Theoretical study on Reaction Mechanism of methylene amidogen H$_2$CN with OH radical

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Abstract. We performed the theoretical potential energy surface investigation on the mechanism of H$_2$CN + OH at the CCSD(T)/6-311++G(2df,p), G3B3, CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ single-point levels using the B3LYP/6-31++G(d,p), BH&HLYP/6-31++G(d,p), and QCISD/6-311++G(d,p) optimized geometries. We found that two reaction channels were feasible: 1) the quasi hydrogen abstraction of H$_2$CN by OH to form product HCN + H$_2$O via NC(H)HꞏꞏꞏOH, and 2) the addition elimination to form HCN + H$_2$O.

1. Introduction

The methylene amidogen radical (H$_2$CN) was first discovered in 1962 by Cochran et al.\(^1\) Since then, its structures and spectra have been the subject of extensive attention both experimentally and theoretically.\(^2\)-\(^14\) The H$_2$CN radical is important in the combustion chemistry of hydrocarbon flames containing nitrogen\(^15\),\(^16\) and in the reburning of NO.\(^17\) Moreover, the H$_2$CN radical has been considered as a key reactive intermediate in combustion of energetic molecules CH$_2$NNO$_2$\(^3\) and (CH$_2$NNO$_2$)$_2$\(^4\).\(^18\)-\(^21\) Its chemical fate and environmental effect have been of much interest to people.\(^22\),\(^23\) In addition, H$_2$CN was detected in the interstellar cloud TMC-1.\(^24\) In particular, the photochemistry of N$_2$ and CH$_4$, which have abundant existence in atmosphere of Titan\(^25\) and Earth, can take place to form $^4$N and CH$_3$. The experimental and theoretical studies\(^26\),\(^28\) have shown that $^4$N+CH$_3$ reaction would prevalently generate the H$_2$CN radical. Thus, besides the relevance in combustion chemistry, the H$_2$CN radical might have potential in astrophysical chemistry.

Recently, a series of experimental or theoretical calculations have shown that the H$_2$CN reaction with itself (intra-molecular evolution)\(^29\),\(^33\) or the reactions towards a number of stable molecules\(^5\),\(^34\)-\(^35\) as O$_2$, C$_3$H$_4$, CO, CH$_4$, H$_2$, NO, and N$_2$O, are very slow, due to the high overall energy barriers and low rate constant values. Thus, the radical-radical reaction should reflect the chemical fate of H$_2$CN radical. As we all know, hydroxyl radical (OH) is one of the key intermediates in a number interstellar processes and combustion reactions and even in explosion processes of HMX and RDX\(^21\). It is the important oxidant in the troposphere and can oxidize the atmospheric volatile organic compounds\(^36\). Thus, it would be very desirable to carry out a detailed study on the evolution mechanism of the H$_2$CN+OH reaction both the hydrogen-abstraction and addition-elimination processes. Such knowledge should be important for better understanding the chemical fate and potential role of the
H$_2$CN radical in some chemical processes.

2. Theoretical Methods
The calculations were carried out using the Gaussian 03$^{37}$ and Gaussian 98$^{38}$ The B3LYP/6-31++G(d,p), BH&HLYP/6-31++G(d,p), and QCISD/6-311++G(d,p) methods were applied for geometrical optimization. At the 6-31++G(d,p)-B3LYP and BH&HLYP structures and 6-311++G(d,p)-QCISD structures for the reactants, transition states, isomers, and products, the single-point energy calculations were carried out at the CCSD(T)/6-31+G(2df,p) level as well as at the composite G3B3 level and highly cost-expensive CCSD(T) method with the aug-cc-pVTZ and aug-cc-pVQZ basis set (for selected species).

3. Results and Discussions
In table 1, we lists the single-point energy data at the CCSD(T)/6-311++G(2df,p), G3B3, CCSD(T)/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVQZ levels using B3LYP/6-31++G(d,p), BH&HLYP/6-31++G(d,p) and QCISD/6-311++G(d,p) structures. The structural parameters of the reactants, intermediates, and most important transition states and products are shown in Figure 1. The singlet and triplet PESs of the H$_2$CN+OH reaction are presented in Figure 2 and Figure 3, respectively. The energy of the reactant R H$_2$CN+OH is set at zero. Here, the symbol L$_n$ means an isomer. The symbols L$_{nt}$ and L$_{nc}$ mean the trans-L$_n$ and cis-L$_n$, respectively.

Table 1: Total (a.u.) and relative energies (kcal/mol) of the reactant and for products, selected intermediate isomers, and transition states at the CCSD(T)/6-311++G(2df,p), G3B3, CCSD(T)/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVQZ levels. The geometries were optimized using B3LYP/6-31++G(d,p) (in Normal), BH&HLYP/6-31++G(d,p) (in parentheses), and QCISD(T)/6-311++G(d,p) (in bracket) levels.

| species      | CCSD(T)/6-311++G(2df,p) +ZPVE | G3B3 | CCSD(T)/aug-cc-pVTZ+ZPVE | CCSD(T)/aug-cc-pVQZ+ZPVE |
|--------------|--------------------------------|------|--------------------------|--------------------------|
| R CH$_2$N+OH | -169.4115217 0.0               | -169.615461 0.0 | -169.4414691 0.0         | [-169.4820376] [0.0]     |
|              | (-169.4096962) (0.0)           | 4 0.0 | (-169.4397235) (0.0)     |                          |
|              | (-169.61396 87) (0.0)          |      |                          |                          |
| TSL/P1$^a$   | (-1.0)                         | (-1.1) | (-1.2)                   | [----]                   |
|              | (-1.8)                         | (-2.2) | (-2.6)                   | [-2.2]                   |
|              | (-1.8)                         | (-2.2) | (-2.6)                   | [-2.2]                   |
| L$_{1t}$     | -57.2                          | -58.8 | -57.5                    | [-59.1]                  |
|              | (-56.5)                        | (-58.2) | (-56.7)                 |                          |
| L$_{1c}$     | -52.2                          | -53.9 | -52.7                    | [-54.4]                  |
|              | (-51.5)                        | (-53.2) | (-51.9)                 |                          |
| TSL1/P1$^b$  | -0.5                           | -2.2  | -2.1                     | [-3.3]                   |
| P$_1$ HCN+H  | -0.5                           | -2.2  | -2.1                     | [-3.3]                   |
|              | (-0.5)                         | (-0.5) | (-0.6)                  | [-0.6]                   |
|              | (-2.5)                         | (-2.5) | (-2.5)                  | [-2.5]                   |
| O$_2$        | -20.6                          | -93.0 | -91.6                    | [-93.4]                  |
|              | (-90.5)                        | (-92.8) | (-91.4)                |                          |

$^a$ The relative energies are calculated using UBH&HLYP and UQCISD-optimized geometries and ZPVE.
Figure 1: Optimized geometries of reactants, important isomers, product and transition states for the 
H₂CN+OH reaction at the B3LYP/6-31++G(d,p) (in Normal), BH&HLYP/6-31++G(d,p) (in 
parentheses), and QCISD/6-311++G(d,p) (in brackets) levels (UBH&HLYP and UQCISD for 
L and 
TSL/P1).

3.1 Singlet Potential Energy Surface

As shown in Figure 2, for the interaction between the H₂CN radical and the OH radical, four kinds of 
entrance pathways were identified on the singlet PES as: (1) quasi-direct H abstraction of H₂CN by 
OH to the P1 HCN + H₂O (-90.6, -90.5) via TSL/P1 (-1.0); (2) direct H-abstraction of OH by H₂CN to form the high-energy product P4 CH₂NH+O (13.2, 13.5); (3) radical-radical combination to form the low-lying isomers L1t CH₂NOH (-57.2, -56.5) and 
L1c CH₂NOH (-52.2, -51.5) via a barrierless exothermic process; and (4) O-addition to the C=N bond to 
form the high-energy three-membered ring isomer L4 r-CH₂NOH (10.8, 11.5). The normal and italic 
values in parentheses are ZPVE-corrected CCSD(T)/6-311++G(2df,p) energies based on the 
6-31++G(d,p)-B3LYP and BH&HLYP geometries and frequencies, respectively, with reference to R 
(0.0, 0.0). Generally, B3LYP and BH&HLYP predict close values to each other except for the 
weakly-bound complex L and the hydrogen-abstraction TSL/P1. It is obvious that the channels (2) and 
(4) can be excluded due to the high energy of isomer L4 (10.8, 11.5) and fragment P4 (13.2, 13.5). 
Both the H-abstraction channel (1) and the radical-radical combination channel (2) appear to be 
thermodynamically and kinetically favorable. Their competition need to be determined with dynamic 
calculations, as will be shown in the latter sections.
Starting from the isomer $L_{1c}$ or $L_{1t}$ CH$_2$NOH, 8 reaction pathways were identified as follows: (i) H$_2$O-extrusion forming P1 HCN+H$_2$O (-90.6, -90.5) via TSL1t/P1 (-0.5, 1.0); (ii) 1,2-H shift leading to L2 CH$_2$NHO (-45.3, -44.6) via TSL1t/L2 (-3.2, 2.5); (iii) H$_2$-extrusion forming P2 HCNO+H$_2$ (-26.0, -25.6) via TSL1c/P2 (7.9, 8.4); (iv) 1,3-H shift leading to L3 CH$_3$NO (-46.1, -45.5) via TSL1c/L3 (13.7, 14.3); (v) forming a three membered ring L4 r-CH$_2$NOH (10.8, 11.5) via TSL1t/L4 (18.1, 18.4); (vi) H-extrusion forming P5 CH$_2$NO+H (23.0, 22.8); (vii) 1,2-shift leading to L5 CHNHOH (-17.8, -17.3) via TSL1t/L5 (28.3, 29.1); and (viii) H-extrusion forming P6 HCNOH+H (44.4, 44.6). Processes iii-viii should have little contribution to the eventual product distribution due to the high energy of the products or transition state relative to the reactants. Therefore, further transformations do not need to be considered. Although formation of the isomer L2 CH$_2$NHO in pathway (ii) has the lowest barrier, its further conversion is unfavorable, i.e., the formation isomer L3 CH$_3$NO (-46.1, -45.5) via TSL2/L3 (5.2, 5.8) is the most favorable. However, the transition state in energy is higher than reactants. Therefore, pathway (ii) is expected to have little contribution to the final fragmentation. The most favorable channel from L1 CH$_2$NOH is then the pathway (i), in which a concerted CH and NO bond rupture takes place to generate the product P1 HCN+H$_2$O.

### 3.2 Singlet Potential Energy Surface

For the H$_2$CN+OH reaction between two doublet radicals (H$_2$CN and OH), it’s desirable to inspect the triplet PES. As shown in Figure 3, three triplet entrance pathways were found. The direct H-abstraction can lead to $^3P_1$ $^3$HCN+H$_2$O (18.5, 18.8) via the transition state $^3$TSR/P1 (22.5, 21.9). The other one is formation of $^3L_1$ ($^3$L1t: 3.1, 3.3 and $^3$L1c: 5.7, 6.1) via the transition state $^3$TSR/L1 (10.4, 10.5).
Figure 3: Potential energy surface of the H$_2$CN+OH reaction in triplet at CCSD(T)/6-311++G(2df,p)//B3LYP/6-31++G(d,p)+ZPVE (in Normal) and CCSD(T)/6-311++G(2df,p)//BH&HLYP/6-31++G(d,p)+ZPVE (in Italic) levels.

All the above discussions indicate that the favorable reaction channel for the CH$_2$N+OH reaction can be summarized as:

**Path 1:** R $\rightarrow$ L NC(H)...OH $\rightarrow$ P1 HCN+H$_2$O

**Path 2:** R $\rightarrow$ L1 CH$_2$NOH $\rightarrow$ P1’ HCN+H$_2$O

(The simple “’” on the top right corner of P1’ in **Path 2** is to make difference from the product P1 in **Path 1**.)

It is desirable to compare the G3B3 method, which comprises a series of high level single point energy calculations$^{39,40}$, with the costly CCSD(T)/aug-cc-pVQZ and even more costly CCSD(T)/aug-cc-pVTZ single-point energy calculations for the 6 most important species R H$_2$CN+OH, L, TSL/P1, L1, TSL1/P1’, and P1 HCN+H$_2$O (UCCSD(T) for L and TSL/P1). The QCISD method with triple zeta basis set [6-311++G(d,p)] were performed for the above species (UQCISD for TSL/P1). We note that the geometrical optimization of the weakly-bound complex L at the UQCISD/6-311++G(d,p) level always met with the convergence problems. Luckily, the transition state TSL/P1 at the G3B3// UBH&HLYP/6-31++G(d,p), UCCSD(T)/aug-cc-pVTZ//UQCISD/6-311++G(d,p) +ZPVE and G3B3//UQCISD/6-311++G(d,p) levels all have negative relative energies, i.e., -2.2, -2.2 and -1.8 kcal/mol, respectively, indicating that the H-transfer **Path 1** is in fact an exothermic process. As seen in Table 1, the CCSD(T)/aug-cc-pVQZ//QCISD/6-311++G(d,p) +ZPVE energy is very close to the G3B3//B3LYP/6-31++G(d,p) value. The largest deviation lies in the transition state TSL1/P1, for which the CCSD(T)/aug-cc-pVQZ relative energy is 1.1 kcal/mol lower than the G3B3 value, which is in the range of quantum chemical computational error. We considered the five products (P1-P4, P7).

As shown in Table 2, the inexpensive G3B3 (using B3LYP/6-31++G(d,p) and QCISD/6-311++G(d,p) geometric structures) results and the very costly CCSD(T)/aug-cc-pVQZ//QCISD/6-311++G(d,p)+ZPVE results are generally close to each other and all agree with the available experimental data. Moreover, our calculated formation enthalpies (in parentheses) of the species H$_2$CN (56.38, 56.51 kcal/mol), OH (8.18, 8.23 kcal/mol), HCN (30.43, 30.33 kcal/mol) and H$_2$O (-57.79, -57.60 kcal/mol) at the G3B3//B3LYP/6-31++G(d,p) and G3B3//QCISD/6-311++G(d,p) levels are in good accord with available experimental or accurate theoretical values 56.0$^{43}$, 8.9$^{44}$,31.5$^{45}$, and -57.8$^{46}$ kcal/mol, respectively.
Table 2: Comparison on the thermochemical data (kcal/mol) from literatures and calculation [at the G3B3//B3LYP/6-31++G(d,p) level and the CCSD(T)/aug-cc-pVQZ//QCISD/6-311++G(d,p)+ZPVE level] for some reaction pathways.

| Experiments | G3B3//B3LYP/6-31++G(d,p) | G3B3//QCISD/6-311++G(d,p) | CCSD(T)/aug-cc-pVQZ//QCISD/6-311++G(d,p)+ZPVE |
|-------------|--------------------------|--------------------------|---------------------------------|
| R: H₂CN(56.0)⁷⁻OH(8.9)⁷ | -91.2 | -91.9 | -92.0 | -92.2 |
| P1: HCN(31.5)⁴ | -24.3 | -26.3 | -26.7 | -24.8 |
| ³¹⁰O(-57.8)⁸ | -8.5 | -9.0 | -9.3 | -9.4 |
| P3: CH₃(34.8)⁺+NO(21.6)⁶ | 15.7 | 15.9 | 15.8 | 13.9 |
| P4: CH₂NH(21.0)⁺+O(59.6)⁸ | 51.2 | 52.7 | 52.7 | 52.3 |

⁷See Ref. 41; ⁸See Ref. 42; ⁹See Ref. 43; ⁴See Ref. 44; ⁵See Ref. 45; ⁶See Ref. 46; ⁷See Ref. 47.

Due to the unique potential energy surface of the H₂CN+OH reaction, i.e., coexistence of a quasi-direct hydrogen-transfer path via a very loose complex L (Path 1) and an addition-elimination path via a very deep intermediate L₁ (Path 2) as shown in Fig. 2, it’s highly desirable to add further reasoning comments on the resulted kinetic information. In general, for a complex reaction, the eventual reaction mechanism and rate constants are determined by three steps, i.e., entrance, intermediate isomerization, and final fragmentation. For the H₂CN+OH reaction, since the transition state energies of subsequent steps starting from L and L₁ lie lower or close in energy, the step that governs the competition between Path 1 and Path 2 is not the fragmentation (i.e., L→P1 (via TSL/P1) and L₁→P1 (via TSL₁/P1), respectively), but the entrance (i.e., R→L and R→L₁, respectively). That is to say, formation of L and L₁ is the respective rate-determining step of Path 1 and Path 2. Clearly, since the entrance rate of R→L₁ is far higher than that of R→L, the kinetically dominant channel starting from R should reasonably be the addition-elimination Path 2, rather than the quasi-direct H-abstraction Path 1.

4. Conclusions
We have reported a combined quantum chemical on the mechanism of the H₂CN+OH reaction. The results are summarized as follows: The potential energy surface study showed that there are two thermodynamically feasible channels. One is the quasi hydrogen-abstraction to form HCN+H₂O via a weakly bound complex NC(H)HꞏꞏꞏOH, the other is the addition elimination to form HCN+H₂O.

The theoretical results presented here are expected to provide a useful basis for further experiment investigation and to be helpful for understanding the nitrogen-recycling process in the conflagrant and astrophysical chemistry.

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