Thermokinetic study of the isomerization of isocyanic acid

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Abstract

In this work, the detailed study on the mechanism, kinetics and thermochemistry of the isomerization of isocyanic is described. Theoretical study was carried out by ab initio molecular orbital theory based on the CCSD(T) and B3LYP/6-311++G(3df,2p) methods in conjunction with statistical theoretical kinetic Rice-Ramsperger-Kassel-Marcus (RRKM) Master equation calculations. The potential energy surface (PES) for the isomeric reactions was also examined. At 760 Torr pressure, temperature dependent rate constants of the isomeric reactions HNCO → HOCN (a), HNCO → H(CNO) (b) and HNCO → H(NCO) (c) were: k(T) (a) = $10^{-37.70}.T^{13.09}.e^{-93.30kcal/mol/RT}$, k(T) (b) = $10^{3.46}.T^{1.76}.e^{-93.98kcal/mol/RT}$, k(T) (c) = $10^{-28.50}.T^{10.61}.e^{-91.16kcal/mol/RT}$ respectively. Calculated results show that the isomerization of isocyanic acid may take place via three mechanisms and have very high barriers; all rate constants of them are very small in the temperature range from 300 to 2000 K.

Keywords. Potential energy surface, isocyanic acid, density function theory, isomerization.

1. INTRODUCTION

Isocyanic acid (HNCO) is known as the simplest organic compound which has full four most important biogenic elements C, H, N, O in organic chemistry. This molecule has sixteen valence electrons, symmetric group C_S. Its electronic configuration in ground state is given by $(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(1a'')^2(8a')^2(9a')^2(2a'')^2(10a')^0$ [1, 2]. In daily life, the major source forming isocyanic acid is from tobacco smoke, biomass burning, fuel burning at low temperature, forest fires, etc. At concentration over 1 ppbv (parts per billion by volume), isocyanic acid can cause cataract, heart failure and other chronic diseases efor example rheumatoid arthritis [3]. Isocyanic acid is also formed from dissociative photoionization reaction of urea [4].

$$CO(NH_2)_2 + h\nu \rightarrow NH_3^+ + HNCO + e^-$$
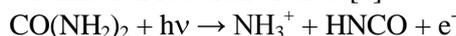
Fulminic acid (iosomer of isocyanic acid) plays an important role in the combustion chemistry due to its involvement in the NO-reburning process for the reduction of NO_x pollutants. It is also one of the components of photochemical smog. Fulminic acid is formed primarily by the combustion of fossil fuels whose normal products include water vapor, CO_2 and some pollutant gas such as CO, and NO_x, [3, 5, 6]. Therefore, the understanding of the isomerization of HNCO isomers has particular significance for environmental research.

The study on the HNCO isomerization were performed firstly by Dieter Poppinger et al. in 1976 by using Roothaan' method with STO-3G, 4-31G, and 6- 31G* basis sets. Seven minima found on the potential energy surface is isocyanic acid, cyanic acid, fulminic acid, isofulminic acid, formylnitrene, oxazirine, and oxaziridinylidene. However, the structures of formylnitrene, oxazirine were only found at very small STO-3G basis set, with a larger basis set these structures did not exist. In addition, this potential energy surface was not indicated fully. The HCON and HNOC isomers had not been mentioned on the potential energy surface [7]. Recently, some of the properties of electrons and magnetic properties of four stable isomers including isocyanic acid, cyanic acid, fulminic acid, and isofulminic acid were also studied in the ground state [8-10]. On the other hand, the kinetics of the isomerization of HCN, CH_3NC had been studied [11-14] but without any kinetics of isocyanic acid isomerization. A full theoretical study on the potential energy surface of the isomerization at higher level as well as their kinetics is very necessary.

2. COMPUTATIONAL METHODS

Geometric optimizations for the eight isomers and ten

transition states (TS) were carried out at the B3LYP level of density functional theory (DFT) using the 6-311++G(3df,2p) basis set. The vibrational frequencies of the transition state were calculated at the same level. The symbol TS **i/j** is used to denote the transition state connecting isomers (**i**) and (**j**). All of the stationary points were confirmed to be local minima or transition states by harmonic vibrational analysis. Single point energy (SP) calculations of all species were performed at the CCSD(T)/6-311++G(3df,2p) level using the B3LYP/6-311++G(3df,2p) optimized geometries. Natural bond orbital (NBO) analysis was calculated at HF/STO-3G level. All calculations were carried out using the GAUSSIAN-03 program packages [15].

The thermodynamic parameters and vibrational frequencies that were scaled down by 0.989 [16] were used to calculate kinetic by using RRKM theory and ChemRate program [17, 18]. This is the RRKM formula:

$$k(T) = \frac{\sigma}{hQ(T)} \int_{E_0}^{\infty} \frac{N^{\ddagger}(E - E_0)e^{-E/k_BT}}{1 + k(E)/\omega} dE$$

where $k(T)$ is the rate constant, T is the temperature, h is Plank's constant, k_B is Boltzmann's constant, σ is the reaction symmetry factor, Q is the partition function, E is the reactant internal energy, E_0 is the critical energy of the reaction, $N^{\ddagger}$ is the sum of the TS states, ω is the collisional frequency, $k(E)$ is the microcanonical rate constant.

The Lennard-Jone parameters for HNCO isomers and Ar bath gas were: σ_{HNCO} = 4.42 Å, ε_{HNCO} = 258 K, σ_{Ar} = 3.47 Å, ε_{Ar} = 116 K [19]. In the present work, temperature was taken in the range from 300-3000 K, at 760 Torr Ar pressure.

3. RESULTS AND DISCUSSION

3.1. Potential energy surface

Figure 1 depicts the structures of isomers and transition states. All structures have singlet electronic ground state. Isocyanic acid, HNCO has the lowest relative energy (E_{rel}) among all CHNO isomers on potential energy surface (PES) [H, C, N, O]. Cyanic acid, fulminic acid and isofulminic acid lie respectively, 25.03, 69.21 and 83.41 kcal/mol higher in energy than isocyanic acid. Our results agree well with the previous study results of Michael S. Schuurman that are 24.7, 70.7 and 84.1 kcal/mol respectively [20]. The four acid isomers above have the lowest relative energy on the PES. Therefore, they are the most stable isomers. Isofulminic acid (HONC) is the least stable of the four acid isomers. These are in good agreement with Dieter Poppinger'

prediction [7]. The oxaziridinylidene H(NCO) (**6**) structure is a three-membered ring, relative energy of which is 105.84 kcal/mol. The oxazirine H(CNO) (**5**) structure is also a three-membered ring. Its relative energy is nearly 2 kcal/mol higher than isofulminic acid. We also established the reaction pathway for the structure (**7**) that was predicted but not finished by Dieter Poppinger [7].

Analyzing NBO at HF/STO-3G level shows that in the N-O bond of (**7**) structure, the distribution of O atom is 84.05%, only 15.95% for N atom. This means that the structure (**7**) is very similar to a complex compound which contains a N←O donor – acceptor bond. This N←O bond length is 1,47 Å (figure 1) longer than a normal N-O bond length. Therefore, the (**7**) structure is unstable, ready to go (CO+NH) formation. This suggested a new pathway for forming (CO+NH): fulminic acid → TS**6/3** → oxaziridinylidene → TS**6/7** → HNOC → (NH + CO). The data in figure 1 show that barriers of this pathway are not much higher than the barriers of the path recommended by J. K. Yu group, fulminic acid → TS**5/3** → H(CNO) → TS**1/5** → HNCO → TS→ (NH + CO) when they studied the photolysis of fulminic acid at 248 nm ultraviolet wavelength [21].

With the acyclic compound (**8**) – HCON, it was predicted and optimized at STO-3G level by Dieter Poppinger et al. [7] but not successfully at higher basis set due to converting to (**1**), (**2**) or (**4**). We optimized successfully (**8**) with a very large 6-311++G(3df, 2p) basis set, which is also the minimum has the highest relative energy on the PES, thus, the viability of (**8**) isomer is very small at low temperature.

As mentioned in the preceding section, the three lowest relative energy structures including isocyanic acid, cyanic acid and fulminic acid have very high barrier in isomeric reactions. The isomerization of isocyanic acid has three mechanisms, either via TS **1/2** (140.58 kcal/mol) to form cyanic acid, or via TS **1/5** (106.37 kcal/mol) to form (**5**) (85.3 kcal/mol), or via TS **1/6** (129.41kcal/mol) to form (**6**) (105.84 kcal/mol). Among these mechanisms, the one via TS **1/5** with the lowest barrier will occur in the easiest way. For cyanic acid (25.03 kcal/mol), there are only two isomeric mechanisms, via TS **1/2** to come back isocyanic acid or via TS **2/4** (109.89 kcal/mol) to form isofulminic acid (83.41 kcal/mol). Likewise, fulminic acid (69.21 kcal/mol) also has only two isomeric mechanisms, via TS **6/3** (136.10 kcal/mol) to form (**6**) or via TS **5/3** (137.21 kcal/mol) to form (**5**). The data on PES in figure 1 show that all isomerizations will have to overcome very high barriers. Therefore, the isomeric ability of (**1**), (**2**), (**3**) is impossible under normal

condition. The quantitative result of these processes   will be considered further at the later kinetic section.
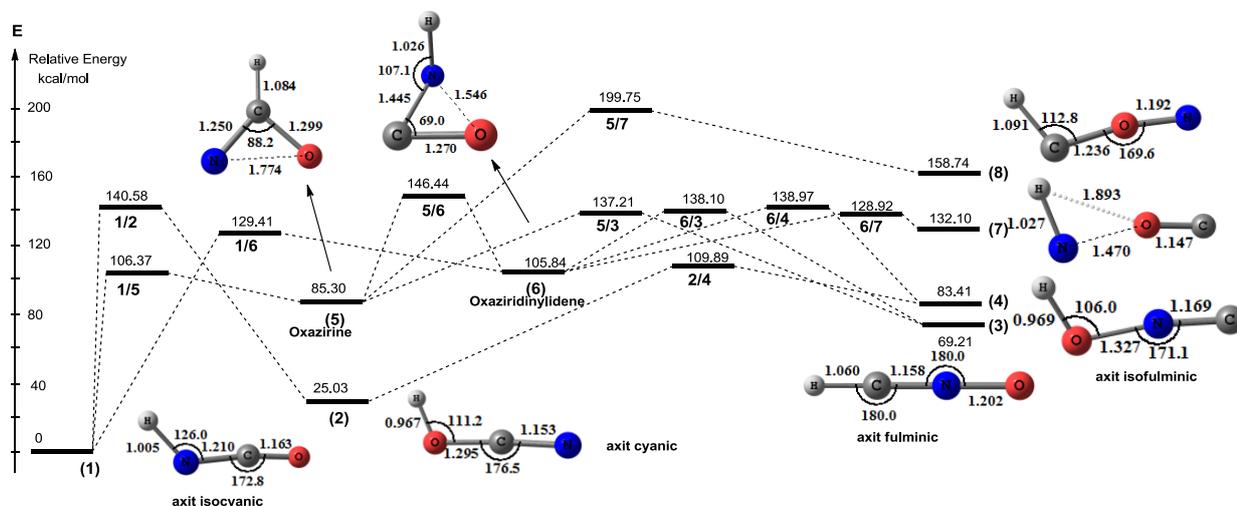
Figure 1: Detailed PES (kcal.mol^{-1}) of the isomers [H, C, N, O] obtained at the CCSD(T)/6-311++G(3df,2p) level of theory. The optimized geometries at the B3LYP/6-311++G(3df,2p). Bond distances in (Å), bond angles in degrees

Table 1: ZPE, SP (a.u.), E_{rel}, $\Delta H_{f\,0K}^{0}$, $\Delta H_{f\,298K}^{0}$ (kcal/mol) of isomers and transition states

Species	ZPE	SP	E_{rel}	$\Delta H_{f\,0K}^{0}$	$\Delta H_{f\,298K}^{0}$
(1) HNCO Isocyanic acid	0.021327	-168.434757	0.00	-27.99 (-27.9±1) [16] −(27.8±0.3) [4]	-28.74 ≥ (-27.7±1.1) [22] (-27.8±0.4) [23] (-28.5±0.3) [4]
(2) HOCN Cyanic acid	0.021568	-168.3951152	25.03	-3.12	-3.80 (-3.55±0.24) [24]
(3) HCNO Fulminic acid	0.019933	-168.3230662	69.21	42.09	41.63 (40.26±0.29) [24]
(4) HONC Isofulminic acid	0.020368	-168.3008765	83.41	56.02	55.58 (55.72±0.24) [24]
(5) H(CNO) Oxazirine	0.019896	-168.2973992	85.30	58.20	57.40
(6) H(NCO) Oxaziridinylidene	0.019567	-168.2643246	105.84	78.96	78.13
(7) HNOC	0.017903	-168.2208136	132.10	106.26	105.93
(8) HCON	0.018257	-168.1787261	158.74	132.67	131.99
5/6	0.014168	-168.1942293	146.44	122.94	122.14
6/3	0.017783	-168.2111434	138.10	112.33	111.41
2/4	0.018603	-168.2569079	109.89	83.61	82.81
1/5	0.016805	-168.2607305	106.37	81.21	80.28
1/2	0.013512	-168.2029086	140.58	117.49	116.75
5/3	0.015893	-168.2106653	137.21	112.63	111.86
1/6	0.017175	-168.2243748	129.41	104.02	103.13
5/8	0.014591	-168.1096919	199.75	175.99	175.35
6/7	0.015236	-168.2232176	128.92	104.75	104.52
6/4	0.014664	-168.2066894	138.93	115.12	114.36

3.2. Thermodynamic properties

By spectroscopy techniques, in 1995, Zhang et al. detemined the heat of formation of isocyanic acid $\Delta H^0_{f\,K}(HNCO, g) = -(27.9\pm1.0)$ kJ.mol^{-1} [16]. In 1996, Steven S. Brown and coworkers via calculation the N-H and C-O binding energy of HNCO molecule gave $\Delta H^0_f(HNCO, g) \geq -(27.7\pm1.1)$ kcal.mol^{-1} [22]. Also in 1996, M. Zyrianov et al. using photodissociation specified $\Delta H^0_f(HNCO, g) = -27.8\pm0.4$ kcal.mol^{-1} [23]. Most recently, in 2013, Andras Bodi et al. using dissociative photoionization technology reported $\Delta H^0_{f\,0K}(HNCO, g) = -(27.8\pm0.3)$ kcal.mol^{-1}, $\Delta H^0_f(HNCO, g) = -(28.5\pm0.3)$ kcal.mol^{-1} [4]. Comparing with heat of formation reported previously, our theoretical result $\Delta H^0_{f\,0K}(HNCO, g) = -27.99$ kcal.mol^{-1}, $\Delta H^0_f(HNCO, g) = -28.74$ kcal.mol^{-1} are in good agreement. As shown in table 1, the heat of formation values of cyanic acid, fulminic acid, isofulmic acid are also not much different with experimental values. Remarkably, only heat of formation of isocyanic and cyanic acid are negative. These are also energetically lowest lying iosmers on PES. Therefore, they are the stablest isomers. Whereas, fulminic acid and isofulminic acid, their heat of formation and relative energy are much higher. The results of calculation Gibbs free energy for three isocyanic acid isomeric reactions:

HNCO → HOCN   (a) $\Delta G^0_{298K} = 24.88$ kcal/mol
HNCO → H(CNO)   (b) $\Delta G^0_{298K} = 84.74$ kcal/mol
HNCO → H(NCO)   (c) $\Delta G^0_{298K} = 105.35$ kcal/mol
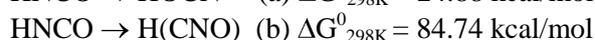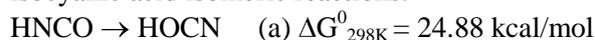
At standart condition, Gibbs free energy (ΔG^0_{298K}) of the reactions (a, b, c) are quite positive. Hence, (a), (b) and (c) are likely not to occur at 298 K thermodynamically.

3.3. Rate constant

In order to test the validity of the present ab initio chemical kinetic predictive approach by RRKM calculations, we have computed the rate constant for the CH$_3$NC→ CH$_3$CN isomeric reaction. The result in table 2 showed that obtained theoretical rate constant k = 5.88×10^{-4} [s^{-1}] at T = 500 K; P = 13 bar was in good agreement with experimental values. Thus, using the CCSD(T)/B3LYP/6-311++G(3df,2p) methods in conjunction with statistical theoretical kinetic RRKM Master equation calculations is very appropriate for computing kinetics of the isomerizations.

Table 2: Rate constant k(T) [s^{-1}] at 500K of the reaction CH$_3$NC → CH$_3$CN

T (K)	k(T) [s^{-1}]			
	2.67E-3 - 0.13 Bar	1.33E-3 - 13.33 Bar	Infinite pressure	13.00 Bar
500	4.71E-4	6.86E-4	7.81E-4	5.88E-04
Literature	[11]	[12]	[13]	This work

Table 3: Rate constant k(T) [s^{-1}] in the temperature range 2100-3000K of the HNCO isomeric reactions

T (K)	$k_{(1\to TS\,1/2)}$	$k_{1\to TS\,1/5}$	$k_{1\to TS\,1/6}$	T (K)	$k_{(1\to TS\,1/2)}$	$k_{1\to TS\,1/5}$	$k_{1\to TS\,1/6}$
2100	0.000122	0.347449	0.001927	2600	0.146886	38.50341	1.241308
2200	0.000618	1.049844	0.008524	2700	0.469952	80.72601	3.561637
2300	0.002798	2.891444	0.033826	2800	1.407905	160.9078	9.612161
2400	0.011436	7.342240	0.122000	2900	3.974057	306.4966	24.54340
2500	0.042683	17.35576	0.404186	3000	10.62645	560.4015	59.59463

The predicted rate constants of the (a, b, c) isomeric reactions given in units of s^{-1} at 760 Torr Ar pressure in the temperature range 300-3000K can be represented by:

$$k(T)\,(a) = 10^{-37.70}.T^{13.09}.e^{-93.30 kcal/mol/RT},$$
$$k(T)\,(b) = 10^{3.46}.T^{1.76}.e^{-93.98 kcal/mol/RT},$$
$$k(T)\,(c) = 10^{-28.50}.T^{10.61}.e^{-91.16 kcal/mol/RT}.$$

The specific values of rate constants of three above isomeric reactions at different temperature in table 3 and figure 2 showed that it was very difficult for the isomeric reactions to occur in the temperature range 300-2000 K. The reactions only occur considerably at T > 2000 K and the direction of forming H(CNO) oxazirine three-membered ring isomer via transition state TS **1/5** is more favorable.
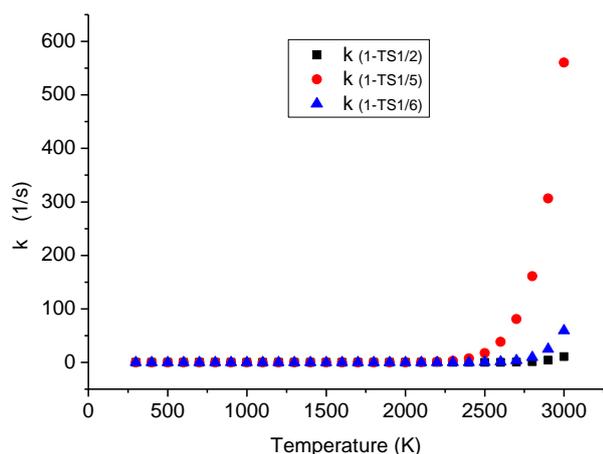
Figure 2: Temperature dependence of rate constants of the HNCO isomeric reactions

4. CONCLUSION

There are eight existent feasible isomers on the potential energy surface [H, N, C, O], in which isocyanic acid and cyanic acid are the most stable isomers. The HNOC isomer contains a N←O unstable donor – acceptor bond is intermediate complex forming CO, NH products. Isomerizations are difficult to occur at normal temperature and pressure condition. Isomerization isocyanic acid is easier above 2000 K and favorable to generate H(CNO) ring compound before forming the other isomer products.

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