

Theoretical study on the mechanism of OH + HCNO reaction

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Abstract A detailed mechanistic study of the OH+HCNO reaction, in which the products \mathbf{P}_i with $i = 1, 2, \dots, 7$ are involved, is carried out by means of CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPVE computational method to determine a set of reasonable pathways. It is shown that $\mathbf{P}_6(\text{CO} + \text{H}_2\text{NO})$ and $\mathbf{P}_3(\text{HNO} + \text{HCO})$ are the major product channels with a minor contribution from $\mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$, whereas the other channels for $\mathbf{P}_1(\text{H}_2\text{O} + \text{NCO})$, $\mathbf{P}_2(\text{NH}_2 + \text{CO}_2)$, $\mathbf{P}_4(\text{HCN} + \text{HO}_2)$ and $\mathbf{P}_7(\text{CO} + \text{H}_2 + \text{NO})$ are less favorable. All these theoretical results are in harmony with experimental facts.

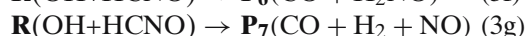
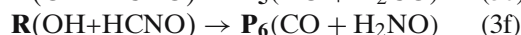
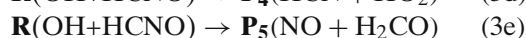
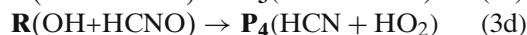
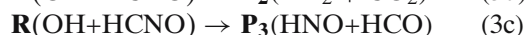
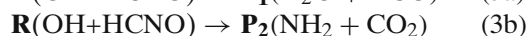
Keywords Reaction mechanism · Potential energy surface (PES) · Reaction OH + HCNO

1 Introduction

It is known that the fulminic acid HCNO, which can be synthesized by vacuum pyrolysis of 3-phenyl-4-oximinoisoxazol-5-(4H)-one as described in the literature [1–3], has recently been identified as an important intermediate in NO-reburning processes for the reduction of NO_x pollutants from fossil-fuel combustion emissions [4]. In particular, the OH + HCNO reaction, identified as a crucial step, has been modeled [4] by means of the computational method at HL1 level [5] to give the potential

energy surface (PES) associated with an estimated rate constant $k = 3.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with no temperature dependence. This valuable PES has been built up to give the reaction coordinate diagram that covers a number of pathways for the OH+HCNO reaction.

The first and direct experimental study of the OH+HCNO reaction [6] has been carried out by the use of laser-induced fluorescence and IR diode absorption spectroscopy to give a temperature-dependent rate constant $k = 2.69 \pm 0.41 \times 10^{-12} \exp [(750.2 \pm 49.8)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–386 K, with a value $k = (3.39 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K. Through these measurements, the products of the OH+HCNO reaction



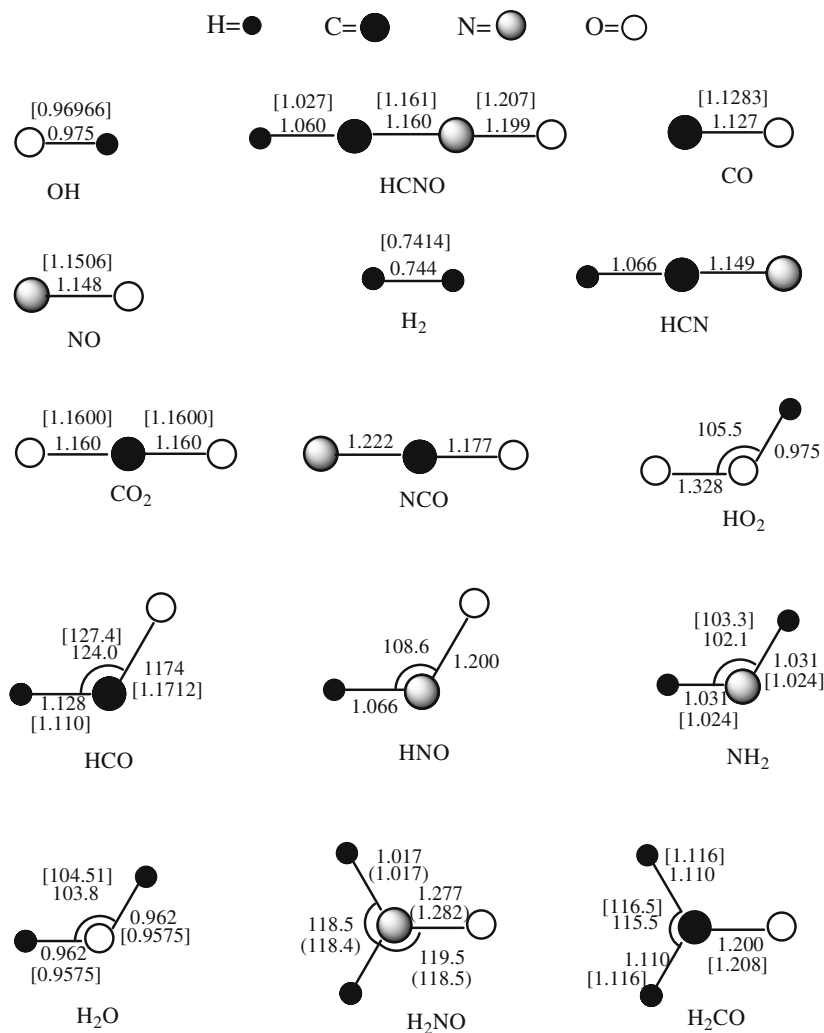
have been determined [6], leading to the major product channels $\mathbf{P}_6(\text{CO} + \text{H}_2\text{NO})$ and $\mathbf{P}_3(\text{HNO} + \text{HCO})$, with a minor contribution from $\mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$. Note that the symbols (3a), (3b), ..., (3g) are used in the literature [6].

It was pointed out [6] that, for the reaction OH + HCNO, the PES [4] covered the product channels $\mathbf{P}_1(\text{H}_2\text{O} + \text{NCO})$, $\mathbf{P}_3(\text{HNO} + \text{HCO})$ and $\mathbf{P}_7(\text{CO} + \text{H}_2 + \text{NO})$, but the study of product channels [4] did not consider the possibility of the major channel $\mathbf{P}_6(\text{CO} + \text{H}_2\text{NO})$, which was investigated in the literature [6]; the mechanistic study [4] predicted that there was a

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Fig. 1 B3LYP/6-311G(d,p) optimized geometries for the reactant R(OH+HCNO) and the products **P**₁(H₂O+NCO), **P**₂(NH₂+CO₂), **P**₃(HNO+HCO), **P**₄(HCN+HO₂), **P**₅(NO+H₂CO), **P**₆(CO+H₂NO), and **P**₇(CO+H₂+NO). Bond lengths are in angstrom and angles in degrees. Values in parentheses correspond from Ref. [8]. Values in square brackets correspond from Ref. [9]



moderate yield of NCO-forming channel **P**₁, but the experiments [6]; indicated that the formation of NCO might be at most a very minor pathway in the reaction; also, the mechanistic study [4] predicted that the **P**₇ channel was a low-energy pathway to the product (CO + H₂ + NO), but the observation of very low NO yields reported in literature [6], suggested that the **P**₇ channel might not be a major one.

As mentioned above, a deeper understanding of the pathways involving the products **P**₁, **P**₂, . . . , **P**₇ may be required. Therefore, a detailed mechanistic study for the OH+HCNO reaction is presented in this work by means of CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) +ZPVE computational method.

2 Computations methods

For the reaction OH + HCNO, all calculations are carried out using Gaussian 98 program packages [7]. The geometries of the reactants, products, intermediates, and

transition states are optimized using hybrid density functional B3LYP method with the 6-311G(d,p) basis set. To confirm that the transition states connects designated intermediates, we also perform intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-311G(d,p) level. In addition, single-point calculations are performed at the CCSD(T)/6-311G(d,p) level for the B3LYP/6-311G(d,p) optimized geometries of all species. B3LYP/6-311G(d,p) zero-point vibrational energies (ZPVE) are included.

In order to make the contents discussed easier, let us introduce the most part of the optimized geometries for the reactant and products, the intermediates, and the transition states, respectively, as shown in Figs. 1, 2 and 3.

Figure 1 shows the B3LYP/6-311G(d,p) optimized geometries for the reactant R(OH+HCNO) and the products **P**₁(H₂O + NCO), **P**₂(NH₂ + CO₂), **P**₃(HNO + HCO), **P**₄(HCN + HO₂), **P**₅(NO + H₂CO), **P**₆(CO + H₂NO), and **P**₇(CO + H₂ + NO).

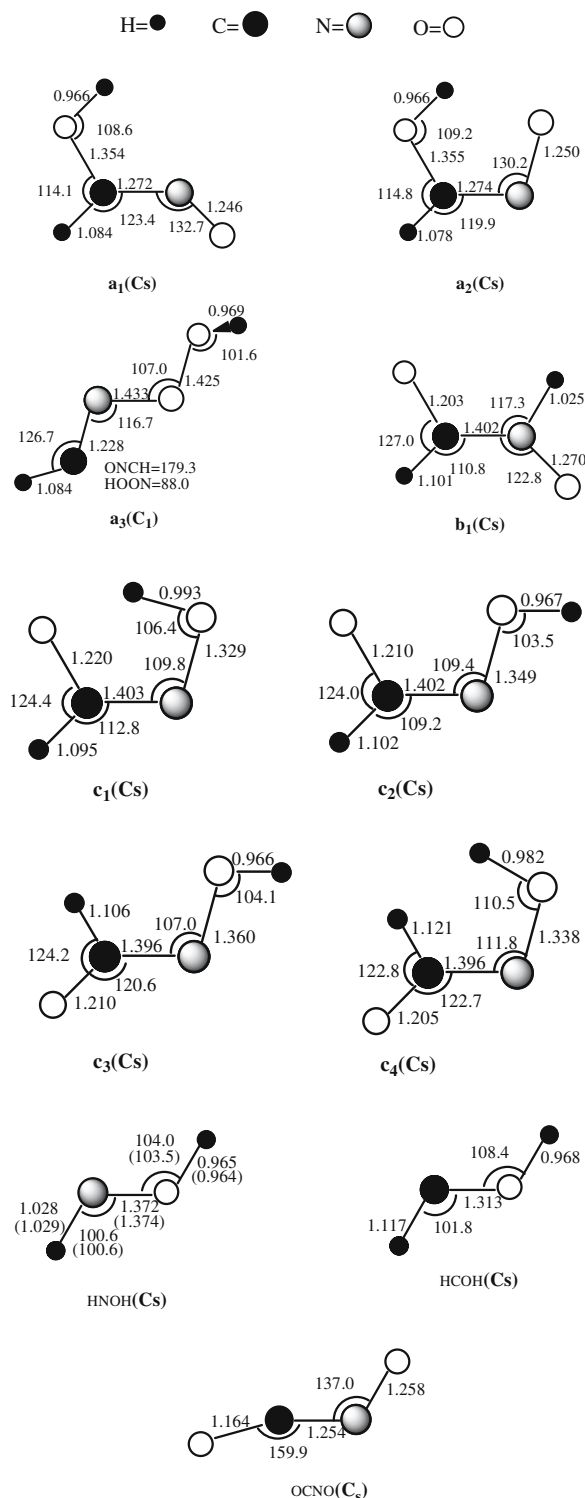
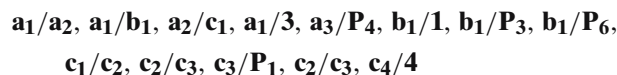


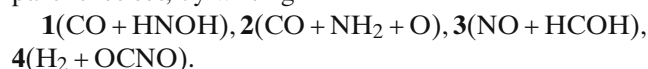
Fig. 2 B3LYP/6-311G(d,p) optimized geometries for intermediates. And most of the six-atom intermediates are isomers, i.e., the isomers **a₁** and **a₂** characterized by HC(OH)NO, the isomer **a₃** by HCNOOH and the isomers **c₁**, **c₂**, **c₃**, and **c₄** by HC(O)NOH. The intermediate **b₁** takes the form **b₁**(HC(O)N(O)H). Also, the four-atom intermediates, HNOH, HCOH and OCNO, are presented. Bond lengths are in angstroms and angles in degrees. Values in parentheses correspond from Ref. [8]

Figure 2 shows that the B3LYP/6-311G(d,p) optimized geometries for intermediates are described in detail, where most of the intermediates are isomers, i.e., the isomers **a₁** and **a₂** are characterized by HC(OH)NO, the isomer **a₃** by HCNOOH and the isomers **c₁**, **c₂**, **c₃**, and **c₄** by HC(O)NOH. The intermediate **b₁** takes the form **b₁**(HC(O)N(O)H). Also, the intermediates which are composed of four atoms such as HNOH, HCOH and OCNO, are presented in Fig. 2.

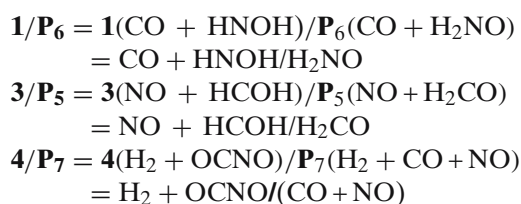
Figure 3 shows the B3LYP/6-311G(d,p) optimized geometries for transition states. In Fig. 3, there are 13 transition states, which are composed of six atoms, denoted by



where the symbol **x/y** is used to denote the transition states, in which **x** and **y** are the corresponding intermediates or products, and where the symbols **1**, **2**, **3**, and **4** are used to denote the species, which are put in the parentheses, by writing



Alternatively, we still have three transition states defined as **1/P₆**, **3/P₅** and **4/P₇**, which can be expressed, respectively, in terms of the four-atom transition states HNOH/H₂NO, HCOH/H₂CO, and OCNO/(CO + NO), i.e.,



We shall see later that the three molecules CO, NO and H₂ in **1/P₆**, **3/P₅** and **4/P₇** will keep unchanged, respectively, in the sub-processes **1**→**P₆**, **3**→**P₅** and **4**→**P₇**.

Also, Table 1 lists the theoretical prediction of the total energy, and the relative energies for the reactant, products, intermediates and transition states at different levels of theory.

3 Results and discussion

The potential energy surface (PES) involving the main structures of the OH+HCNO reaction calculated at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPVE level is shown in Fig. 4, where the optimized geometries of the reactant together with the products, the intermediates and the transition states, respectively, are shown

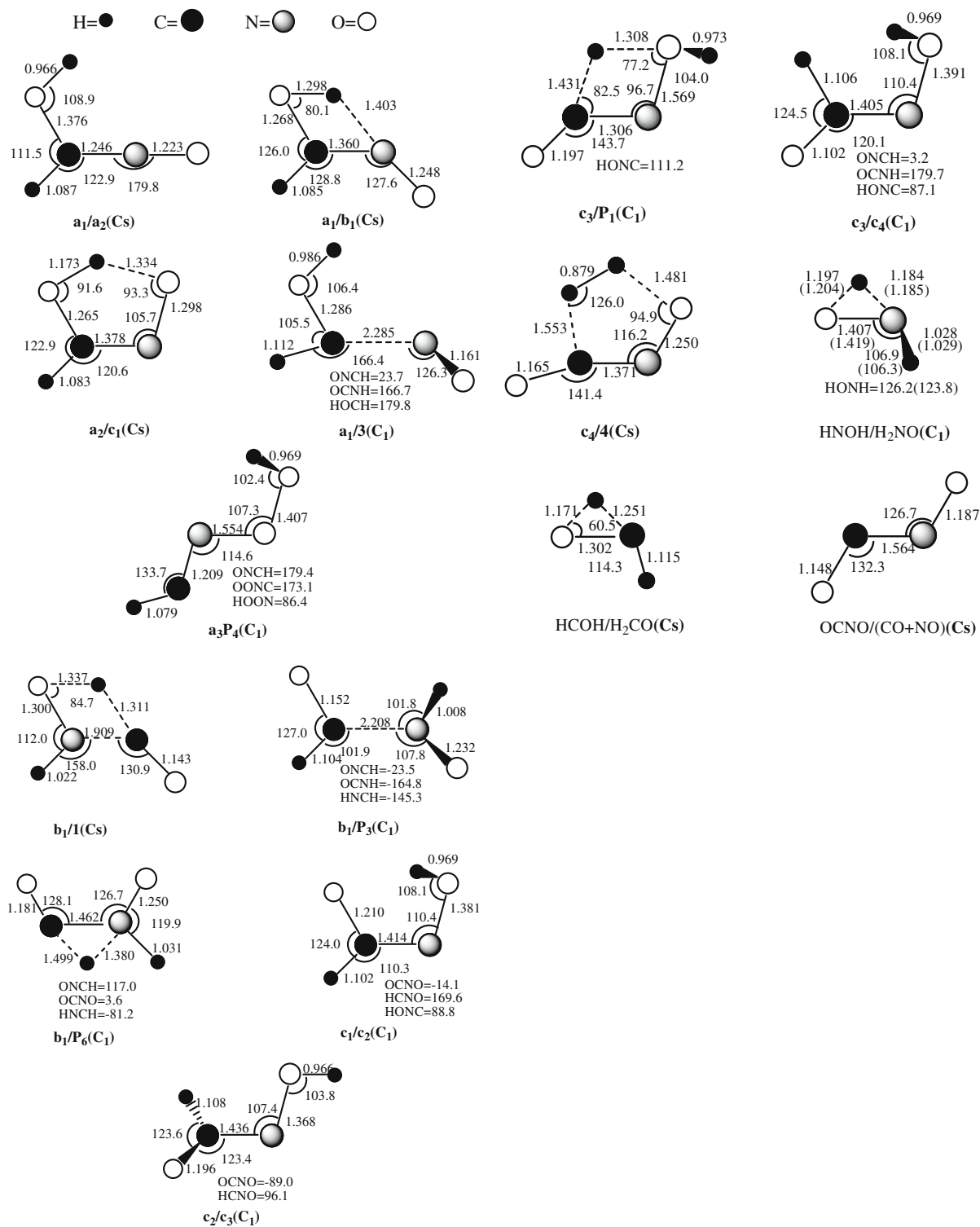


Fig. 3 B3LYP/6-311G(d,p) optimized geometries for transition states. The 13 six-atom transition states are denoted as **a₁/a₂**, **a₁/b₁**, **a₂/c₁**, **a₁/3**, **a₃/P₄**, **b₁/I**, **b₁/P₃**, **b₁/P₆**, **c₁/c₂**, **c₂/c₃**, **c₃/P₁**, **c₂/c₃**, **c₄/4**, where the **1**, **2**, **3** and **4** species are defined as **1**(CO + HNOH), **2**(CO + NH₂ + O), **3**(NO + HCOH) and **4**(H₂ + OCNO), and where the symbol **x/y** is used to denote the transition states, in which **x** and **y** are the corresponding intermediates or products. There are 3 transition

states defined as **1/P₆** = **1**(CO + HNOH)/**P₆**(CO + H₂NO) = CO + HNOH/H₂NO, **3/P₅** = **3**(NO + HCOH)/**P₅**(NO + H₂CO) = NO + HCOH/H₂CO and **4/P₇** = **4**(H₂ + OCNO)/**P₇**(H₂ + CO + NO) = H₂ + OCNO/(CO + NO), where HNOH/H₂NO, HCOH/H₂CO, and OCNO/(CO + NO) are the four-atom transition states. Bond lengths are in angstroms and angles in degrees. Values in parentheses correspond from Ref. [8].

Table 1 Theoretical prediction of the total energy (Hartree), ZPVE (Hartree/ particle), and relative energies ΔE (kcal/mol) for reactant, products, intermediates and transition states of the OH+HCNO reaction at different levels of theory

Species	Total energy		ZPVE	ΔE /(kcal/mol)
	B3LYP/6-311G(d,p)	CCSD(T)/6-311G(d,p)	B3LYP/6-311G(d,p)	CCSD(T)/6-311G(d,p)
R (OH+HCNO)	-244.3771296	-243.8030137	0.027886	0.0
P ₁ (H ₂ O+NCO)	-244.4974039	-243.9277656	0.029973	-76.9735
P ₂ (NH ₂ + CO ₂)	-244.5362062	-243.968428	0.029072	-103.055
P ₃ (HNO+HCO)	-244.3955063	-243.8320645	0.026776	-18.9262
P ₄ (HCN+HO ₂)	-244.4024152	-243.8344311	0.028807	-19.1368
P ₅ (NO+H ₂ CO)	-244.4630436	-243.9005305	0.031017	-59.228
P ₆ (CO+H ₂ NO)	-244.1627996	-243.9093631	0.031469	-64.4869
P ₇ (CO+H ₂ + NO)	-244.4525086	-243.9012879	0.019651	-66.8356
1 (CO+HNOH)	-244.4618077	-243.901684	0.032102	-59.271
2 (CO+NH ₂ +O)	-244.3267153	-243.7812419	0.023927	11.17771
3 (NO+HCOH)	-244.3788034	-243.8183999	0.031241	-7.5497
4 (H ₂ +OCNO)	-244.4294518	-243.8478044	0.023108	-31.1049
a ₁	-244.4699493	-243.8890495	0.036989	-48.2761
a ₂	-244.47236	-243.8918402	0.037351	-49.8001
a ₃	-244.3371774	-243.7609565	0.033346	29.81752
b ₁	-244.4975159	-243.9174644	0.037442	-65.8225
c ₁	-244.4820242	-243.9061369	0.037541	-58.6522
c ₂	-244.4747243	-243.8995379	0.037255	-54.6908
c ₃	-244.4765462	-243.9013819	0.036913	-56.0625
c ₄	-244.4681461	-243.8920467	0.036099	-50.7154
a ₁ / a ₂	-244.4540737	-243.869792	0.035874	-36.8915
a ₁ / b ₁	-244.4242973	-243.8414984	0.032225	-21.4268
a ₁ / 3	-244.3886396	-243.8165175	0.032993	-5.26908
a ₂ / c ₁	-244.4632921	-243.8858355	0.033711	-48.3163
a ₃ / P ₄	-244.3362762	-243.7579024	0.031896	30.82411
b ₁ / 1	-244.4215736	-243.8442636	0.030537	-24.2212
b ₁ / P ₃	-243.0998673	-243.819822	0.031673	-8.171
b ₁ / P ₆	-244.3651191	-243.7806862	0.031246	16.11916
c ₁ / c ₂	-244.4487407	-243.8747683	0.034448	-40.909
c ₂ / c ₃	-244.4601148	-243.8878048	0.036057	-48.0799
c ₃ / P ₁	-244.3925294	-243.8114053	0.029865	-4.02397
c ₃ / c ₄	-244.4498038	-243.8756942	0.034254	-41.6118
c ₄ / 4	-244.4173204	-243.8354536	0.028348	-20.0665
1 / P ₆ (CO+HNOH/H ₂ NO)	-244.3869141	-243.8244449	0.025981	-14.6437
3 / P ₅ (NO+HCOH/H ₂ CO)	-244.3238013	-243.7615882	0.02503	24.20275
4 / P ₇ (H ₂ + OCNO)/(CO+NO))	-244.4175568	-243.8442877	0.021002	-30.2196

in Figs. 1, 2, and 3, and where the values of relative energies in the parentheses are taken from Table 1. Note that the symbol **x/y** is used to denote the transition state, where **x** and **y** are the corresponding intermediates or products.

3.1 The scanned procedure for the starting step $R \rightarrow a_1$

Now let us begin to discuss, as shown in PES, the step $R \rightarrow a_1$ which are taken as the common starting step for some pathways in the reaction OH + HCNO. Taking into consideration of the reactant R(OH + HCNO) as starting point located at (0,0), an intermediate **a**₁(HC(OH)NO) at (-48.3) is formed from attacking the carbon atom in HCNO by OH. It can be demonstrated, as shown in Fig. 5, by the dissociation curve with

respect to the dissociation of the C–O bond in **a**₁. And the starting step described by the scanned procedure just mentioned above is abbreviated as $R \rightarrow a_1$. Clearly, $R \rightarrow a_1$ is an energy rich step.

3.2 The pathways related to $R \rightarrow a_1$

Also, the PES shows that there are five pathways which acted as branches from **a**₁, and it is sketched as follows:

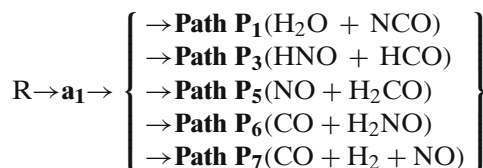


Fig. 4 The potential energy surface for the OH+HCNO reaction. The relative energies ΔE (kcal/mol), taken from Table 1, are calculated at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPVE level. Values in parentheses correspond from Ref. [8]. The reactant and products, the intermediates and the transition states, respectively, are shown in Figs. 1, 2 and 3. The origin of the energy is -243.7751277 Hartree

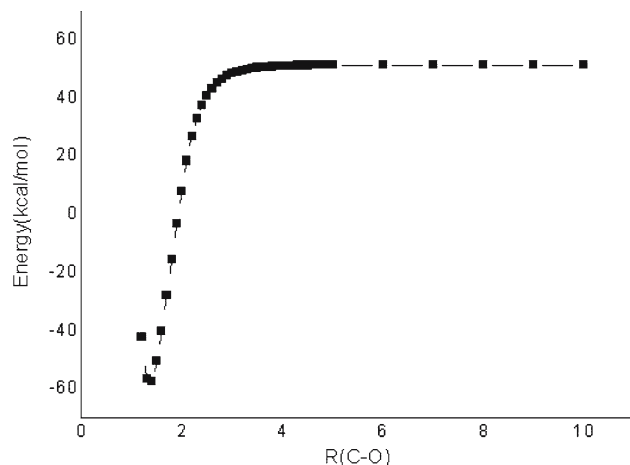
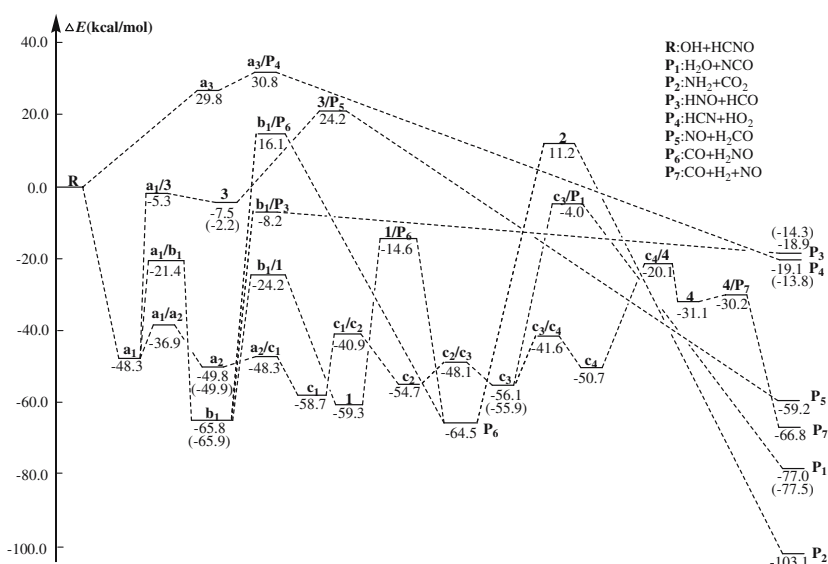
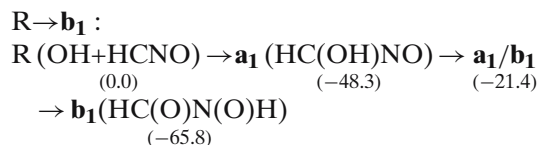


Fig. 5 The dissociation curve with respect to the dissociation of the C–O bond in the isomer $\mathbf{a}_1 \rightarrow \mathbf{R}$ at the B3LYP/6-311G(d,p) level. The origin of the energy is -244.3771296 Hartree

We shall proceed subsequently to the discussions, in which the pathways \mathbf{P}_6 , \mathbf{P}_3 , \mathbf{P}_5 , \mathbf{P}_1 and \mathbf{P}_7 are involved, to give that both pathways \mathbf{P}_6 and \mathbf{P}_3 are the major channels, the pathway \mathbf{P}_5 the minor one, while the other two pathways \mathbf{P}_1 and \mathbf{P}_7 at most the very minor channels.

3.3 A common division $\mathbf{R} \rightarrow \mathbf{b}_1$ of the pathways \mathbf{P}_6 and \mathbf{P}_3 , the major channels

In order to make our discussion easier, let us use the symbol $\mathbf{R} \rightarrow \mathbf{b}_1$ to denote the common division of the pathways \mathbf{P}_6 and \mathbf{P}_3 , such that



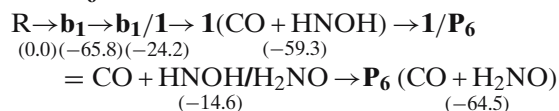
where $\mathbf{a}_1/\mathbf{b}_1$, as shown in Fig. 3, is a four-center transition state connected with the complexes \mathbf{a}_1 and \mathbf{b}_1 . Via the transition state $\mathbf{a}_1/\mathbf{b}_1$, the hydrogen atom H in \mathbf{a}_1 (HC(OH)NO) migrates from the place, where the O–H bond is cleaved, to link with the intramolecular N to produce \mathbf{b}_1 .

From the relative energies listed in the parentheses in $\mathbf{R} \rightarrow \mathbf{b}_1$, it is easily seen that the energy rich step $\mathbf{R}(0.0) \rightarrow \mathbf{a}_1(-48.3)$ can help the sub-process $\mathbf{a}_1(-48.3) \rightarrow \mathbf{a}_1/\mathbf{b}_1(-21.4) \rightarrow \mathbf{b}_1(-65.8)$ to proceed easily via the four-center transition state $\mathbf{a}_1/\mathbf{b}_1$. Obviously, the division $\mathbf{R} \rightarrow \mathbf{b}_1$ is also an energy-rich step, where the step means, in essence, a section.

3.4 Pathway \mathbf{P}_6 , a major product channel

The PES in Fig. 4 shows that the pathway \mathbf{P}_6 takes the common division $\mathbf{R} \rightarrow \mathbf{b}_1$ as starting to give

Path \mathbf{P}_6 :



where the CO molecule keeps unchanged in the sub-process $\mathbf{1} \rightarrow \mathbf{P}_6$. It is clear that the barriers of the transition state $\mathbf{1}/\mathbf{P}_6 = \text{CO} + \text{HNOH}/\text{H}_2\text{NO}$ associated with $\mathbf{1}(\text{CO} + \text{HNOH})$ and $\mathbf{P}_6(\text{CO} + \text{H}_2\text{NO})$ are identical with those of the four-atom transition state HNOH/H₂NO associated with HNOH and H₂NO. Via the four-atom transition state HNOH/H₂NO, the hydrogen atom H in HNOH migrates from the place, where the O–H bond is cleaved, to link with the intramolecular N to produce H₂NO.

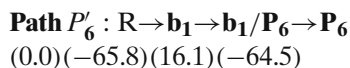
As shown in **Path \mathbf{P}_6** , there is also a loose four-center transition state $\mathbf{b}_1/\mathbf{1}$, as shown in Fig. 3, at (-24.2) , and

it possesses six atoms. Via the transition state $\mathbf{b}_1/\mathbf{1}$, the intermediate $\mathbf{b}_1(\text{HC}(\text{O})\text{N}(\text{O})\text{H})$ is decomposed into two parts CO and HNOH denoted by $\mathbf{1}(\text{CO} + \text{HNOH})$, due to the two bonds N–C and C–H in \mathbf{b}_1 split.

To examine the relative energies listed in the pathway \mathbf{P}_6 , we are led to the energy-rich division $\text{R}(0.0) \rightarrow \mathbf{b}_1$ (–65.8) in **Path \mathbf{P}_6** can promote the sub-process \mathbf{b}_1 (–65.8) $\rightarrow \mathbf{b}_1/\mathbf{1}$ (–24.2) $\rightarrow \mathbf{1}$ (–59.3) $\rightarrow \mathbf{1}/\mathbf{P}_6$ (–14.6) $\rightarrow \mathbf{P}_6$ (–64.5) to proceed in easy way and it is energetically feasible, so that the Path \mathbf{P}_6 is a major product channel.

It seems redundant to give a comparison of the pathway \mathbf{P}_6 to some others, and then to come to the prediction that the Path \mathbf{P}_6 is a major product channel, since this prediction has already been proposed and tested by the first and direct experimental observation reported in the literature [6].

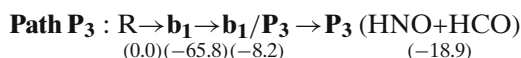
Alternatively, an another pathway \mathbf{P}'_6 is suggested as follows:



where $\mathbf{b}_1/\mathbf{P}_6$ is a three-center transition state, as shown in Fig. 3, composed of six atoms. Since the relative energy of the transition state $\mathbf{b}_1/\mathbf{P}_6$ is located at (16.1) over that of the reactant R at (0.0), this may make the **Path \mathbf{P}'_6** less favorable than the Path \mathbf{P}_6 .

3.5 Pathway \mathbf{P}_3 , a major product channel

By taking the common division $\text{R} \rightarrow \mathbf{b}_1$ as starting, it is easy to write down, from the PES as shown in Fig. 4, the **path \mathbf{P}_3** in the form



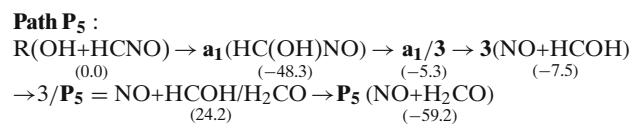
where, as shown in Fig. 3, the transition state $\mathbf{b}_1/\mathbf{P}_3$ at (–8.2) possesses a loose C \cdots N bond with bond length 2.208 Å to join the two groups HCO and HNO like $\text{HC}(\text{O})\cdots\text{N}(\text{O})\text{H}$. Via the transition state $\mathbf{b}_1/\mathbf{P}_3$, the intermediate $\mathbf{b}_1(\text{HC}(\text{O})\text{N}(\text{O})\text{H})$ is decomposed into two parts HCO and HNO to produce the product \mathbf{P}_3 (HNO+HCO), due to the C–N bond in \mathbf{b}_1 split.

It is worth to examine, in Path \mathbf{P}_3 , the relative energies of the sub-process from \mathbf{b}_1 to \mathbf{P}_3 , which are placed after the common division $\text{R} \rightarrow \mathbf{b}_1$, to give that the energy rich division $\text{R}(0.0) \rightarrow \mathbf{b}_1$ (–65.8) can help the sub-process \mathbf{b}_1 (–65.8) $\rightarrow \mathbf{b}_1/\mathbf{P}_3$ (–8.2) $\rightarrow \mathbf{P}_3$ (–18.9) to go forward to the product \mathbf{P}_3 in easy manner, so that the pathway \mathbf{P}_3 is also a major product channel. And it is in

harmony with the experimental result reported in the literature [6].

3.6 Pathway \mathbf{P}_5 , a minor product channel

The PES in Fig. 4 shows that the pathway \mathbf{P}_5 takes the form



where HCOH and H_2CO are shown in Figs. 2 and 1, respectively. Note that the NO molecule keeps unchanged in the sub-process $\mathbf{3} \rightarrow \mathbf{P}_5$.

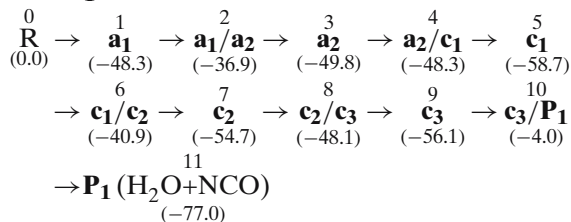
In Path \mathbf{P}_5 , the transition state $\mathbf{a}_1/\mathbf{3}$ in Fig. 3 at (–5.3) is a loose molecular species to join the two groups HCOH and NO through a loose C \cdots N bond with bond length 2.285 Å. Via the transition state $\mathbf{a}_1/\mathbf{3}$, the intermediate $\mathbf{a}_1(\text{HC}(\text{OH})\text{NO})$ is decomposed into two parts NO and HCOH denoted as $\mathbf{3}(\text{NO} + \text{HCOH})$, due to the C–N bond in \mathbf{a}_1 split.

Also in **Path \mathbf{P}_5** , the transition state $\text{HCOH}/\text{H}_2\text{CO}$ in Fig. 3 is a three-center transition state associated with HCOH and H_2CO . It is obvious that the barriers of the transition state $\text{HCOH}/\text{H}_2\text{CO}$ associated with HCOH and H_2CO are identical with those of the transition state $\mathbf{3}/\mathbf{P}_5 = \text{NO} + \text{HCOH}/\text{H}_2\text{CO}$ associated with $\mathbf{3}(\text{NO} + \text{HCOH})$ and $\mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$. Via the transition state $\text{HCOH}/\text{H}_2\text{CO}$, the hydrogen atom H in HCOH migrates from the place, where the O–H bond is cleaved, to link with the intramolecular C to produce H_2CO .

To examine the relative energies in Path \mathbf{P}_5 , it can be seen that the energy-rich step $\text{R}(0.0) \rightarrow \mathbf{a}_1$ (–48.3) can promote the sub-process \mathbf{a}_1 (–48.3) $\rightarrow \mathbf{a}_1/\mathbf{3}$ (–5.3) $\rightarrow \mathbf{3}(\text{NO} + \text{HCOH})$ (–7.5) to proceed without difficulty. Let us consider the subsequent steps $\mathbf{3}(\text{NO} + \text{HCOH})$ (–7.5) $\rightarrow \mathbf{3}/\mathbf{P}_5$ (24.2) $\rightarrow \mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$ (–59.2). Note that the relative energy of the transition state $\mathbf{3}/\mathbf{P}_5$ at (24.2) is over that of the reactant R at (0.0). Since the relative energy of $\mathbf{3}/\mathbf{P}_5$ at (24.2) is not so high, it seems that the temperature factor can help to bring about the sub-process $\mathbf{3}(\text{NO} + \text{HCOH})$ (–7.5) $\rightarrow \mathbf{3}/\mathbf{P}_5$ (24.2) $\rightarrow \mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$ (–59.5) to approach the product \mathbf{P}_5 . Indeed, a temperature-dependent rate constant $k = 2.69 \pm 0.41 \times 10^{-12} \exp [(750.2 \pm 49.8)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–386 K has been obtained via the experimental study of the OH + HCNO reaction [6]. And it enables us to believe that the pathway \mathbf{P}_5 may be a minor product channel, and this prediction is in harmony with the experimental result reported in the literature [6].

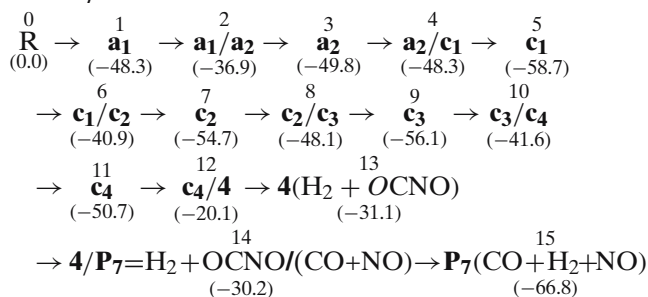
3.7 Pathways of P₁ and P₇

From the PES in Fig. 4, the pathway P₁(H₂O + NCO) takes the form, by writing,

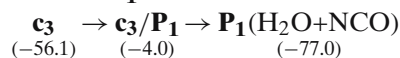
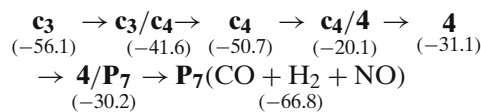
Path P₁ :

where the reactant R(OH + HCNO) together with the product P₁(H₂O + NCO), the intermediates (a₁, a₂, c₁, c₁, c₃), and the transition states (a₁/a₂, a₂/c₁, c₁/c₂, c₂/c₃, c₃/P₁), respectively, are shown in Figs. 1, 2, and 3. By inspecting and comparing the relative energies from R to P₁, we may get the information that the pathway P₁ is a low-energy channel. But the complicated situation of the 11 steps involved in the pathway P₁(H₂O + NCO) may make the channel progressing uneasy. The experiments [6] indicated that the formation of NCO might be at most a very minor channel in the OH + HCNO reaction.

Now let us discuss the pathway P₇(H₂ + CO + NO) and it can be written, from PES in Fig. 4, as

Path P₇ :

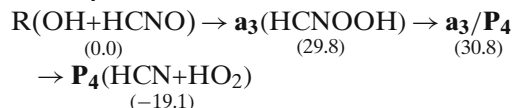
Note that the H₂ molecule keeps unchanged in the sub-process 4 → P₇. Let us discuss the transition states, etc. that are not appearing in Path P₁. In Path P₇, the transition states c₃/c₄, c₄/4 and OCNO/(CO + NO) in 4/P₇ are shown in Fig. 3, where the intermediates c₄ and OCNO are shown in Fig. 2. It is easily seen that the pathway P₇ possesses 15 steps from R to P₇. By comparing the pathway P₇ with the pathway P₁, it is easy to find that the two pathways possess the same steps from R to c₃, i.e., nine steps and, for the purpose of comparison, the difference in steps are also given as follows:

for **Path P₁ :**for **Path P₇ :**

The same and the difference in steps just mentioned above may indicate that the pathway P₇(CO + H₂ + NO) is also a low-energy channel, but it is in the manner more less favorable like that of the pathway P₁(H₂O + NCO) exhibited. As reported in the literature [6], the experiment observed very low NO yields.

3.8 Pathway P₄

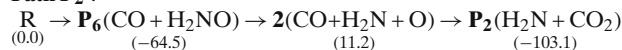
From PES in Fig. 4, it is easy to write down the pathway P₄ in the form

Path P₄ :

The scanned procedure for the first step from R at (0.0) to a₃ at (29.8) is shown in Fig. 6, that is the dissociation curve with respect to the dissociation of the O–O bond in a₃(HCNOOH). Since the relative energy of a₃ at (29.8) is very close to that of the transition state a₃/P₄ at (30.8), R → a₃ → a₃/P₄ can approximately be regarded as one step R → a₃/P₄ to have a high barrier, about 30.8 kcal/mol needed to overcome. It was reported in the literature [6] that pathways to other product channels, such as P₄(HCN + HO₂), were predicted to have high energy barriers.

3.9 Pathway P₂

As shown in PES in Fig. 4, there is a possible way involving a few steps, i.e., through the pathway P₆, across the intermediates 2(CO + NH₂ + O) and down to the product (H₂N + CO₂), such that

Path P₂ :

where the notation R → P₆ stands for the pathway P₆, and it is a major product channel, as illustrated in Sect. 3.4, to have the product P₆(CO + H₂NO) in a steady manner so that the product P₆ does not possess enough energy about 75.7 kcal/mol to cross the intermediates 2(CO + H₂N + O) to produce the product

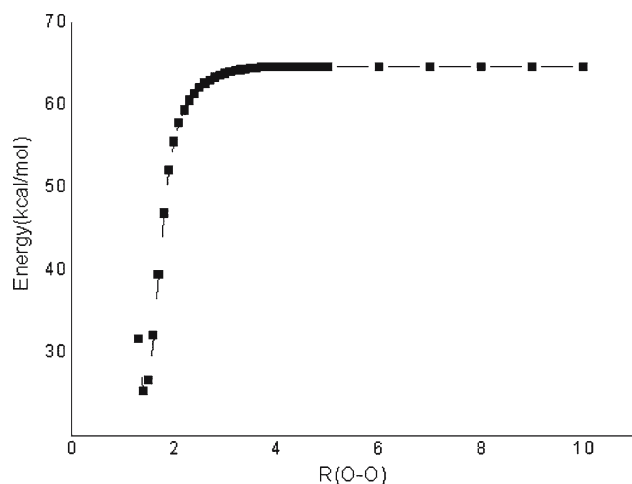


Fig. 6 The dissociation curve with respect to the dissociation of the O–O bond in the isomer $\mathbf{a}_3 \rightarrow \mathbf{R}$ at the B3LYP/6-311G(d,p) level. The origin of the energy is -244.3771296 Hartree

$\mathbf{P}_2(\text{NH}_2 + \text{CO}_2)$, via $\text{CO} + \text{O} \rightarrow \text{CO}_2$. For brevity, the scanned procedure with respect to $\mathbf{P}_6 \rightarrow \mathbf{2}$ is omitted here.

4 Conclusions

All calculations in the present work are carried out using Gaussian 98 program packages [7] and the practical computations are performed by means of CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) + ZPVE.

For the reaction $\text{OH} + \text{HCNO}$, the PES, in which there are seven pathways from \mathbf{P}_1 to \mathbf{P}_7 involved, is built up to show the product channels whether to proceed in the energetically favorable or less or unfavorable manner. It is shown that both pathways $\mathbf{P}_6(\text{CO} + \text{H}_2\text{NO})$ and $\mathbf{P}_3(\text{HNO} + \text{HCO})$ are energetically favorable and

they are of, by experiments, the major channels; the pathway $\mathbf{P}_5(\text{NO} + \text{H}_2\text{CO})$ is the less favorable and it is of, by experiments, the minor one; the two pathways $\mathbf{P}_1(\text{H}_2\text{O} + \text{NCO})$ and $\mathbf{P}_7(\text{CO} + \text{H}_2 + \text{NO})$ are the more less favorable and, by experiments, they are at most the very minor channels; the pathways $\mathbf{P}_4(\text{HCN} + \text{HO}_2)$ and $\mathbf{P}_2(\text{NH}_2 + \text{CO}_2)$, which possess high barriers needed to overcome, proceeded uneasily, and they are energetically unfavorable.

The above theoretical results are in harmony with the first and direct experimental observations [6], in the study of reaction $\text{OH} + \text{HCNO}$, by means of laser-induced fluorescence and IR diode absorption spectroscopy.

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