−0.01	−0.11	−0.02	−0.03	−0.66	0.23
H(5)	−0.97	−0.14	−0.01	0.07	−0.02	−0.12	−0.01	−0.11	0.02	−0.03	−0.66	−0.23
H(6)	0.00	0.13	−0.06	0.47	−0.82	0.27	0.99	0.00	0.00	0.00	0.02	0.00
Transition states	TS5			TS6			TS7			TS8		
Imaginary frequencies/cm^{-1}	718.7362i			392.6493i			98.4653i			356.3885i		
Coordinates	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
O(1)	0.31	−0.04	0.00	0.24	−0.02	0.00	−0.09	0.11	0.00	0.10	0.02	0.00
N(2)	−0.16	0.07	0.00	−0.12	0.01	0.00	0.07	0.03	0.00	−0.10	0.11	0.00
N(3)	−0.11	−0.04	0.00	−0.06	−0.03	0.00	0.02	−0.07	0.00	−0.03	−0.03	0.00
H(4)	0.05	0.01	0.00	−0.05	0.02	0.00	0.20	0.09	0.00	0.06	−0.77	0.00
H(5)	−0.63	0.14	0.09	−0.61	0.30	−0.05	−0.05	−0.68	0.00	0.20	−0.45	0.00
H(6)	−0.63	0.14	−0.09	−0.61	0.30	0.05	−0.05	−0.68	0.00	−0.10	−0.34	0.00

Table 2 Energies of all stationary points on the potential energy surface of reaction

System	E^a /a.u.	*Z-PC*^{b} /a.u.	$E_0{}^c$ /a.u.	$E_R{}^d$ /a.u.	$E_R{}^d$ /(kJ•mol^{-1})
R	−186.01815	0.02685	−185.99130	0.00000	0
IM1	−186.30907	0.04220	−186.26687	−0.27557	−726.2762
TS1	−186.14033	0.03976	−186.10057	−0.10927	−287.9857
IM2	−186.22256	0.04706	−186.17550	−0.18420	−485.4667
TS2	−186.18602	0.04445	−186.14157	−0.15027	−396.0429
IM3	−186.20328	0.04632	−186.15696	−0.16566	−436.6039
TS3	−186.12125	0.04007	−186.08118	−0.08988	−236.8825
TS4	−186.07018	0.03434	−186.03584	−0.04454	−117.3871
TS5	−186.08851	0.03233	−186.05618	−0.06488	−170.9940
TS6	−185.99006	0.03087	−185.95919	0.03211	84.6278
IM4	−185.99044	0.03139	−185.95905	0.03225	84.9962
TS7	−185.98902	0.03127	−185.95775	0.03355	88.4224
IM5	−185.99638	0.03181	−185.96457	0.02673	70.4480
TS8	−185.97169	0.02932	−185.94237	0.04893	128.9570
P1	−186.22538	0.04375	−186.18163	−0.19033	−501.6228
P2	−186.13043	0.03467	−186.09576	−0.10446	−275.3087

[a] Uncorrected energies; [b] zero-point correction; [c] sum of electronic and zero-point energies; [d] relative energies to reactants.

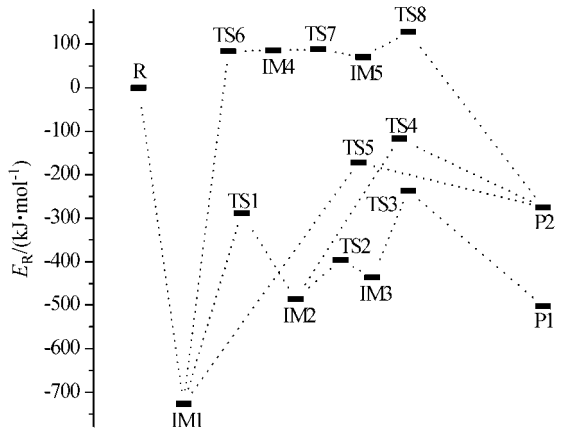

Figure 2 Variation of energy along the pathways.

the heat of 501.62 kJ/mol is set out to produce P1. The isomerization between IM2 and IM3 will be discussed in the following text.

P2 ($NNOH^+ + H_2$) can be obtained along three routes.

(2.1) R→IM1→TS1→IM2→TS4→P2

(2.2) R→IM1→TS5→P2

(2.3) R→IM1→TS6→IM4→TS7→IM5→TS8→P2

As for route 2.1, similar to channel (1), the process of R→IM1→TS1→IM2 comes through at the first and equal barrier height is overcome, and then two H atoms connected with N(2) are gradually dissociated and P2 is generated via TS4 with a heat energy of 275.31 kJ/mol released. P2 can also be achieved through route 2.2, via IM1 and TS5. The energy of TS5 is 555.28 kJ/mol higher than IM1. The third possible route to generate P2 is R→IM1→TS6→IM4→TS7→IM5→TS8→P2. TS6 has the energy of 641.75 kJ/mol higher than IM1, and the activation energy is 203.46 kJ/mol higher than route (1) and 2.1, 86.47 kJ/mol higher than route 2.2.

Isomerization of intermediates

The step IM2→TS2→IM3 involves a typical isomerisation of the two intermediates. The isomerization steps are important in determining the overall rate and yield,[12,13] so we will discuss the isomerization process in detail. There is an energy barrier of 89.43 kJ/mol for N—O bond rotation step IM2→TS2 whereas the barrier for IM3→TS2 is 40.56 kJ/mol. The variation of energy and important geometry parameters are shown in Figure 3. From the figure, we can see that only ∠6132 changes much during N—O bond rotation, and IM2 is much more stable than IM3 because of its faint spatial repulsion.

Energy changes on the pathways

To obtain the variation of energy along the path of the reaction, IRC calculations at the level of B3LYP/6-311 + G** were carried out. Calculations were started from all transition states by a step-length of 0.1 amu$^{(1/2)}$·Bohr, following the least energy path forward and backward scanning 100 points. Taking the reactant energy as zero, we calculated relative energy for each stationary point. Energy change along the reaction path is shown in Figure 3, which describes the mechanism of the collision reaction among protons, N_2 and water vapor.

Conclusion

The title reaction is a multi-channel and exothermic process. The reaction can be represented as the steps below:

(1) R→IM1→TS1→IM2→TS2→IM3→TS3→P1

(2.1) R→IM1→TS1→IM2→TS4→P2

(2.2) R→IM1→TS5→P2

(2.3) R→IM1→TS6→IM4→TS7→IM5→TS8→P2

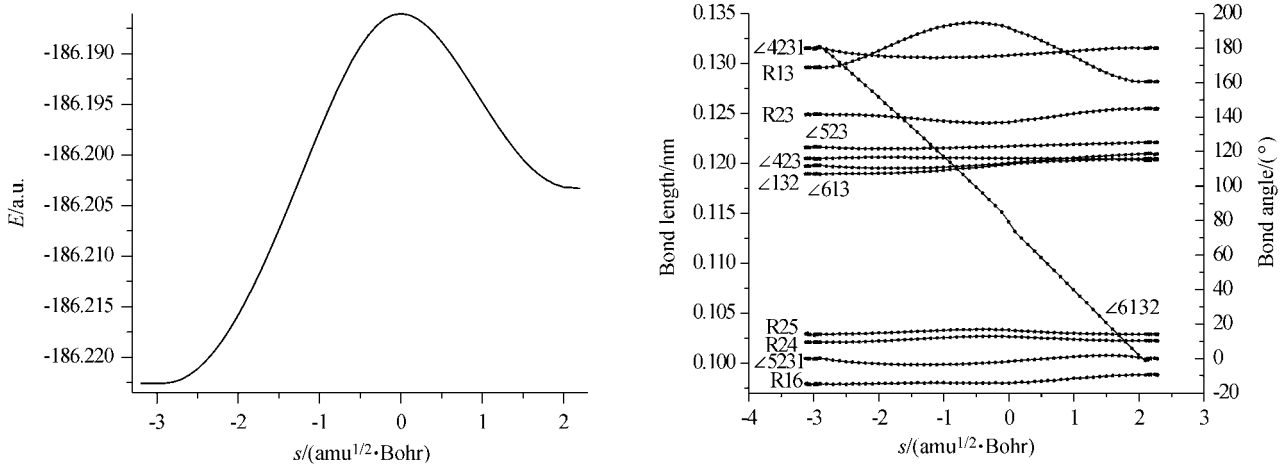

Figure 3 Variation of energy during isomerization process IM2→TS2→IM3 and variation of important geometry parameters.

IM1→TS1 is the rate-determining step of route (1). The energy barrier height of this route is the lowest and P1 is more stable than P2, and therefore route (1) is the optimal route for this reaction. Considering its higher energy and insurmountable activation energies, P2 is not considered as the optimistic product, although P2 can be achieved via three routes and its branch ratio is larger than that for P1.

Our investigation in the present paper may be prospective to contribute to the study on interstellar molecular reactions.

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