Study on mechanism of isomerization between ammonium thiocyanate and thiourea

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A B S T R A C T

Application of ammonium thiocyanate that can be separated from wastewater in coking plant is limited. It may isomerize to thiourea which has widely applied in industry. However, the isomerization yield is low. Moreover, the isomerization temperature is more than 145 °C. In this paper, the isomerization was investigated. The mechanism of the isomerization was supposed based on quantum chemistry calculations. Ammonia was employed as a catalyst to lower isomerization temperature and improved the yield of thiourea in the isomerization reaction. Results of quantum chemical calculation and experiments support the supposed mechanism. The mechanism can be applied in production of thiourea from isomerization of ammonium thiocyanate. The paper suggests a useful way of resourcizing ammonium thiocyanate in wastewater.

1. Introduction

Thiourea (TU), an industrially and physiologically significant compound [1], has popularly been used as plastic additives, a rubber accelerator and an extractant for precious metals, etc [2]. TU has also been applied in the production of pharmaceuticals, such as sulfothiazoles and thiobarbiturates [3], and electronic devices, such as luminescent sensors, due to its nonlinear optical properties [4]. Annual requirement of TU is more than 100,000 tons in the world [5]. Currently, TU is mainly produced by chemical synthesis [6]. A large of energy is consumed in the production process. Moreover, solid waste is unavoidably produced. Therefore, it is interesting that a convenient and environment-friendly method would be developed to produce thiourea from isomerization of NH$_4$SCN [7—10]. Pang et al. reported that NH$_4$SCN would isomerize to TU at the temperature range from 100 °C to 170 °C [11]. However, TU is difficultly separated from the isomerization mixture of NH$_4$SCN and TU due to low percentage of TU (6.70%—34.89%). In order to improve the isomerization yield of TU from NH$_4$SCN and develop a new production method of TU from resource of coke-oven wastewater, NH$_4$SCN, mechanism of isomerization has to be investigated.

In this article, experiments of isomerization of NH$_4$SCN were performed. Geometries of NH$_4$SCN, TU, supposed intermediate and transition state structures were optimized with the density functional theory (DFT) calculations using Gaussian03 [12] software at the B3LYP/6-31G(d) level [13—15]. The mechanism of isomerization is suggested based on quantum chemistry calculations and experimental results. This paper suggests a useful isomerization way for synthesizing TU from the resourcized NH$_4$SCN.

2. Experimental

2.1. Materials

NH$_4$SCN was purchased from Suzhou Jiuwang Environmental Technology Co. Ltd. All other chemicals were purchased from Sigma-Aldrich Co. Ltd and used without further purification. The Fourier transform infrared (FT-IR) spectrum of TU in KBr pellet was recorded using a Bruker Vector 22 Fourier transform infrared (FT-IR) spectrometer.

2.2. Methods

2.2.1. Isomerization of NH$_4$SCN

Five NH$_4$SCN (20 g, 0.26 mol) samples were respectively added into five autoclaves and heated at 140 °C, 150 °C, 160 °C, 170 °C and 180 °C for 2 h. The yield of the isomerization was determined by Liquid Chromatography-Mass Spectrometer (LC-MS).

2.2.2. Isomerization of NH₄SCN in ammonia water

NH₄SCN (20 g, 0.26 mol) and ammonia water (5 mL, 25.0 wt%) were added into an autoclave and heated at 80 °C for 2 h. The yield of the isomerization determined by LC-MS is 45.3%. White crystals were obtained by recrystallization from ethanol.

2.2.3. Calculation details

The mechanism of the isomerization has been examined as implemented in Gaussian 03 package [12] and the electronic structure calculations using DFT method at B3LYP with 6-31G (d) basis set [13–15]. The theoretical FT-IR spectrum of TU was calculated using DFT method at B3LYP with 6−311++G (2d, 2p) basis set. The calculated vibrational wavenumbers of TU would be larger than the experimental vibrational wavenumbers, therefore the calculated wavenumbers were scaled by the factors of 0.981 (below 1800 cm⁻¹) and 0.961 (above 1800 cm⁻¹) [16–19]. The nature of the stationary points was determined by using frequency calculations for the minimum energy structures and for the transition states. The quadratic synchronous transit (QST) protocol was used to locate the transition state (TS) structures. The identification of the TS structures was obtained through the normal-mode analysis by having a single imaginary frequency. Intrinsic reaction coordinate (IRC) [20] calculations were carried to verify that the transition state connected reactants and products [21].

The thermodynamic parameters, enthalpy, entropy and Gibbs free energy, were acquired by frequency calculations at 140 °C, 145 °C, 150 °C, 155 °C, 160 °C, 165 °C, 170 °C, 175 °C and 180 °C under 1 atm. The changes of free energy (ΔG), enthalpy (ΔH), entropy (ΔS) and were calculated by the following equations,

$$\Delta G = G_{TU} - G_{R2} \tag{1}$$

$$\Delta H = H_{TU} - H_{R2} \tag{2}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{3}$$

$$\ln K = -\Delta G/RT + C \tag{4}$$

where T is thermodynamic temperature (K), R is the universal gas constant (R = 8.314 J mol⁻¹ K⁻¹).

3. Results and discussion

3.1. The yield of TU in process of conversion from NH₄SCN to TU

The yield values of TU in processes of conversion from NH₄SCN to TU were collected in Table 1. These experimental results are according with literature [11,22].

The yield of TU in processes of conversion from NH₄SCN to TU decreases from 34.89% to 25.30% with isomerization temperature increasing from 140 °C to 180 °C. It is attributed to the fact that the isomerization processes are exothermic reaction.

3.2. FT-IR spectrum

The theoretical spectrum of the crystal TU has been calculated using crystal data of TU as input files [23]. The experimental and theoretical FT-IR spectra of TU are shown in Fig. 1.

Table 1
Isomerization temperature and the yield of TU.

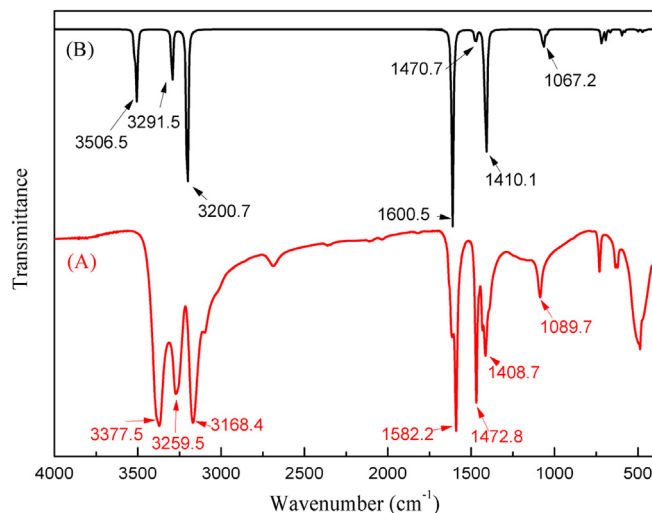| Temperture/°C	140	150	160	170	180
Yield/%	34.89	30.30	29.00	26.70	25.30

Fig. 1. Experimental (A) and theoretical (B) FT-IR spectra of TU.

In Fig. 1, experimental FT-IR spectrum exhibits absorption peaks located at 3377.5, 3259.5, 3168.4, 1582.2, 1472.8, 1408.7 and 1089.7 cm⁻¹, respectively. The strong peaks located at 3377.5 and 3259.5 cm⁻¹ are N−H asymmetric stretching vibration modes of NH₂ group in TU. A very strong peak located at 3168.4 cm⁻¹ is the N−H symmetric stretching vibration mode of NH₂ group in TU. The peak located at 1582.2 cm⁻¹ is the bending vibration mode of N−H due to NH₂ group in TU [24]. The peaks located at 1472.8 and 1408.7 cm⁻¹ are asymmetric and symmetric stretching vibration modes of C−N, respectively [25]. A peak located at 1089.7 cm⁻¹ is stretching vibration mode of C=S. These absorption peaks are in accordance with those in literature [26].

Theoretical FT-IR spectrum exhibits absorption peaks located at 3506.5, 3291.5, 3200.7, 1600.5, 1470.7, 1410.1 and 1067.2 cm⁻¹, respectively. The peaks located at 3506.5 and 3291.5 cm⁻¹ are N−H asymmetric stretching vibration modes of NH₂ group in TU. A hydrogen bond is formed between a hydrogen atom of an ammonia group and a sulfur atom in an adjacent TU molecule [27]. A very strong peak located at 3200.7 cm⁻¹ is N−H symmetric stretching vibration mode. The peak located at 1600.5 cm⁻¹ is the bending vibration mode of N−H. The peaks located at 1470.7 and 1410.1 cm⁻¹ are asymmetric and symmetric stretching vibration modes of C−N, respectively. The peak located at 1067.2 cm⁻¹ is stretching vibration mode of C=S. The theoretical absorption peaks coincide with the experimental absorption peaks. Therefore, the product would be the crystal TU. The experimental and theoretical FT-IR spectra show that H atoms of NH₂ groups in a TU molecule can interact with sulfur atom in an adjacent TU molecule to form S···H−N hydrogen bonding [28].

3.3. Mechanism of the isomerization reaction

The mechanism of the isomerization reaction has been assumed in Scheme 1.

To study the mechanism of isomerization, resonance structures of NH₄SCN were supposed. Structure of NH₄SCN is popularly considered as R1 [29]. Because SCN⁻ anion may rearrange to give NCS⁻ anion [30], structures of NH₄SCN also are R2 and R3. Therefore, NH₄SCN has three possible resonance structures R1, R2 and R3.

The natural bond orbital (NBO) charge [31] distributions and geometrical parameters of these structures are collected in Table 2 and Table 3, respectively.

Firstly, ammonium thiocyanate (R1) isomerizes to give