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THERMOKINETIC STUDY OF FORMATION OF CARBON MONOXIDE IN THE DIMERISATION OF ISOCYANIC ACID

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Abstract. The mechanism of the dimerisation of HNCO was investigated using the *ab initio* method. The barrier heights, reaction energies and geometrical parameters of the reactants, intermediates and transition state, and products were studied. It was found that there were possibly three reaction channels. The B3LYP 6-311++G(3df,2p)//CCSD(T) 6-311++G(d,p) calculated barriers showed that the reaction of formation of four-membered ring O=CNHNHC=O was more favourable than the formation of CO_2 or CO. The formation of carbon monoxide from the dimerisation of isocyanic acid was a new pathway. Its rate constant was very small, $k = 2.62\times10^{-19}$ cm^3/molecule/s at 2,500 K and 1 atm, which was about 2,000 times as small as the rate constant of formation of CO with a bimolecular mechanism of HNCO with Ar.

Keywords: Potential energy surface, isocyanic acid, density function theory, dimerisation

1 Introduction

Emissions of CO to the atmosphere come from a range of sources, but mostly as a by-product of incomplete combustion, whether it is biomass burning, domestic heating systems or vehicle exhausts. Therefore, the understanding of the formation of CO from various sources can help to find a more simple solution for reducing the concentration of CO in the environment. This is always an interesting topic for scientists [10, 15, 21]. At present, the formation of CO from the bimolecular reaction of isocyanic acid has not been studied yet.

Isocyanic acid (HNCO) can be prepared in the pure form by reaction of KOCN or NaOCN with stearic or oxalic acid [8]

$$\mathrm{MOCN + R\text{–}COOH \rightarrow HNCO + R\text{–}COOM}$$

$$\mathrm{2\ MOCN + (COOH)_2 \rightarrow 2\ HNCO + (COOM)_2}$$

$$\mathrm{(M = Na, K;\ R = C_{17}H_{35})}$$

The identification, characterisation and investigation of the thermal stability of HNCO and the evidence for a possible existence of “dicyanic acid” $(HNCO)_2$ have been studied in the gas phase, liquid and solid state in the temperature range of –80 °C to 160 °C by vibrational and

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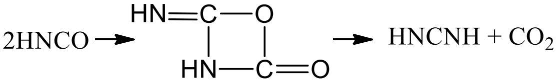
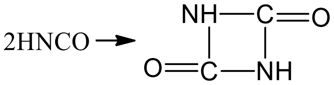
NMR spectroscopy and mass spectrometry by Fischer et al. [8]. The polymerisation of HNCO can produce a mixture of cyanuric acid (trimmer of HNCO) and cyamelide $(HNCO)_n$. Isocyanic acid and its isomers play an important role in the $RAPRENO_x$ (RAPid REduction of Nitrogen Oxides) process for NO reduction in combustion [16] and are a source of formation of NH – one of the intermediates in the formation of NH_3 upon sequential hydrogenation of N atoms [13, 5]. Isocyanic acid can form strong hydrogen bonds, therefore, its dimer can be easily generated [18]. In the temperature range of 823–1,220 K, a number of differential reaction mechanisms were proposed by researchers. He and Liu suggested a two-step bimolecular mechanism explaining the formation of CO_2 [6]



(1)

According to this mechanism, reaction (1) consists of two steps: (I) the two molecules of HNCO first react with each other to form a four-membered ring intermediate; (II) the intermediate then decomposes to form the products, namely CO_2 and HNCNH.

In 1995, Feng et al. used the *ab initio* MP2/6-31G* method to suggested a reaction mechanism of two molecules of isocyanic acid to get another four-membered ring [6]



(2)

Feng et al. concluded that the reactive ability of reaction (2) was higher than that of reaction (1). Many groups of researchers showed that, at high temperature (T > 1,800 K), the HNCO dimerisation can follow a bimolecular mechanism with an Ar bath gas to produce carbon monoxide [12, 14, 20]. Is there the formation of CO in the bimolecular reaction of HNCO if the bath gas is not used? The purpose of this study is to answer this question by using quantum computational chemistry and at the same time again confirm a more favourable reaction pathway of the dimerisation of HNCO by calculation of the thermodynamic and kinetic properties with high accurate methods such as B3LYP/6-311++G(3df,2p) and CCSD(T)/6-311++G(d,p).

2 Computational methods

Density functional theory (DFT) approaches, especially those using hybrid functionals, have evolved to a powerful and very reliable tool, being routinely used for the determination of various molecular properties. The B3LYP function has been shown to provide an excellent compromise between accuracy and computational spectra for organic molecules [11, 22]. In this work, all of the geometrical structures were optimised. The zero point energy and vibrational frequencies were calculated using DFT with the B3LYP functional in conjunction with 6-311++G(3df,2p) basis set. To achieve more reliable energies of various species along the potential energy surface (PES), we have employed the CCSD(T)/6-311++G(d,p) method to obtain the single point energy (SP) based on the optimised geometries. The data of the SP are shown in Table 1. Our calculation results for geometrical parameters of isocyanic acid, intermediates, transition states (TS), and products are shown in Fig. 2. The values of the bond lengths and angles of isocyanic acid are in a good agreement between experimental and theoretical results. Therefore, the used methods in this study are appropriate. All calculations were carried out using the GAUSSIAN-09 program packages [7].

The calculated DFT vibrational frequencies were scaled using factor 0.9614 [23]. These frequencies and thermodynamic parameters were used to determine the kinetics by using the transition state theory (TST) [17] and the KisThelp program [2]. According to TST, for the bimolecular reaction $A + B \rightarrow C + D$, rate constant k is computed using the following formula

$$k = \kappa \frac{k_b T}{h} \frac{q^{\ddagger}}{q_A q_B} \exp\left(\frac{-E_0}{RT}\right)$$

where k is the rate constant, T is the temperature (K), h is the Plank's constant, k_B is the Boltzmann's constant, R is the gas constant, κ is the transmission coefficient, E_0 is the critical energy and is found from the potential energy surface, $q^{\ddagger}$ is the partition function per unit volume for TS, q_A and q_B are partition functions per unit volume for the reactants. Then, the rate constant was scaled by Eckart tunneling factor [4]. In the present work, the temperature was taken in the range from 500–2,500 K at 1 atm pressure.

3 Results and discussion

3.1 Potential energy surface

As shown in Fig. 1, the dimerisation of HNCO can take place with three channels. The first channel consists of two steps: (I) the two molecules of HNCO react to form a four-membered ring intermediate (Int) (15.21 kcal/mol) through TS1 (40.04 kcal/mol); (II) Int then decomposes to products P1 (–2.73 kcal/mol), namely H_2N_2C and CO_2 via a TS2 with an energy barrier of 39.53 kcal/mol, not much different from the barrier of TS1. The second channel forms product P2 (1.06 kcal/mol) via TS3 (32.80 kcal/mol). The barrier of TS3 is lower than the barriers of TS1 and TS2. Both products P2 and TS3 belong to the C_{2h} point group – the highest symmetry point group on PES. Hence, our result is similar to the that of Feng et al. [6], which means that the barrier of reaction (2) is lower than that of reaction (1). Reaction (2) is more favourable.

The third channel via TS4 (79.62 kcal/mol) forms product P3 (54,15 kcal/mol), namely H_2N_2CO and CO. According to our knowledge, this pathway has not been reported previously. Its barrier is much higher than that of reactions (1) and (2). Thus, the third pathway is difficult to take place.

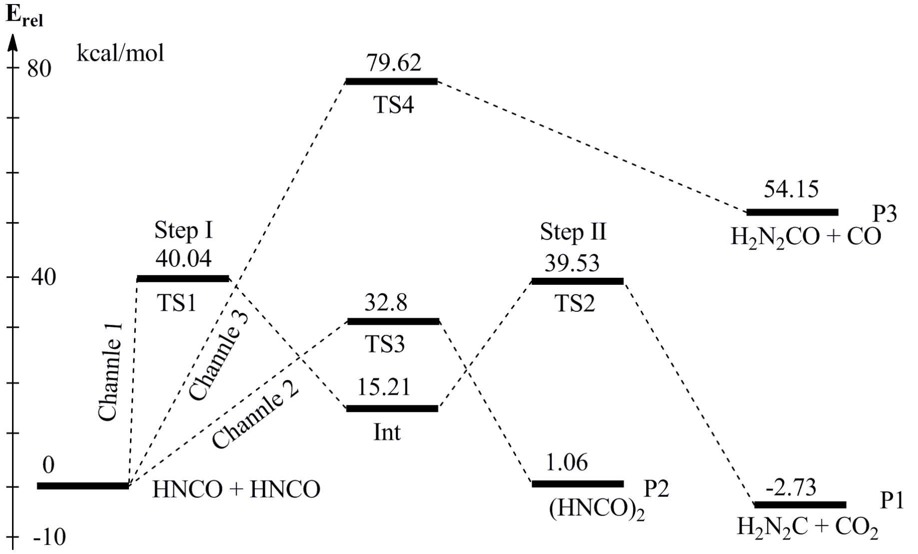


Fig. 1. Potential energy surface of the reaction channels for the dimerisation of HNCO
E_{rel} is the relative energies (kcal·mol^{-1}) at the CCSD(T)/6-311++G(d,p) level

3.2 Thermodynamic properties and rate constant

The change of enthalpy ΔH^0_{298} and Gibbs free energy ΔG^0_{298} in kcal/mol of the reactions (1, 2, 3) are

$$2\ HNCO \rightarrow H_2N_2C + CO_2 \quad (\mathbf{P1});\quad \Delta H_1 = -3.00;\ \Delta G_1 = -1.67$$

$$2\ HNCO \rightarrow (HNCO)_2 \quad (\mathbf{P2});\quad \Delta H_2 = -0.52;\ \Delta G_2 = 12.10$$

$$2\ HNCO \rightarrow H_2N_2CO + CO \quad (\mathbf{P3});\quad \Delta H_3 = 53.80;\ \Delta G_3 = 54.86$$

It is clearly seen that based on thermodynamic laws, reaction (3) is difficult to occur because both the standard enthalpy and Gibbs free energy changes are very positive. However, reaction (1) is more favourable than reaction (2) because the standard enthalpy change and Gibbs free energy change are negative. This result is in contradiction with the PES analysis above.

Table 1. *ZPE*, *SP* (a.u.), E_{rel} (kcal/mol) of HNCO, intermediate, products and transition states

Structures	*ZPE*	$SP_{CCSD(T)}$	E_{rel}
HNCO	0.021327	–168.3339128	
IM	0.045814	–336.650756	12.69

Structures	***ZPE***	$SP_{CCSD(T)}$	E_{rel}
TS1	0.046348	–336.6077129	40.04
TS2	0.045814	–336.6079964	39.53
TS3	0.045831	–336.6187346	32.80
TS4	0.043849	–336.5421357	79.62
P2	0.050295	–336.6737763	1.06
CO_2	0.011722	–188.221156	
H_2N_2C	0.032664	–148.4527577	
$H_2N_2C+CO_2$	0.044386	–336.6739137	–2.73
H_2N_2CO	0.038919	–223.4867392	
CO	0.00505	–113.0961062	
H_2N_2CO+CO	0.043969	–336.5828454	54.15

Table 2. Rate constant $k(T)$ (in cm^3/molecule/s) in the temperature range 500–2500 K of the dimerisation HNCO

T(K)	k_1 Ref. [19]	k_1 Ref. [9]	k_1	k_2	k_3	k_4	HNCO→ CO+ NH in Ar bath gas Ref. [20]
500	4.24E–32		4.73E–32	477.8786	1.92E–28	1.27E–48	
600	4.97E–29		4.33E–29	36001.33	5.58E–26	1.01E–42	
700	7.73E–27		6.01E–27	806133.8	3.42E–24	1.77E–38	
800	3.41E–25		2.55E–25	8401636	7.88E–23	2.86E–35	
900	6.47E–24	6.77E–24	4.91E–24	5.23E+07	9.42E–22	9.35E–33	
1000	6.82E–23	7.13E–23	5.40E–23	2.27E+08	7.07E–21	9.95E–31	
1100	4.69E–22	4.90E–22	3.95E–22	7.57E+08	3.79E–20	4.67E–29	
1200	2.34E–21	2.44E–21	2.12E–21	2.07E+09	1.57E–19	1.18E–27	
1300	9.09E–21		8.94E–21	4.85E+09	5.30E–19	1.85E–26	
1400	2.92E–20		3.13E–20	1.00E+10	1.55E–18	2.00E–25	
1500	8.00E–20		9.35E–20	1.91E+10	3.92E–18	1.60E–24	
1600	1.94E–19		2.49E–19	3.34E+10	8.97E–18	9.95E–24	

T(K)	k_1 Ref. [19]	k_1 Ref. [9]	k_1	k_2	k_3	k_4	HNCO→ CO+ NH in Ar bath gas Ref. [20]
1700	4.22E–19		6.00E–19	5.43E+10	1.91E–17	5.04E–23	
1800	8.43E–19		1.32E–18	8.40E+10	3.75E–17	2.16E–22	
1900	1.57E–18		2.68E–18	1.25E+11	6.86E–17	8.01E–22	
2000	2.74E–18		5.05E–18	1.79E+11	1.19E–16	2.65E–21	
2100	4.54E–18		9.12E–18	2.40E+11	2.00E–16	7.91E–21	
2200	7.18E–18		1.61E–17	3.23E+11	3.23E–16	2.10E–20	5.93E–17
2300	1.09E–17		2.62E–17	4.30E+11	5.05E–16	5.22E–20	1.30E–16
2400	1.60E–17		4.20E–17	5.30E+11	7.34E–16	1.24E–19	2.68E–16
2500	2.28E–17		6.54E–17	6.87E+11	1.08E–15	2.62E–19	5.20E–16

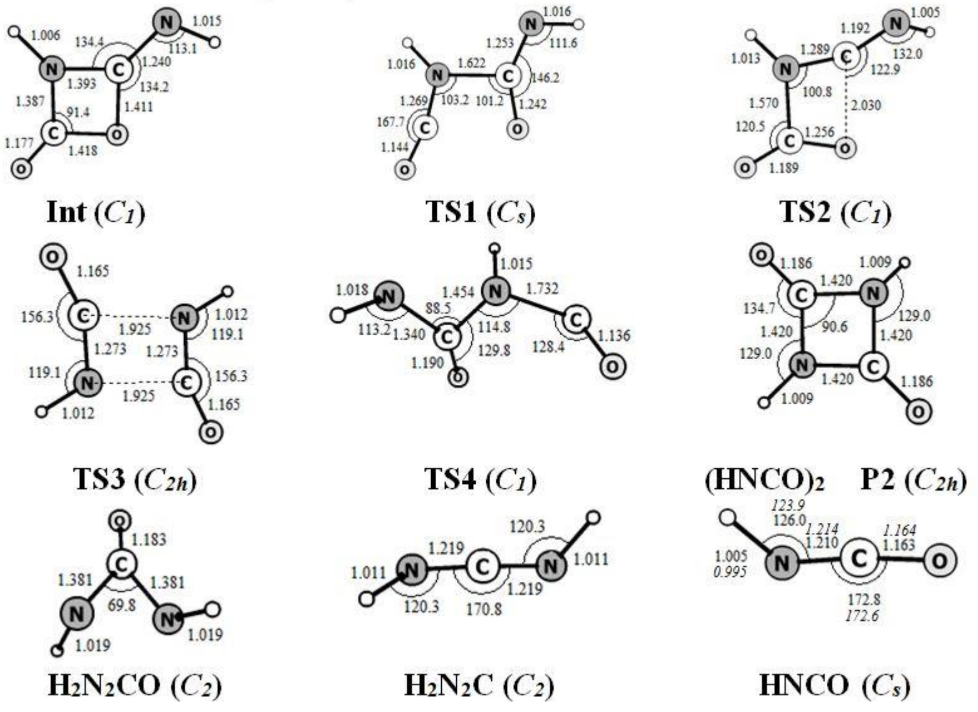


Fig. 2. The optimised geometries and symmetry point groups of TS, intermediate, products at the B3LYP/6-311++G(3df,2p) level. Bond distances are given in (Å), bond angles in degrees. The experimental values are given in italics from [1, 3]

We have examined the kinetics of the dimerisation of HNCO. The data in Table 2 show that reaction (1) consists of two steps. In step II, the rate constant k_2 of the formation of products P1 is much higher than the rate constant k_1 of the formation of Int. This is the proof that step II is fast and in equilibrium and step I determines the value of the rate constant of reaction (1). The values k_1 of reaction (1) are in a good agreement with the experimental results reported in the literature [9, 19]. Therefore, the methods we used are appropriate. At the same condition, rate constant k_3 of reaction (2) is much higher than the rate constant k_1 of reaction (1). For example, at 2,500 K (in cm^3/molecule/s), $k_3 = 1.08\times10^{-15} >> k_1 = 6.54\times10^{-17}$.

The new pathway (3) for the formation of the product P3, namely H_2N_2CO and CO has not been reported so far. The rate constant k_4 is very small compared to k_1 or k_3. At 2,500 K, $k_4 = 2.62\times10^{-19}$ cm^3/molecule/s, about 2,000 times as small as the rate constant of formation CO from the bimolecular mechanism of HNCO with Ar suggested by Wu et al. [20]. The plot in Fig. 3 shows that $k_3 > k_1 >> k_4$ at the same temperature. The variation of the yields of products as a function of temperature in Fig. 4 also shows that when temperature increases, the yield of P2 decreases but the yield of P1 or P3 increases negligibly. At the highest temperature in this work, the yields were as follows: 5.71 % for P1, only 0.02 % for P3, the remainder 94.27 % for P2.

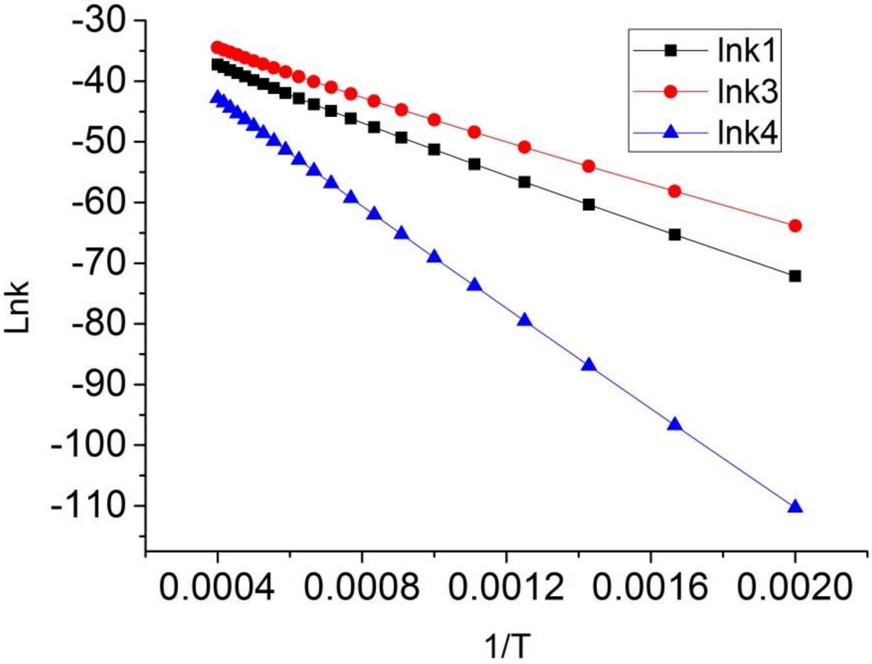


Fig. 3. Temperature dependence of the rate constant in the dimerisation of HNCO

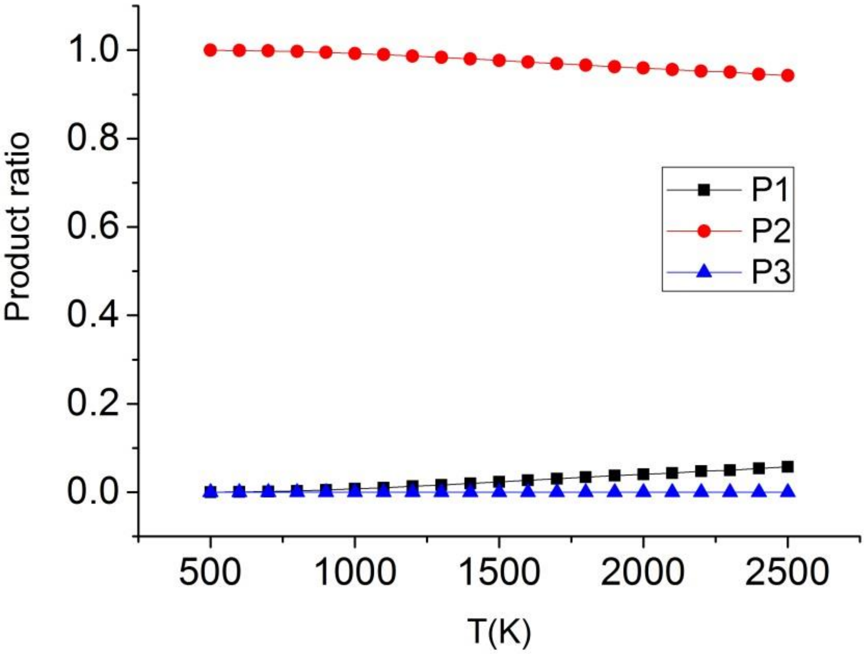


Fig. 4. Predicted yields of the products in the dimerisation of HNCO as a function of temperature

4 Conclusion

By using the density functional theory, CCSD(T) and the transition state theory methods, we found that there were three differential reactions of dimerisation of isocyanic acid. The channel for the formation of four-membered ring O=CNHNHC=O with C_{2h} symmetry point group is the dominant reaction pathway, with a yield up to 94 %. Carbon monoxide was only produced with a negligible yield of 0.02 % following the bimolecular mechanism without the Ar bath gas.

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