

Thermal Stability and Thermodynamics in the Process of Synthesising 1, 3-dimethylurea

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The present work aims to study the thermal stability and thermodynamics in the process of synthesizing 1, 3-dimethylurea. The HPLC spectrograms were used to study the impacts of reaction time and temperature on the thermal behaviour of the ammonolysis reaction system. Rate equation of the ammonolysis reaction can be summed up as $c(t) = 1016.24 \cdot e^{-(t/47.9403)} + 16.1935$. Thermal stability curve also can be determined. Experimental results revealed that the process of synthesizing 1, 3-dimethylurea was of pseudo-first-order reaction kinetics and k value was 0.0163 min^{-1} . Thermodynamics results indicated that enthalpy was -1.92 kJ/mol , Gibbs free energy was -8.51 J/mol , and entropy was $15.96 \text{ J/mol} \cdot \text{K}$. The reaction was an exothermic, spontaneous and entropy increasing process. Based on thermal stability and thermodynamics study, synthesis of 1, 3-dimethylurea was unfavourable at higher temperature as well as long reaction time.

1. Introduction

1, 3-dimethylurea is widely used in the printing, food and preservative industries. In industrial production, urea is utilized for the production of 1, 3-dimethylurea through ammonolysis reaction with methylamine. (Novaes et al., 2017). However, in this reaction urea and urea compounds have poor thermal stability, which can result in side reactions. Impurities produced by side reactions are the source of pollution once evacuated into the environment (Koyuncu et al., 2001), the treatment of impurities also consumes high cost and energy. For above reasons, it is extremely important to study thermal behavior in the process of synthesizing 1, 3-dimethylurea to reduce the generation of impurities. In this work, thermal stability and thermodynamics were studied to evaluate the thermal behaviour.

Since 1,3-dimethylurea have widespread applications in medicine and polymer industry, many papers focus on the pharmaceutical synthesis, analysis, and applications of its downstream products. In 1952, The rate constants and the activation energies of the thermal dissociation of sym-dimethylurea, asym-dimethylurea and asym-phenylethylurea in Butyric Acid were studied (Hoshino et al., 1952). While in 1984, the initial decomposition temperatures of various ureas by using thermal gravimetry and infrared analyses (Skuches et al., 1984). However, to the best our knowledge, there is no report on thermal behaviour of synthesizing 1,3-dimethylurea. At present, the big flaw of using urea and methylamine to produce 1,3-dimethylurea is the thermal instability of products. In this research, as shown in Figure 3, thermal stability curve not only showed the reaction boundary of temperature but also revealed the thermal behaviour of synthesizing 1,3-dimethylurea. Only a few data are available on the kinetics and thermodynamics data. In 1978, Shigeru systematically studied the kinetics and thermodynamics of synthesizing N, N'-dimethylurea from monomethyl amine and carbon. In this work, as shown in section 3.2, the kinetic model can be described a pseudo-first-model which response to the previous work. The parameters obtained can help to predict the kinetics and thermodynamics of other ways to synthesize 1, 3-dimethylurea. In this study, kinetics and thermodynamics of synthesizing 1,3-dimethylurea were explored to help to understand the trend, degree and driving force of the reaction, and they also play an important role to explain the characteristics, laws and possible mechanisms (Boutemak et al., 2019). The kinetic study contains reaction order and rate constant (Aieta et al., 1986). HPLC spectrograms were used to study the impacts of reaction time and temperature on the thermal behaviour of

the ammonolysis reaction system. The main objective of this study is to develop a thermal stability curve from the ammonolysis reaction of urea with methylamine, to provide guidance for energy saving and emission reduction.

2. Materials and methods

2.1 Materials

Saturated methylamine solution was supplied by Xinhua Pharmaceutical (Shou Guang) Co., Ltd. Urea (A.R.) was purchased from Shandong Lianmeng Chemical Group Co.,Ltd. Calcium oxide(A.R.) was purchased from Damao Chemical factory. Acetonitrile (G.R.) and triethylamine (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphoric acid (A.R.) was purchased from Shanghai Ail Chemical Reagent Co.,Ltd

2.2 Characterization

The reactant concentrations, product concentrations, reaction temperature and reaction time, were determined. The concentrations in the mixture were measured by a constant gradient reversed-phase high-performance liquid chromatography (LC-100; Exformma Technologies, China): The wavelength of the detector was set at 205 nm. A ZORBAX Eclipse XDB-C18 column (5 μ m, 4.6 \times 250 mm) was used for compound separation. The mobile phase consisted of 2 % triethylamine in water, add phosphoric acid to pH=3 (A) and acetonitrile (B). The proportion (v/v) of solvent A: B = 96: 4. The flow rate was 1.0 mL/min and the injection volume was 20 μ L. All standard samples were prepared for calibration curve construction.

2.3 Experimental

Experiments were carried out in 500 mL four-necks-round-bottom-flask containing 50 g of melting urea at 130 $^{\circ}$ C. An appropriate amount of saturated methylamine solution was added to a gas generator to gain gaseous methylamine. The damp gas was introduced into Calcium oxide desiccator to purification. Purified gas was injected into the melting urea with agitation and the reactor was heated to 140 $^{\circ}$ C for 3 h. In the first hour, samples were tested every 15 min; in the second hour, samples were tested every 20 min; in the third hour, samples were tested every 30 min. After each collecting, samples were analysed by high-performance liquid chromatography methods to measure the concentrations. Based on experimental data, Concentration (c) - Time (t) curve was obtained via regression.

3. Results and Discussion

3.1 Thermal Stability

Effect of reaction time

Table 1 tabulates the concentration of urea for experimental ammonolysis reaction, 140 $^{\circ}$ C, 180 min of reaction time.

Table 1: The concentration of urea for ammonolysis reaction, 140 $^{\circ}$ C, 180 min of reaction time.

Time (min)	Concentration (mg/L)
0	999.9
15	867.9
30	477.4
45	386.5
60	307.5
80	243.5
100	153.2
120	106.5
150	36.4
180	43.5

The concentration-time curve can be fitted as shown in Figure 1.

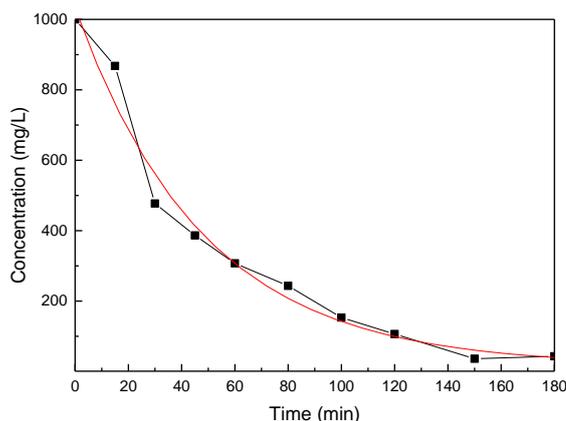


Figure 1: Reactant concentration curve and Polynomial fit

The curve of synthesizing 1, 3-dimethylurea behaved a negative correlation with time. Extending experiment time would result in 100 % conversion but the speed of reaction rate decreased due to the cost of reactant. For this reason, it's efficient and economically viable to study concentration distribution. Via fitted curves, Rate equation of the ammonolysis can be summed up as $c(t) = 1016.24 \cdot e^{-t/47.9403} + 16.1935$. The R^2 value of Figure 1 is 0.97489. According to the fitting equation, the calculated data as Table 2 indicates.

Table 2: The concentration of reactant urea

Time (min)	value	Concentration (mg/L)
t1	10	900
t2	20	700
t3	30	500
t4	60	300
t5	120	100

Effect of reaction temperature

Rather than accelerating the reaction process, higher reaction temperature will bring about the side reactions, especially spontaneous polymerization and self-decomposition in the mixture. Melamine and other impurities can seriously influence the next reaction. These impurities exhibit different peaks and response times in HPLC spectra. Presence of impurities peaks in the result reveals the side reaction happened or not in the given concentration, which directly determines the stability.

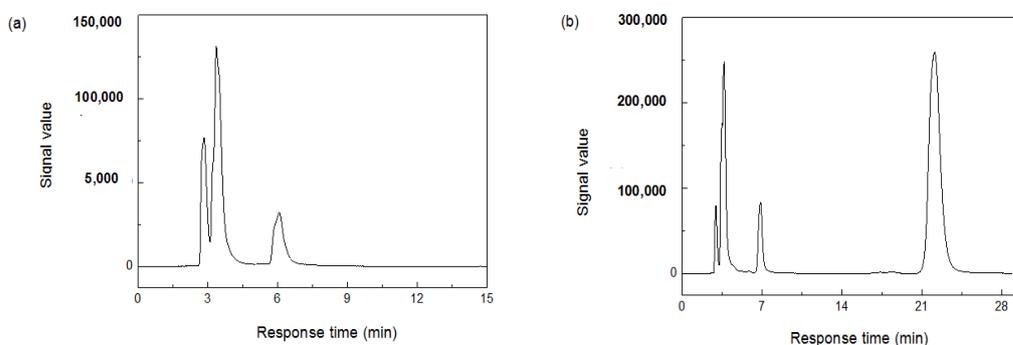


Figure 2: HPLC spectra of (a) reaction taking place at 140 °C, 30 min of reaction time and (b) samples were heated up to 170 °C, 30 min of reaction time

Table 3: Concentration of substance in Figure 2 (a) and Figure 2 (b)

Substance	a (mg/L)	B (mg/L)
Urea	705.8	774.8
Methylamine	78.6	47.5
Dimethylurea	215.5	146.2
Impurities	0	31.4

High-performance liquid chromatography methods were performed to analyse the standard substance of urea, monomethylurea, and dimethyl urea. The response peak time of each standard substance was as follows: urea was 6.4 min; methylamine was 3.15 min and 1, 3-dimethylurea was 4.11 min. The samples in the reaction process were measured by HPLC methods, and the peak response time of each substance was consistent with the standard sample. The spectra of samples which prepared at 140 °C, 30min of reaction time, was shown in Figure 2 (a). It can be observed that the response peak time of impurities was 22 min, which was caused by side reaction as temperature rising from 140 to 170 °C. As shown in Table 2, the heating process accelerates self-decomposition side reaction (Sardeing et al., 2004), which leads to the decrease of product concentrations and the increase of reactant concentrations. Over-temperature leads to the self-decomposition side reaction. Samples were heated up to the gradient temperature (140, 150, 160, 170, 180 °C) with real-time detection.

Table 4: Thermal stability temperature, Concentration of reactant urea, 140 – 170 °C, 125 min of reaction time

Time(min)	Concentration (mg/L)	Temperature(°C)
0	999.9	140
10	887.2	150
20	779.3	160
30	470.5	170
60	312.6	170
120	169.8	180

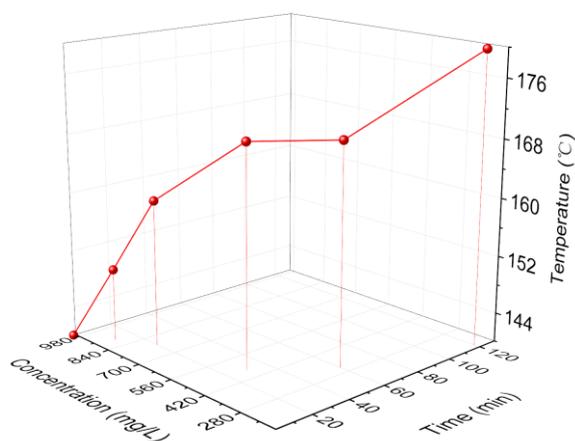


Figure 3: 3D diagram of thermal stability curve, concentration of reactant urea, 140 - 170°C, 125 min of reaction time

The data indicates that thermal stability in the process of synthesizing 1,3-dimethylurea shows a negative correlation with the concentration of reactant urea, while a positive correlation with the reaction temperature. When temperature or concentration of reactant urea exceeded the limitation of thermal stability curve, side reaction can be initiated. For the above results, appropriate reaction time and suitable temperature condition can reduce side reactions.

3.2 Thermodynamics

Ammonolysis reaction of urea with methylamine to produce 1,3-dimethylurea and ammonia can be described by the reaction in Eq(1):



Eq(1) can be simplified as follows:



The rate of reaction for Eq(2) can be described mathematically as Eq(3):

$$-r_A = -d[A]/dt = k_{pos}[A]^a [B]^b - k_{rev}[C]^c [D]^d \quad (3)$$

$-r_A$ is the reaction rate; k_{pos} and k_{rev} are reaction positive constant and reverse constant; $[A]$ and $[B]$ are the concentrations of reactants; $[C]$ and $[D]$ are the concentrations of products; Eq(3) can be simplified based on assumptions: (i) concentration of methylamine is constant due to the excess methylamine in the whole process (ii) the reverse and side reaction can be ignored due to the excessive methylamine (Saimon et al., 2020). For the above reasons, $[B]^b$ can be assumed fixed and $k_{pos}[B]^b$ can be symbolized k . The simplification as follow:

$$-r_A = -d[A]/dt = k[A]^a \quad (4)$$

In order to investigate thermodynamics in the process of synthesizing 1, 3-dimethylurea, the pseudo-first-order model and the pseudo-second-order model were used to fit data (Figure 5). The R^2 value of Figure 4(a) is 0.87573; The R^2 value of Figure 4(b) is 0.99468. There was an obvious linear correlation between the $\ln[C_A/C_{A0}]$ and the reaction time, which demonstrate that it's better to use the pseudo-first-order model to describe the synthesizing process. $[C_A]$ is the concentration of while $[C_{A0}]$ is the initial concentration of reactant, the k value is 0.0163 min^{-1} , $a = 1$.

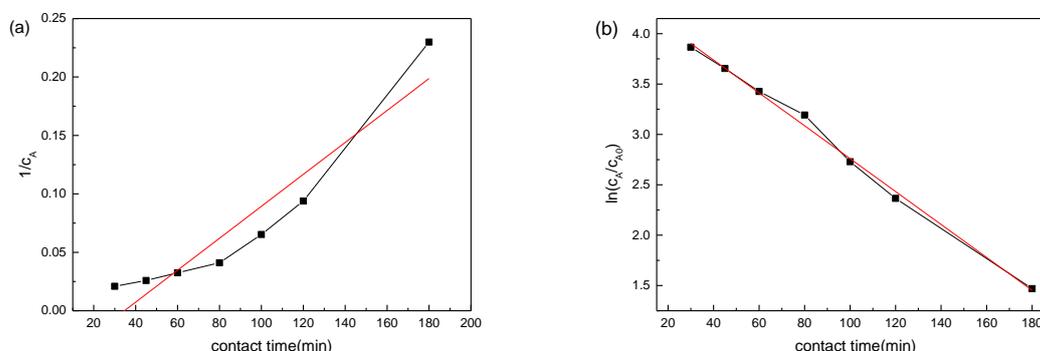


Figure 4: Pseudo-Second-order model (a) and Pseudo-First-order model (b) to Fit Data at 150 °C, 200 min of reaction time.

Parameters: Enthalpy of reaction ΔH , Entropy of reaction ΔS , Free energy of reaction ΔG , Enthalpy of products $\Delta_{pro}H$, Enthalpy of reactants $\Delta_{rea}H$, Entropy of products $\Delta_{pro}S$, Entropy of reactants $\Delta_{rea}S$, Stoichiometric coefficient of products ν_i and reactants ν_j

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$\Delta H = \sum \nu_i \Delta_{pro}H - \sum \nu_j \Delta_{rea}H \quad (6)$$

$$\Delta S = \sum v_i \Delta_{pro} S - \sum v_j \Delta_{red} S \quad (7)$$

Table 5: Enthalpy and Entropy in the process of synthesizing 1,3-dimethylurea

Parameters	ΔH (kJ/mol)	ΔS (J/mol*K)
urea	14.61	35.70
methylamine	6.13	34.13
ammonia	5.66	42.01
dimethylurea	13.62	35.90

According to Eq(6), Eq(7) and Eq(8), when the reaction temperature was 140 °C, Free energy of reaction can be obtained as -8.5148 J/mol. Enthalpy was -1.92 kJ/mol, Entropy was 15.96 J/mol*K. The obtained positive value of ΔS and negative values of ΔH and ΔG revealed that reaction was an exothermic and spontaneous process. Promptly separating can promote the reaction towards the increase of entropy.

4. Conclusions

This study reveals that rate equation of the ammonolysis reaction can be summed up. Thermal stability in the process of synthesizing 1, 3-dimethylurea behaved a negative correlation with the reaction time. Over-temperature would promote the self-decomposition side reaction. Investigations on thermal stability curve of synthesizing 1, 3-dimethylurea were conducted. When temperature and concentration of reactant exceeded the limitation of thermal stability curve, side reactions can be initiated. The curve can be used for not only obtaining stability information but also predicting suitable storage and reaction conditions. Kinetics studies showed that the reaction followed a pseudo-first-order kinetic model, and k value was 0.0163 min⁻¹. Thermodynamics results indicate that the enthalpy was -1.92 kJ/mol, Gibbs free energy was -8.5148 J/mol, and entropy was 15.96 J/mol*K. The reaction was an exothermic, spontaneous and entropy increasing process. Thermal stability and thermodynamics study showed that promptly reaction time and suitable temperature condition can reduce side reactions to save energy and reduce the formation of pollutants.

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