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Computational Studies of the Isomerization Pathways of Isocyanic Acid HNCO

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Paths of isomerizations of isocyanic acid HNCO into various chain isomers via ring intermediates have been investigated by ab initio MO calculations with the MRD-CI procedure employing the 6-31G** basis sets. Geometry optimizations were accomplished at the RHF, UHF, or CASSCF level of theory. It is found that the isomerization from HNCO to cyanic acid HOCN is energetically the most favorable and that it should proceed via successive 1,2-hydrogen migrations rather than by a single 1,3-hydrogen migration. The overall barrier height is calculated to be 423 kJ mol^{-1}, which is ca. 60 kJ mol^{-1} higher than the critical energy for the main decomposition channel, HNCO→NH($^3\Sigma$)+CO. Implications of the results to the kinetics of the thermal decompostion of HNCO at high temperatures are discussed.

Isocyanic acid HNCO decomposes mainly into NH ($^3\Sigma$)+CO in the temperature region above 2000 K.[1-3] Another bond dissociation channel to produce H+NCO has been reported to contribute by less than 5% to the total HNCO consumption.[3] In addition to these two dissociation channels, we observed an indication of the occurrence of an apparent "direct" decomposition leading to CN+OH at higher temperatures.[4]

$$\Delta H^\circ_0/\mathrm{kJ\ mol^{-1}}$$

$$\mathrm{HNCO+M \longrightarrow NH(^3\Sigma^-)+CO+M} \qquad 361 \qquad \text{(1a)}$$

$$\mathrm{ \longrightarrow H+NCO+M} \qquad 474 \qquad \text{(1b)}$$

$$\mathrm{ \longrightarrow CN+OH+M} \qquad 574 \qquad \text{(1c)}$$

This last process must involve an initial isomerization of HNCO into HOCN or HONC. Characteristics of the saddle points for the isomerizations are of particular interest in this connection.

Potential energy surfaces for various isomers of the four-atomic HCNO entity were first studied by Poppinger, Radom, and Pople[5] using ab initio MO calculations at the RHF/4-31G level of theory. Their study has revealed that the surfaces are complicated with many potential wells corresponding to various chain isomers and ring isomers. Thus, a number of isomerization pathways would have to be considered in order to clarify the dynamical mechanism of reaction (1c).

The isomerizations we will consider in the present work include the following:

$$\mathrm{HNCO \longrightarrow H\overline{CON} \longrightarrow HOCN} \qquad \text{(2a)}$$

$$\mathrm{\phantom{HNCO \longrightarrow H\overline{CON}} \longrightarrow HONC} \qquad \text{(2b)}$$

$$\mathrm{\phantom{HNCO \longrightarrow H\overline{CON}} \longrightarrow HCNO} \qquad \text{(2c)}$$

$$\mathrm{HNCO \longrightarrow H\overline{NCO} \longrightarrow HOCN} \qquad \text{(2d)}$$

where both $\mathrm{H\overline{CON}}$ and $\mathrm{H\overline{NCO}}$ denote ring structures while the remaining species are chain isomers. Theoretical assessments of the relative eases of the various isomerization processes at the split-valence+polarization+correlation level are the principal concern of this work.

Method

Geometry optimizations for the minimum energy structures and the saddle points were carried out by the SCF procedure with the energy gradient technique. For a ring intermediate and the relevant transition states(TS), the complete-active-space (CAS) SCF procedure was utilized.

At all the stationary points located, the multi-reference single- and double-excitation (MRD) configuration-interaction (CI) calculations were carried out to obtain the electronic correlation energy. For singlet state the configurations whose contributions $|c_i|^2$ to a state exceed 0.25% were all regarded as the main (reference) configurations. In the case of triplet states, however, we were obliged to loosen the weight limit to $|c_i|^2=1.0\%$ because of otherwise too many configurations selected for handling properly. Triplet state energies might thus be somewhat inaccurate. At any rate, the lowest configuration-selection threshold T was deliberately assigned a value between 1 and 30 μhartree, so that the maximal dimension of the configurational space fell in the region 7000—9000. Four successive threshold values increasing stepwise by 5 μhartree each were used to obtain the CI energy extrapolated to $T=0$ hartree. Further, the generalized Langhoff–Davidson approximation[6,7] was used to correct for possible errors which might arise from the use of a limited number of reference configurations. The CI energies thus corrected are regarded as estimates of full CI values,[7,8] which will be denoted as E_{CI}. The iterative natural-orbital CI method was applied occasionally with two or three cycles at each state.

All calculations were done by using the 6-31G** basis set. The Gaussian 86[9] and HONDO7[10] programs were used for SCF optimization calculations, and the TABLE

MRD-CI program furnished by Buenker[11,12] was used for CI calculations.

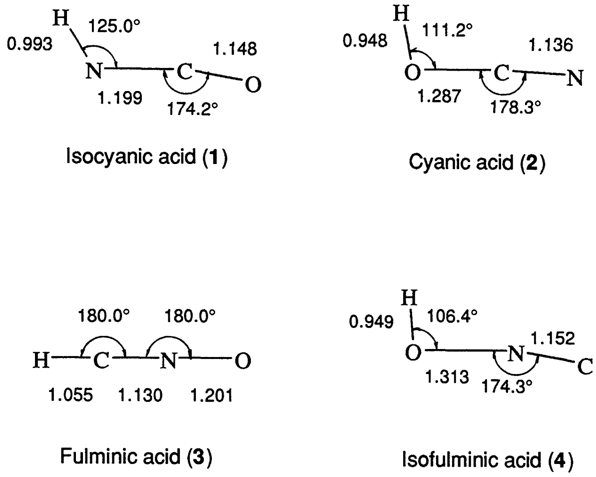
Results

(A) Chain Isomers. For molecular entities constituted of one each of the H, C, N, and O atoms, several isomeric structures are conceivable. Under the constraint that the H atom is attached to the terminal heavy atom (C, N, or O), one can anticipate six chain structures as follows:

HNCO	HOCN	HCNO
1	**2**	**3**
HNOC	HONC	HCON
6	**4**	**5**

Preliminary STO-3G calculations have shown that the entities **1**—**4** indeed possess the restricted Hartree–Fock (RHF) SCF minima at their respective chain structures. By contrast, the entity **6** is liable to dissociate into NH+CO, and the entity **5** tends to cyclize into the form $\mathrm{H}\overline{\mathrm{CON}}$ upon geometry optimizations. Although the four chain isomers have already been the matter of thorough investigations by Teles et al.,[14] we also treat these molecules here for the sake of quantitative considerations of the potential energy profiles for isomerizations.

Geometries of the four chain isomers **1**—**4** optimized by the restricted Hartree–Fock (RHF) SCF procedure employing the 6-31G** functions are shown in Fig. 1. Their energies at the RHF and MRD-CI levels are listed in Table 1. HNCO (**1**, isocyanic acid) is a well-known stable entity, and HCNO (**3**, fulminic acid) has been recognized as an isomer that can exist in the gas phase. However, HOCN (**2**, cyanic acid) and HONC (**4**, isofulminic acid) have been observed only in the rare gas matrices.[14,15] The relatively low total energy calculated for **2** suggests the possibility that it could be detected in the gas phase. The quasi-degeneracy noted between **3** and **4** at the RHF SCF level is released at the CI level. The relative energies deduced by the present CI calculations agree reasonably well with the coupled-



Isocyanic acid (**1**) Cyanic acid (**2**)

Fulminic acid (**3**) Isofulminic acid (**4**)

Fig. 1. Optimized geometries of the chain isomers. The bond lengths are given in units of Å.

Table 1. Total and Relative Energies of the HNCO Chain Isomers

Isomer	Energy		Relative energy		
	hartree		kJ mol^{-1}		
	E_{RHF}+167	E_{CI}+168	ΔE_{RHF}	ΔE_{CI}	ΔE_{CCD}[a)]
HNCO (**1**)	−0.76602	−0.24780	0	0	0
HOCN (**2**)	−0.72902	−0.21125	97	96	88
HCNO (**3**)	−0.63260	−0.12193	350	331	308
HONC (**4**)	−0.63273	−0.10221	350	382	340

a) The CCD (coupled-cluster, double-excitation) energy reported by Teles et al.[14]

Table 2. Comparisons of the Dissociation Energies (kJ mol^{-1}) of HNCO Calculated by the MRD-CI Method with the Thermochemical Data

Products	Calcd			Expt[a)]	
	E_{CI}+167	ΔE_{CI}	D_0[b)]	ΔH°_0	ΔH°_{3000}
	hartree	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
NH($^3\Sigma^-$)+CO	−1.11296	354	332	361	359
H+NCO	−1.06639	476	447	474	496
NH($^1\Delta$)+CO	−1.04531	532	510	512	510
CN+OH	−1.02094	596	576	574	366
CH+NO	−0.93877	811	785	779	786

a) Based on the "JANAF Thermochemical Tables."[16] b) Corrected for the vibrational zero-point energy.

cluster double-excitation (CCD) energies reported by Teles et al.[14]

The dissociation energies D_0 calculated for HNCO (**1**) in particular are listed in Table 2, together with the experimental enthalpy change, ΔH°_{0}.[16] Zero-point energy corrections were made by use of the experimental vibrational frequencies.[16] Theoretical dissociation energies D_0 are in fairly good agreement with the experimental ΔH°_{0} values.

(B) Ring and Branched Isomers. For the entities **5** and **6**, we took a step further to carry out the perfect-pairing multi-configuration (PPMC) SCF calculations[13] with the STO-3G basis set. The active space included eight orbitals accommodating six electrons (8,6) with only double excitations permitted.

In the PPMC/STO-3G optimization for the entity HCON (**5**), use of the initial RHF MO's gave an apparent ring structure, whereas use of the initial guess molecular orbital (MO) coefficients prepared from a UHF solution (diradical type MO's) resulted in a curious ring-like structure in which the OCN angle exceeded 90°. The latter form may be visualized as a "branched" structure. The discrepancy is probably because of an unavoidable incompleteness in the configuration space utilized rather than due to the presence of two hardly distinguishable electronic states.

In the RHF/6-31G** optimization of **5**, no ring isomer has been found. All initial guess geometries we tried led to the potential well of HNCO (**1**). The tendency is similar to that reported by Poppinger et al. using the 4-31G basis set.[5] On the other hand, the UHF/6-31G** optimization has given a branched structure with the OCN angle being 123.5°. The branched isomer is strongly spin-polarized and its eigenvalue of the $\hat{S}^2$ operator is $S^2=1.16$, indicative of a strong diradical character. The two odd electrons are localized mainly on the in-plane orbitals of the O and N atoms.

In order to settle this problem, we performed CASSCF/6-31G** optimization in which four frontier orbitals were invoked for four electrons (4,4) to be accommodated. Both the diradical and the closed-shell type MO coefficients were used as initial guess. As a result, the optimized geometries have proved to be identical, showing a structure intermediate between the ring the the branched forms. The electronic structure found is such as described with two major configurations, one being of the diradical type while the other, the closed-shell type:

$$\cdots(1a'')^2(8a')^2(2a'')^2(9a')^1(10a')^1,$$

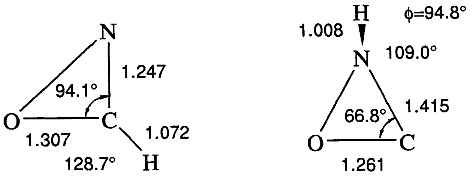
$$\cdots(1a'')^2(8a')^2(2a'')^2(9a')^2.$$

Their CI coefficients are 0.84 and −0.46, respectively.

Figure 2 shows the structure for HCON (**5**) in its electronic ground state optimized by the CASSCF(4,4) procedure assuming Cs symmetry. The remarkable feature is that its OCN angle is 94.1°, with the O–N bond index of ca. 0.5. These values indicate that **5** in its ground state takes a "half-ring structure". The normal ring species called oxazirine, which was proposed as a reaction intermediate in matrix experiments,[17,18] has still been unknown. We will here refer to the half-ring isomer as "oxazirine" and simply regard it as a ring isomer.

Table 3 lists the geometric parameters and the CI energies for the ground-state oxazirine (**5**) and its three excited states. All these excited states are low-lying and have branched structures with the OCN angle of ca. 120°. Both the $^3A''$ and $^1A''$ states to be regarded as formylnitrene have their odd electrons in the nearly degenerate in-plane and out-of-plane p orbitals of the N atom.

The ring isomer in which the H atom is attached to the N atom, HNCO (**7**, oxaziridinylidene), was suggested by



Oxazirine (**5**) Oxaziridinylidene (**7**)

Fig. 2. Optimized geometries of the isomers. The bond lengths are given in units of Å. ϕ indicates the dihedral angle ϕ_{HNCO}.

Table 3. Geometries and Energies of the Cyclic HNCO Isomers

State	Geometry					Energies		
	R_{OC}	R_{CN}	R_{CH}	A_{OCN}	A_{OCH}	$E_{\mathrm{UHF}}+167$	$E_{\mathrm{CI}}+168$	ΔE_{CI}[a)]
	Å	Å	Å	degree	degree	hartree	hartree	kJ mol^{-1}
HCON (**5**)								
$^1A'$	1.307	1.247	1.072	94.1	128.7	−0.70142[b)]	−0.11767	342
$^3A''$	1.236	1.354	1.085	120.8	121.8	−0.69776	−0.09085	412
$^1A''$	1.253	1.326	1.083	121.2	121.2	−0.66954	−0.08716	422
$^3A'$	1.333	1.251	1.086	126.2	111.7	−0.66866	−0.06582	478
HNCO (**7**)	1.261	1.415	1.008[c)]	66.8	109.0[d)]	−0.58786[e)]	−0.05575	504

a) Relative to HNCO (**1**). b) CAS(4,4) energy. c) R_{NH}. d) A_{HNC}. e) RHF energy.

Poppinger et al.[5] We have confirmed that it lies in a potential well on the RHF/6-31G** surface as well. It has a nonplanar structure with the HNCO dihedral angle ϕ=94.8°, as can be seen in Fig. 2. Its CI energy is listed in Table 3. The high energy value (504 kJ mol^{-1} relative to HNCO) makes us suspect that the potential well will be shallow. The situation will be clarifed with the results of MRD-CI calculation for the transition state of its ring opening reaction to form HNCO (**1**).

(C) Isomerizations. We examined four isomerization pathways (2a)—(2d). All these pathways from HNCO (**1**) consist of two steps involving a cyclic intermediate **5** or **7**. We denote the transition state of the cyclization of **1** to **5** as TS1. The transition states from **5** to **2**, **3**, and **4** will be denoted as TS2, TS3, and TS4, respectively. TS5 stands for the transition state for the ring-closure of **1** giving **7**, and TS6 for that of the path from **7** to **2**. All these elementary steps involved are diagrammatically illustrated in Fig. 3.

Since neither UHF nor RHF calculation can describe the electronic state of **5** properly, we have carried out CASSCF(6,10) optimizations to determine the geometries of TS1 and TS2. The geometries obtained are shown in Fig. 4. TS2 on the UHF surface was also examined for the sake of comparison with the CASSCF geometry. It can be seen that the goemetry of TS2 is sensitive to the extent of assessment of correlation energy. Either way, TS2 is structurally more HOCN(**2**)-like than is TS1. TS1 is more HNCO(**1**)-like, as it should be.

Strictly speaking, TS2 was found to be slightly nonplanar at the CASSCF level, the dihedral angle ϕ (HNCO) being 0.5°. Since vibrational analysis at the CASSCF level is a formidable task, we carried out the analysis by the UHF procedure at the planar TS2 (UHF) geometry, to confirm a single imaginary frequency being 2362i cm^{-1}. Assumption of the Cs symmetry for TS2 will cause no serious error.

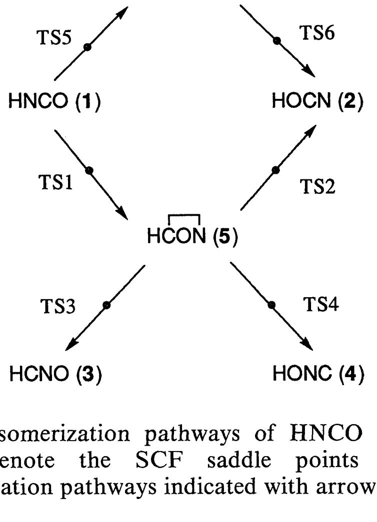


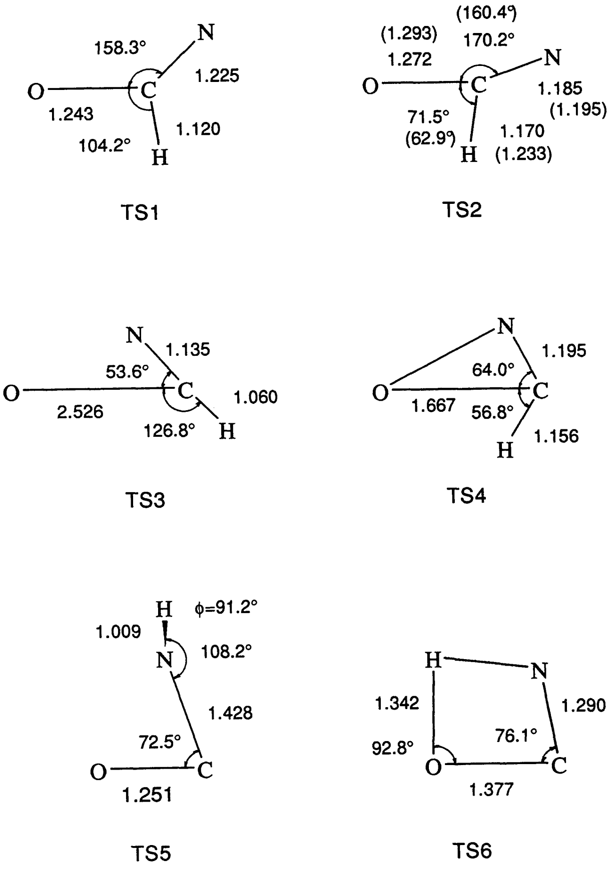
Fig. 3. Isomerization pathways of HNCO (**1**). TS 1—6 denote the SCF saddle points on the isomerization pathways indicated with arrows.

TS3 and TS4 are responsible for the formations of **3** and **4**, respectively, from the cyclic intermediate **5**. Their geometries obtained by the RHF SCF procedure are shown in Fig. 4.

The remaining transition states, TS5 and TS6, are related to the isomerization of **1** to **2** via the cyclic intermediate **7**. The first saddle point, TS5, was found only on the UHF surface and its geometry (Fig. 4) proved to closely resemble that of **7**. On the contrary, TS6 was found on the RHF surface. Its geometry is also shown in Fig. 4. Both TS5 and TS6 were confirmed to have a single imaginary frequency of vibration.

All the transition state structures, TS1 through TS6, were then subjected to the MRD-CI calculations. The CI energies obtained are summarized in Table 4. The relative energies ΔE_{CI} are the values expressed by taking HNCO (**1**) as the common standard.

Figure 5 diagrammatically illustrates the calculated potential energy profiles for all the isomerization pathways considered here. It is apparent that the most favorable isomerization pathway of HNCO (**1**) is reaction (2a), which proceeds through the cyclic intermediate HCON (**5**) to give HOCN (**2**). In a sense, it is a suc-



TS1 TS2

TS3 TS4

TS5 TS6

Fig. 4. Optimized geometries of the transition states for isomerizations. The bond lengths are given in units of Å. The figures given in parentheses for TS2 are the bond lengths and angles obtained by the UHF SCF procedure.

Table 4. MRD-CI Energies for the Transition States of Various Isomerizations

TS	Reaction	Method	E_{SCF}+167 hartree	E_{CI}+167 hartree	ΔE_{CI}a) kJ mol^{-1}
TS1	**1**→**5**	CAS (6,10)	−0.63668	−1.11305	354
TS2	**5**→**2**	CAS (6,10)	−0.62758	−1.08653	423
TS3	**5**→**3**	RHF	−0.54022	−0.98838	681
TS4	**5**→**4**	RHF	−0.50022	−1.00423	639
TS5	**1**→**7**	UHF	−0.58488	−1.05843	497
TS6	**7**→**2**	RHF	−0.51115	−1.00929	626

a) Relative to HNCO (**1**).

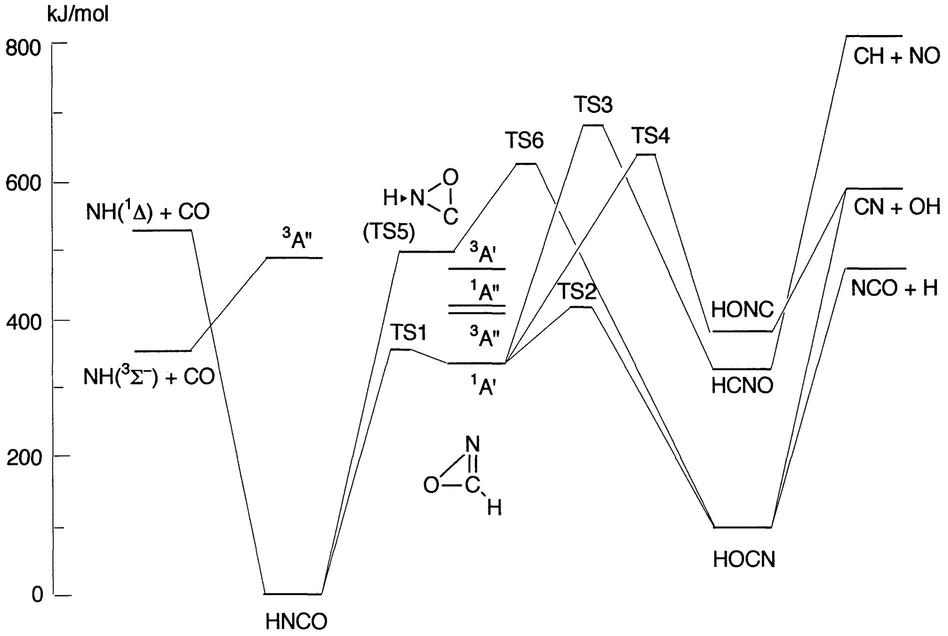


Fig. 5. Potential energy profiles of the HNCO systems calculated by the MRD-CI/6-31G** computations.

cession of two 1,2-hydrogen migrations. Its overall TS is TS2, the net barrier height being 423 kJ mol^{-1}.

Another pathway of isomerization of **1** to **2** is reaction (2d), which involves the cyclic intermediate HNCO (**7**). According to the present CI calculations, however, the TS for the initial cyclization, i.e., TS5, is more stable than **7**. Hence, the existence of **7** as an intermediate is dubious, in contradiction to the conclusion reached by Poppinger et al.5) on the basis of the SCF/4-31G calculations. The overall reaction should thus be regarded as a one-step 1,3-hydrogen migration passing over TS6. Because TS6 lies much higher (626 kJ mol^{-1}) than does TS2, the 1,3-hydrogen migration (2d) will be far less important than reaction (2a).

In both reactions (2b) and (2c), the second steps seem to be rate-controlling. Since the net barriers TS3 and TS4 lie at much higher energy levels (681 and 639 kJ mol^{-1}, respectively) as compared to TS2, reactions (2b) and (2c) will both be much less favorable than reaction (2a).

Discussion

All the isomerization reactions considered in this work have been presumed to proceed through a cyclic intermediate, **5** or **7**. Oxazirine (**5**) is calculated to lie in energy minimum even though the barrier (TS1) preventing its transfomation into HNCO (**1**) is low (only 12 kJ mol^{-1}). On the other hand, oxaziridinylidene (**7**) does not seem to be a stable entity; it is liable to be led to the HNCO (**1**) minimum with no activation barrier at all. It should be noted that both these conclusions based on CI calculations are just opposite to the views presented by Poppinger et al.5) at the SCF level.

Direct isomerizations may deserve attention as well. Among others, the HONC (**4**)-HOCN (**2**) isomerization is likely to be an elementary reaction of the well-documented isonitrile-nitrile rearrangement type.19,20) Practically, however, formation of **4** from **1** requires a high activation energy, so that the direct isomerization in question will have little significance in the present context.

The most important point to be noted in this work is the demonstration that the two-step isomerization reaction of HNCO (**1**) to HOCN (**2**), i.e., reaction (2a), is energetically the most favorable process. The net activation barrier (TS2) lies 423 kJ mol^{-1} above HNCO (**1**). Corrected for the vibrational zero-point energy, the barrier height is slightly lowered to 411 kJ mol^{-1}, which is only modestly higher than the experimental activation energy (355±4 kJ mol^{-1}) reported recently by Wu et al.[3] for the main decomposition reaction (1a) of HNCO. Thus, reaction (2a) could well be an unignorable side reaction of reaction (1a) particularly at high temperatures. HOCN (**2**) thus formed will be liable to decompose into H+NCO, just as HNCO (**1**) is partly led to the same fragments beside the principal decomposition products $\mathrm{NH}(^3\Sigma^-)+\mathrm{CO}$.[3] At still higher temperatures, formation of CN from **2** may be feasible. Our observation of a sizable amount of CN radicals in the shock-heated decomposition of HNCO in the high temperature region (2500—3500 K) could only be rationalized from this view. The anomalously low heat of formation of the CN radical at high temperatures (ΔH°_f at 3000 K being 221.3 kJ mol^{-1} as compared to 436.8 kJ mol^{-1} at 0 K)[16] may assist this formation of CN in the high temperature region.

Conclusion

Ab initio MO calculations based on the MRD-CI method reveal that the isomerization reaction HNCO→HOCN can compete with the primary decomposition channel $\mathrm{HNCO}\rightarrow\mathrm{NH}(^3\Sigma)+\mathrm{CO}$. The isomerization consists of two 1,2-hydrogen migrations with an intermediacy of oxazirine, a half-ring isomer $\mathrm{H\overline{CON}}$. The transition state of the second step $\mathrm{H\overline{CON}}\rightarrow\mathrm{HOCN}$ constitutes the overall barrier top. Both the intermediate and the transition state are sensitive to the degree of assessment of the correlation energy involved.

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