

## ARTICLE

Theoretical Study on the Reaction Mechanism of CH<sub>2</sub>F Radical with HNCO

Lai-cai Li\*, Jing Shang, Jun-ling Liu

Department of Chemistry, Sichuan Normal University, Chengdu 610066, China

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The reaction mechanism of CH<sub>2</sub>F radical with HNCO was investigated by density functional theory (DFT) at the B3LYP/6-311++G(d,p) level. The geometries of the reactants, the intermediates, the transition states and the products were optimized. The transition states were verified through the vibration analysis. The relative energies were calculated at the QCISD(T)/6-311++G\*\*//B3LYP/6-311++G(d,p) level. Seven feasible reaction pathways of the reaction were studied. The results indicate that the pathway (5) is the most favorable to occur, so it is the main pathway of the reaction.

**Key words:** CH<sub>2</sub>F radical, Isocyanic acid, Reaction mechanism, Activation barrier

## I. INTRODUCTION

Isocyanic acid (HNCO) is the main product during cyanuric acid (CA) thermolysis process. HNCO is also a convenient photolysis source in the study of elementary reaction dynamics in laboratory [1-3]. Furthermore, HNCO plays an important role in the study of combustion chemistry and atmosphere chemistry. It can eliminate the hazardous substance from the burning exhaust gas [4-7]. The oxidation reaction between HNCO and hydroxyl radical (OH) is crucial to eliminate NO. Many experimental and theoretical studies have been concentrated on the reactions of HNCO [8-20].

In the typical fuel-lean combustion condition, the reactions of halogenated alkyls with atoms are important in the oxidation process of polyhalogenated hydrocarbons [21]. Halogenated alkanes also can undergo photodecomposition to produce halogenated alkyl radicals. As a simple halogenated alkyl radical, halogenated methyl (CH<sub>2</sub>X) attracted scientist's attention [22,23]. In a word, it has practical and theoretical significance for studying the reaction of HNCO with halogenated alkyl radical. In this work, we used density functional theory (DFT) to explore the reaction mechanism of fluorine-substituting methyl (CH<sub>2</sub>F) radical with HNCO.

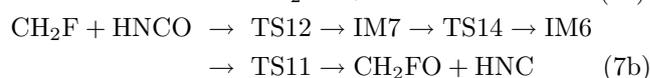
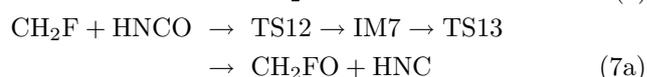
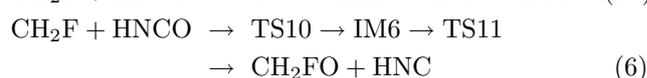
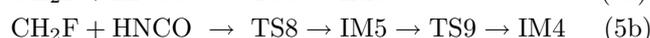
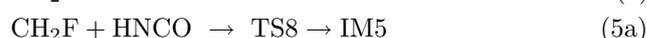
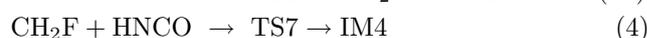
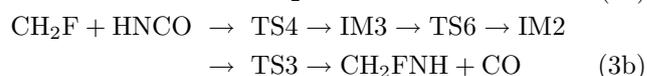
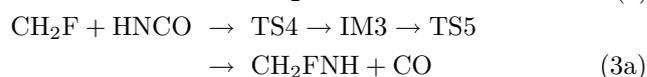
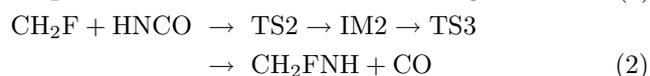
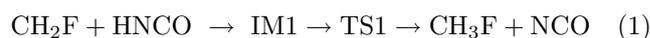
## II. COMPUTATIONAL DETAILS

The geometries of reactants, intermediates, transition states and products were fully optimized at the B3LYP/6-311++G(d,p) level. For each species, the vibration analysis was performed to obtain the zero point energies (ZPE) and verify whether it was a minimum

or a transition state on the potential energy surfaces (PES). To obtain more accurate energies, the single point energies of all structures were calculated at the QCISD(T)/6-311++G(d,p) level. Meanwhile, the wave function of all species were calculated at the B3LYP/6-311++G(d,p) level. Based on the wave function results, the structures of all species were analyzed with AIM 2000 program package [24] to calculate the charge density of some critical points. All calculations were carried out with the Gaussian 98 program [25].

## III. RESULTS AND DISCUSSION

Considering the possible attacking patterns in the CH<sub>2</sub>F+HNCO reaction, seven feasible pathways were investigated, which are respectively:



In these seven pathways, IM represents the intermediate and TS represents the transition state. The op-

\* Author to whom correspondence should be addressed. E-mail: lilcmail@163.com

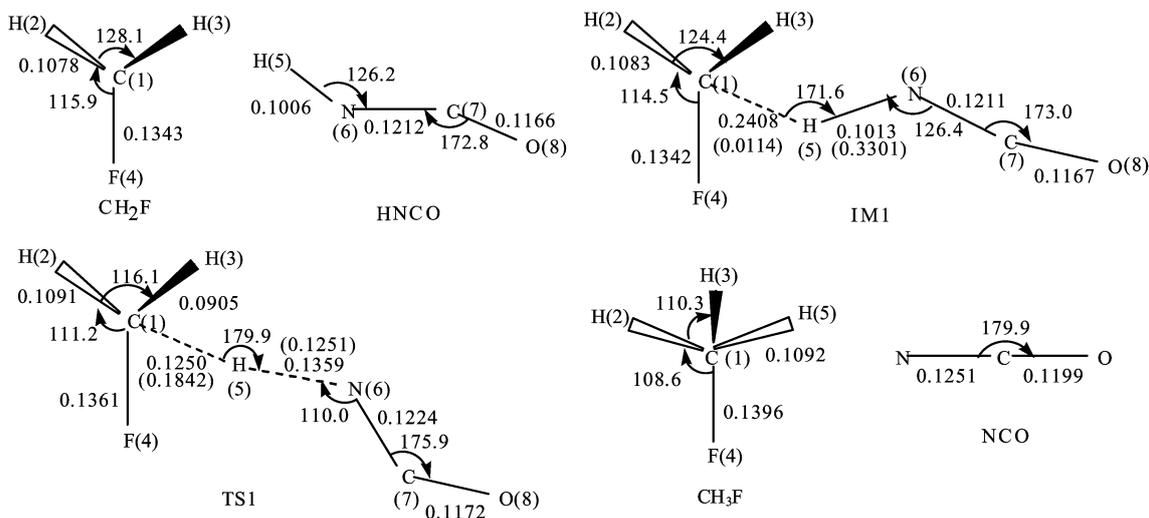


FIG. 1 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (1).

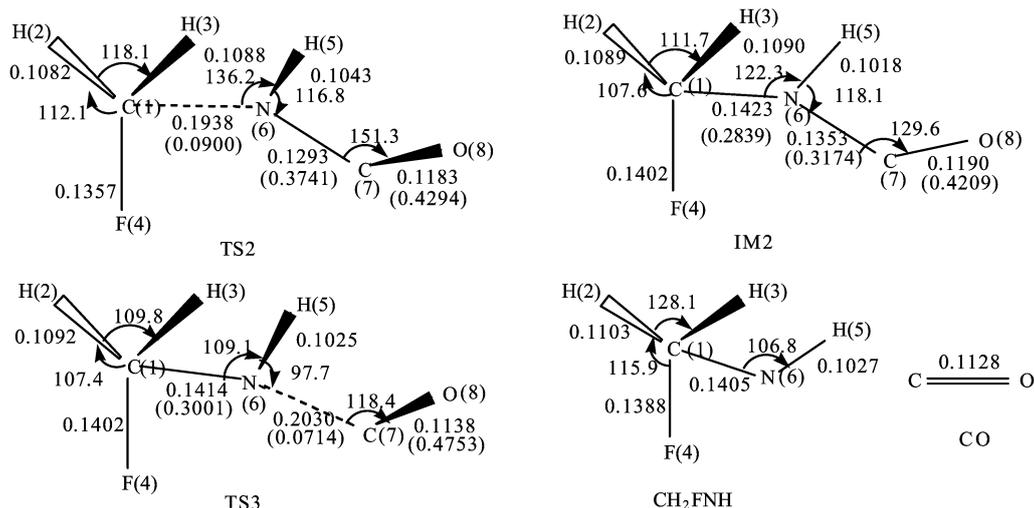


FIG. 2 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (2).

timized geometry parameters (bond length: nm, bond angle: ( $^{\circ}$ )) and the charge density of some critical points (in bracket) of all species are illustrated in Fig.1 to Fig.6. Table I lists the corresponding energies calculated at the B3LYP/6-311++G(d,p) and QCISD(T)/6-311++G(d,p) levels, respectively. And based on the results of QCISD(T)/6-311++G(d,p) level, the relative energies ( $E_{\text{rel}}$ ) are also calculated and listed in Table I. Figure 7 shows the energies of these pathways.

From Table I, we can see that all the vibration frequencies of the intermediates are positive, and the transition states have only one imaginary frequency, which indicates that all intermediates and transition states really exist on the potential energy surface.

Pathway (1): As can be seen in Fig.1, the H(5) atom of HNCO collides with the C(1) atom of  $\text{CH}_2\text{F}$  to form a hydrogen-bonding complex IM1 directly. Then IM1 de-

composes into the  $\text{CH}_3\text{F}$  and NCO radicals through the transition state TS1. It is a hydrogen transferring process. By analyzing the configurations and corresponding charge density of the critical points, one could see that, the bond length of C(1)–H(5) is shortened from 0.2408 nm in IM2 to 0.1250 nm in TS1, and the charge density of the critical point is increased from 0.0114 to 0.1842. And finally it forms a C(1)–H(5) bond. Similarly, the bond length of H(5)–N(6) is increased from 0.1013 nm in IM1 to 0.1360 nm in TS1, and the charge density of the critical point is decreased from 0.3301 to 0.1251. The H(5)–N(6) bond is broken.

In IM1, the length of C(1)–H(5) bond is 0.2408 nm, its charge density of the critical point is 0.0114, and the bond angle of C(1)–H(5)–N(6) is  $171.6^{\circ}$ . All results show that IM1 is a hydrogen-bonding complex. Its stabilization energy is 9.53 kJ/mol.

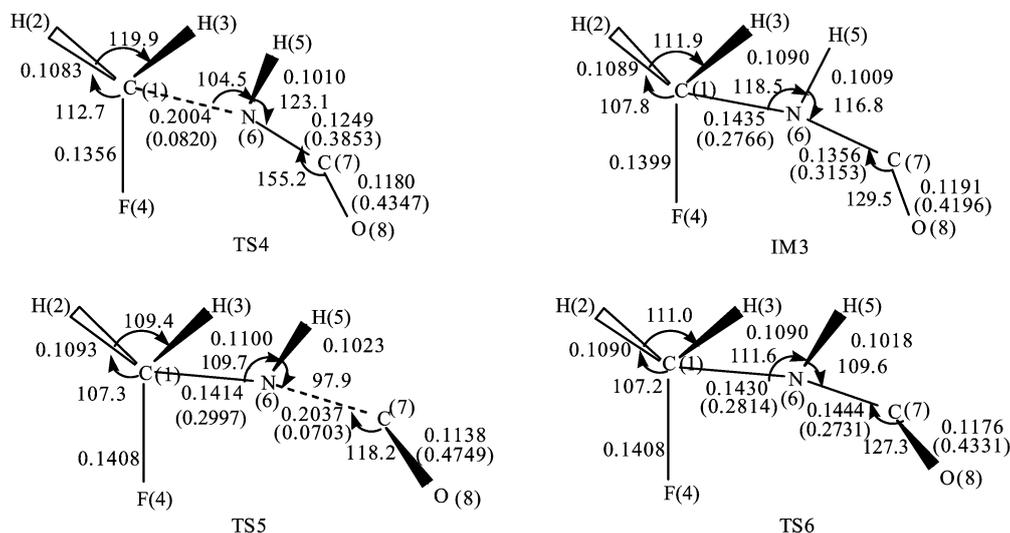


FIG. 3 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (3).

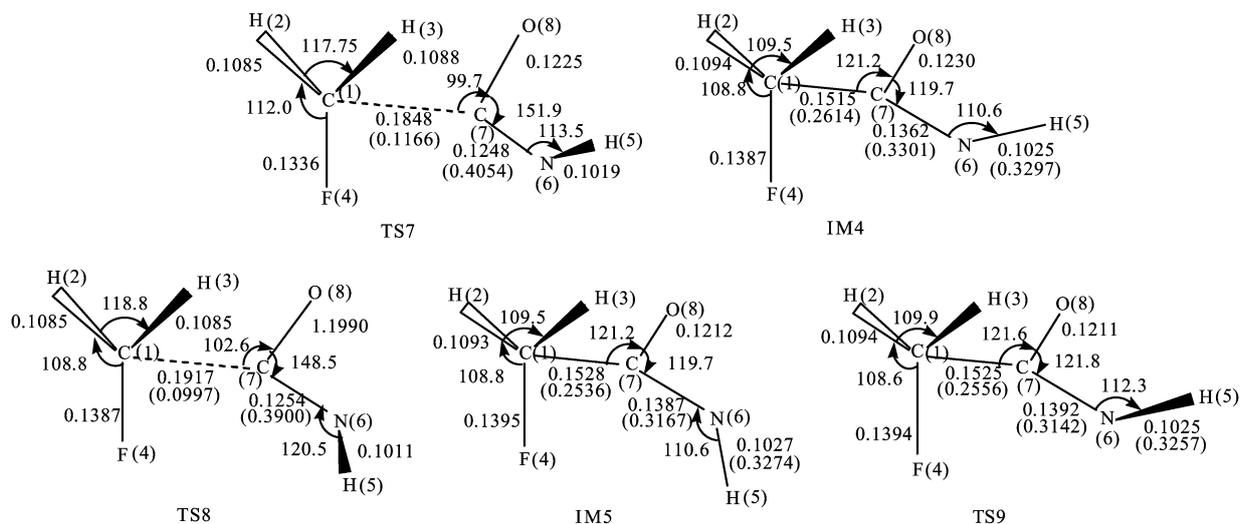


FIG. 4 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (4) and (5).

Pathway (2): Figure 2 shows the N(6) atom of HNCO approaches the C(1) atom of CH<sub>2</sub>F to form the intermediate IM2 through TS2. Then IM2 forms final products CH<sub>2</sub>FNH and CO directly through the transition state TS3. The bond length of C(1)–N(6) is changed from 0.1938 nm in TS2 to 0.1423 nm in IM2, and to 0.1414 nm in TS3, and the charge density of the critical point is increased from 0.0900 to 0.2839, and to 0.3001. Obviously, the C(1)–N(6) bond is formed. Similarly, the bond length of N(6)–C(7) is increased from 0.1293 nm in TS2 to 0.1353 nm in IM2, and to 0.2030 nm in TS3, and the charge density of the critical point is decreased from 0.3741 to 0.3174, and to 0.0714. Distinctly, the N(6)–C(7) bond is cleaved.

Pathway (3): In Fig.3, the N(6) atom of HNCO col-

lides with the C(1) atom of CH<sub>2</sub>F to form the intermediate IM3 through TS4. Then IM3 decomposes into the final products CH<sub>2</sub>FNH and CO through TS5. The bond length of C(1)–N(6) is changed from 0.2004 nm in TS4 to 0.1435 nm in IM3, and to 0.1414 nm in TS5, and the charge density of the critical point is changed from 0.0820 to 0.2766, and to 0.2997. The C(1)–N(6) bond is formed. Similarly, the N(6)–C(7) bond is broken. Meanwhile, as can be seen in Fig.3 and Fig.7, IM3 can isomerize to form IM2 through the transition state TS6. In IM3, TS6 and IM2, the dihedral angle H(5)–N(6)–C(7)–O(8) is the mainly variable. In these three species, they are 180.0°, 115.5° and 0.0°, respectively.

Pathway (4) and Pathway (5): Figure 4 shows the

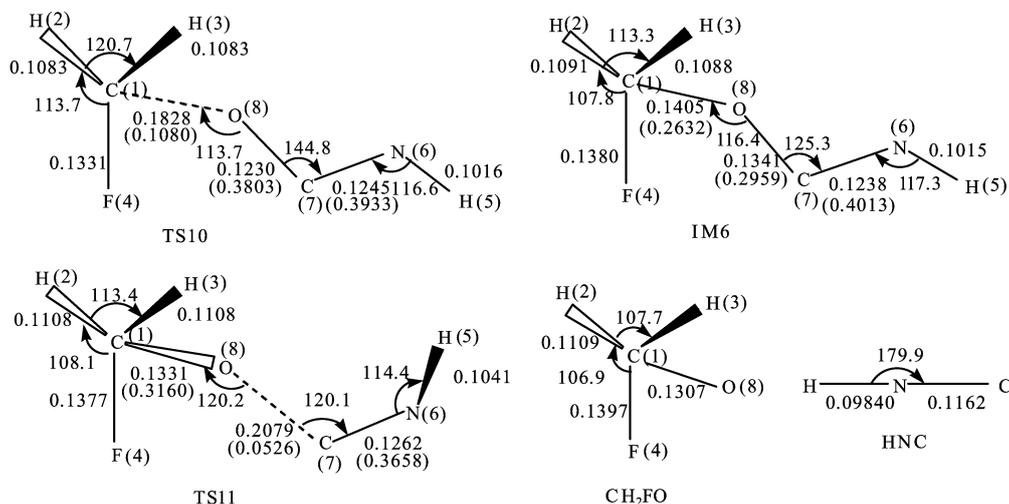


FIG. 5 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (6).

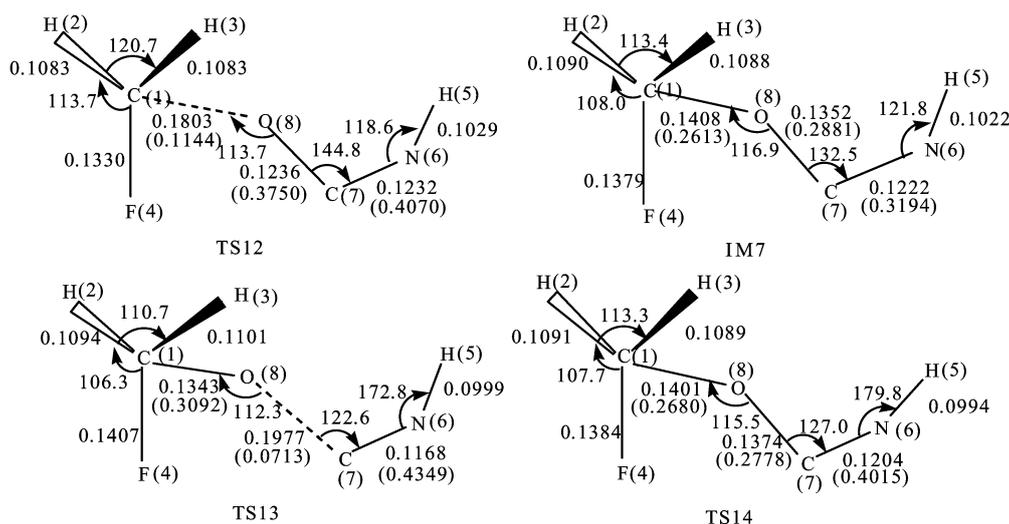


FIG. 6 Optimized structures parameter and the charge density of some critical points (in bracket) of all compounds in pathway (7).

C(7) atom of HNC(O) collides with the C(1) atom of CH<sub>2</sub>F to form the intermediates IM4 and IM5 through TS7 and TS8, respectively. Based on the configurations, IM4 and IM5 are stable molecules, i.e. fluorine-substituting methyl imide (CH<sub>2</sub>FCONH). The bond length of C(1)–C(7) is shortened from 0.1848 nm in TS7 to 0.1515 nm in IM4, and the charge density of the critical point is increased from 0.1166 to 0.2614. Obviously, the C(1)–C(7) bond is formed. Meanwhile, IM5 can isomerize to form IM4 through the transition state TS9. In IM5, TS9 and IM4, the dihedral angle H(5)–N(6)–C(7)–O(8) is the mainly variable, they are 180.0°, 99.3° and 0.0°, respectively.

Pathway (6): As can be seen in Fig.5, the O(8) atom of HNC(O) collides with the C(1) atom of CH<sub>2</sub>F to form the intermediate IM6 through TS10. Then

IM6 decomposes into the final products CH<sub>2</sub>FO and HNC through the transition state TS11. The bond length of C(1)–O(8) is decreased from 0.1828 nm in TS10 to 0.1405 nm in IM6, and to 0.1331 nm in TS11, and the charge density of the critical point is increased from 0.1080 to 0.2632, and to 0.3160. Obviously, the C(1)–O(8) bond is formed. Similarly, the bond length of O(8)–C(7) is increased from 0.1230 nm in TS10 to 0.1341 nm in IM6, and to 0.2079 nm in TS11, and the charge density of the critical point is decreased from 0.3803 to 0.2959, and to 0.0526. Clearly, the O(8)–C(7) bond is cleaved.

Pathway (7): Figure 6 shows the O(8) atom of HNC(O) approaches to the C(1) atom of CH<sub>2</sub>F to form the intermediate IM7 through TS12. Then IM7 forms the final products CH<sub>2</sub>FO and HNC through the transi-

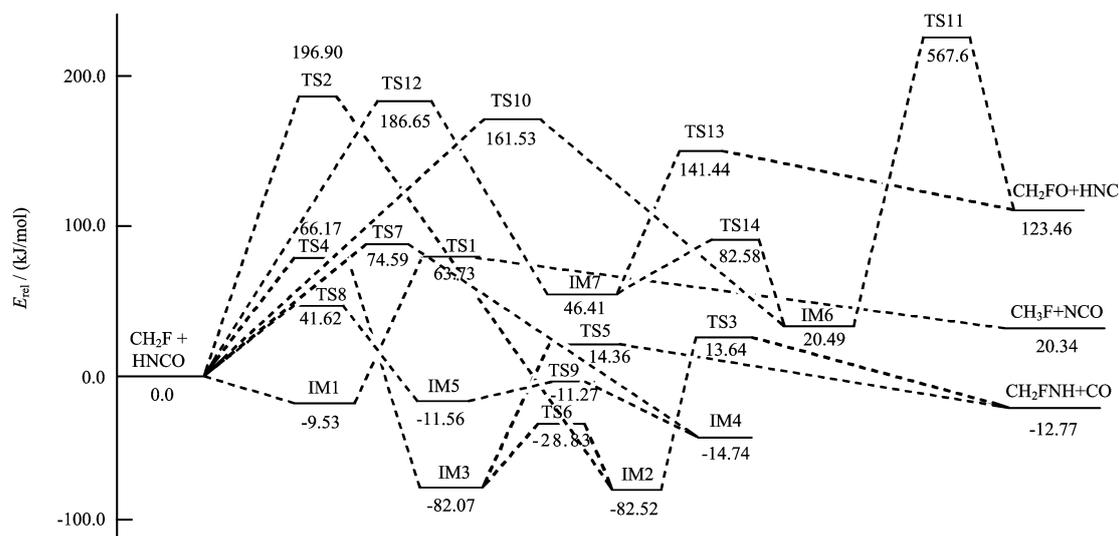


FIG. 7 Energy diagram in the CH<sub>2</sub>F+HNCO reaction.

tion state TS13. The bond length of C(1)–O(8) is shortened from 0.1803 nm in TS12 to 0.1408 nm in IM7, and to 0.1343 nm in TS13, and the charge density of the critical point is increased from 0.1144 to 0.2613, and to 0.3092. Obviously, the C(1)–O(8) bond is formed. Similarly, the bond length of O(8)–C(7) is changed from 0.1236 nm in TS12 to 0.1352 nm in IM7, and to 0.1977 nm in TS13, and the charge density of the critical point is decreased from 0.3750 to 0.2881, to 0.0713. Apparently, the O(8)–C(7) bond is cleaved. Meanwhile, IM7 can isomerize to form IM6 through the transition state TS14. In IM7, TS14 and IM6, the dihedral angle H(5)–N(6)–C(7)–O(8) is the main variable. In these three species, they are 0.0°, 82.9° and 180.0°, respectively.

#### IV. ENERGY ANALYSIS

As can be seen in Table I and Fig.7, the rate-controlling step of pathway (1) is IM1→TS1, whose energy barrier is 73.26 kJ/mol. The rate-controlling step of pathway (2) is CH<sub>2</sub>F+HNCO→TS2, and its energy barrier is 196.90 kJ/mol. The rate-controlling step of pathway (3) is IM3→TS5, and its energy barrier is 96.43 kJ/mol. The rate-controlling step of pathway (4) is CH<sub>2</sub>F+HNCO→TS7, whose energy barrier is 74.59 kJ/mol. The rate-controlling step of pathway (5) is CH<sub>2</sub>F+HNCO→TS8, and its energy barrier is 41.62 kJ/mol. The rate-controlling step of pathway (6) is IM6→TS11, whose energy barrier is 547.11 kJ/mol. The rate-controlling step of pathway (7) is CH<sub>2</sub>F+HNCO→TS12, and its energy barrier is 186.65 kJ/mol.

Obviously, the energy barrier of the rate-controlling step of pathway (5) is the lowest, so it is the easiest to occur. In pathway (5), it can form a stable molecule fluorine-substituting methyl imide (CH<sub>2</sub>FCONH). The

energy barrier of the rate-controlling step in pathway (1) is the second lowest, so it is also possible to occur. The hydrogen-transferring is the main reaction process. The energy barrier of the rate-controlling step in pathway (6) is the greatest, and it is impossible to occur comparatively. At the same time, there is a parallel competitive reaction between pathway (6) and pathway (7), so pathway (6) is not the main pathway to form CH<sub>2</sub>FO and HNC.

#### V. CONCLUSION

The calculation results show that pathway (5), CH<sub>2</sub>F+HNCO→TS8→IM5→TS9→IM4, not only possesses the lowest energy barrier energy, but also forms a stable molecule fluorine-substituting methyl imide. It is the main pathway in this reaction. The previous studies indicated in the reaction of HNCO with other radicals, the hydrogen-transferring process is the main reaction pathway. There is a little difference between the results presented in this work and the previous results. However, in the reaction of HNCO with CH<sub>2</sub>F radical, the energy barrier of the rate-controlling step of hydrogen-transferring is not high (73.26 kJ/mol), so this process is also likely to occur. The calculation results also indicate the energy barrier of the rate-controlling step of pathway (6), CH<sub>2</sub>F+HNCO→TS10→IM6→TS11→CH<sub>2</sub>FO+HNC, is the highest, so it is unlikely to occur.

#### VI. ACKNOWLEDGMENTS

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TABLE I Energies (a.u.) and relative energies (kJ/mol) and frequency ( $\text{cm}^{-1}$ ) of the compounds in the  $\text{CH}_2\text{F}+\text{HNCO}$  reaction

Species	ZPE	B3LYP	QCISD(T)	$E_{\text{rel}}$	Frequency
$\text{CH}_2\text{F}+\text{HNCO}$	0.044637	-307.813497	-307.142703	0.00	—
$\text{CH}_3\text{F}+\text{NCO}$	0.047099	-307.797076	-307.134951	20.34	—
$\text{CH}_2\text{FNH}+\text{CO}$	0.047087	-307.798882	-307.147568	-12.77	—
$\text{CH}_2\text{FO}+\text{HNC}$	0.044202	-307.760277	-307.095653	123.46	—
IM1	0.047232	-307.813619	-307.146335	-9.53	15.8
IM2	0.054741	-307.830172	-307.174153	-82.52	102.1
IM3	0.055123	-307.829036	-307.173980	-82.07	88.8
IM4	0.046928	-307.815752	-307.148661	-14.74	16.9
IM5	0.052143	-307.805549	-307.148319	-11.56	83.9
IM6	0.053609	-307.790657	-307.134893	20.49	96.3
IM7	0.052756	-307.782515	-307.125018	46.41	96.0
TS1	0.044983	-307.794128	-307.118415	63.73	1105.9i
TS2	0.048832	-307.736471	-307.067666	196.90	915.7i
TS3	0.049866	-307.791452	-307.137505	13.64	334.4i
TS4	0.049261	-307.787894	-307.117487	66.17	573.9i
TS5	0.049960	-307.790899	-307.137232	14.36	342.0i
TS6	0.053424	-307.806728	-307.153690	-28.83	310.6i
TS7	0.049836	-307.780703	-307.114277	74.59	394.5i
TS8	0.049937	-307.793040	-307.126840	41.62	360.9i
TS9	0.050816	-307.804358	-307.146997	-11.27	174.2i
TS10	0.049774	-307.752124	-307.081143	161.53	888.8i
TS11	0.045742	-307.594685	-306.926358	567.60	147.4i
TS12	0.049001	-307.744353	-307.071573	186.65	915.4i
TS13	0.048375	-307.752874	-307.088802	141.44	273.2i
TS14	0.051102	-307.772550	-307.111232	82.58	787.9i

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