



Short communication

## Non-isothermal thermal decomposition reaction kinetics of dimethylhexane-1,6-dicarbamate (HDC)

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### ABSTRACT

The thermal decomposition behavior and reaction kinetics of dimethylhexane-1,6-dicarbamate (HDC) were investigated by TG–DTG, DSC and IR techniques. It is shown that the decomposition process can be divided into 3 main stages and the first stage is the thermal decomposition reaction for HDC to dimethylhexane-1,6-diisocyanate (HDI). The main gaseous products of the decomposition are CO<sub>2</sub> and CH<sub>3</sub>OH. The kinetic parameters of the reaction for HDC to HDI are  $E_a = 119.51 \text{ kJ mol}^{-1}$ ,  $\lg(A/s^{-1}) = 14.82$ , respectively. The kinetic equation is  $d(\alpha)/d(t) = 10^{15.12}(1 - \alpha)^{3/2} e^{-1.4375 \times 10^4/T}$ .

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## 1. Introduction

Isocyanates have been widely used in the manufacture of polyurethanes and herbicides [1,2]. They are mainly synthesized by the reaction of amines with phosgene or its derivatives. Many problems may occur during the process, such as the use of extremely toxic reagent phosgene and the seriously corrosive byproduct HCl. Many phosgene-free synthesis routes have been reported, while the thermal decomposition of carbamate is the most promising method. This method contains two steps: the synthesis of carbamate and thermal decomposition of carbamate [3]. Between them decomposition of carbamate to isocyanate is the key process [4–6].

As the decomposition of carbamate is strongly endothermic, great amounts of heat is consumed during the reaction. The reaction should be preceded at high temperature. However, isocyanate is highly active and unstable in high temperature. So, appropriate reactor which could minimize the side-reaction is necessary. Few researches on the study of the decomposition reaction reactor have been reported. Lewandowski and Milchert reported the decomposition of methylene-4,4-diethylphenyl-carbamate (MDC) could be conducted with a conversion of 98% in a reactor filled with aluminum rods [7]. Franz Merger reported the cleavage of HDC in a two-phase mixture by a reactor with baffles [8]. These researches were mainly about the optimization of the reaction

condition. However, the thermal decomposition reaction kinetics of carbamate, which is the key to develop high-efficiency reactor, have not been reported.

It is very difficult to get the isothermal kinetics accurately of thermal decomposition reaction of carbamate for the instability of isocyanate. So in this paper, TG–DTG, DSC and FT-IR techniques, which are effective methods to get the non-isothermal kinetics of the thermal decomposition process [9–11], is used to confirm thermal decomposition mechanism and non-isothermal kinetics parameters of dimethylhexane-1,6-dicarbamate (HDC).

## 2. Experimental

### 2.1. Material

HDC was synthesized by dimethylhexane-1,6-diisocyanate (HDI) and methanol in our laboratory. The reaction condition was:  $n(\text{HDI}):n(\text{methanol}) = 1:10$ ,  $T = 50^\circ\text{C}$ ,  $t = 6 \text{ h}$ . The compound was purified by crystallization in toluene, with a final purity of >99%. The structure of HDC was characterized by GC–MS, elemental analysis, IR spectrometry and H-NMS. The sample was kept in vacuum desiccators before use.

### 2.2. Equipment and conditions

TG–DTG and DSC curves under the condition of nitrogen flow were studied on a TGA/DSC-1 thermal analyzer (Mettler Toledo, Switzerland). The conditions of TG–DTG and DSC were as follows:

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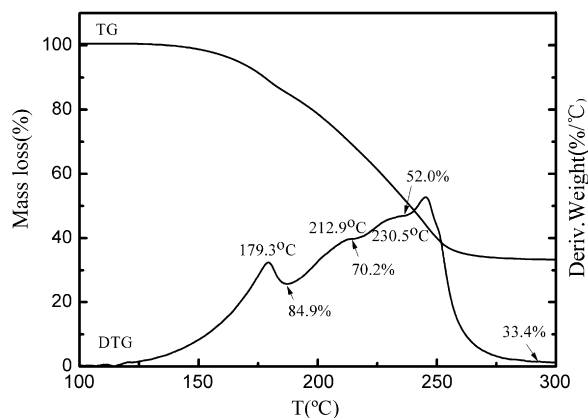


Fig. 1. TG/DTG curve for HDC at a heating rate of 5 °C min<sup>-1</sup>.

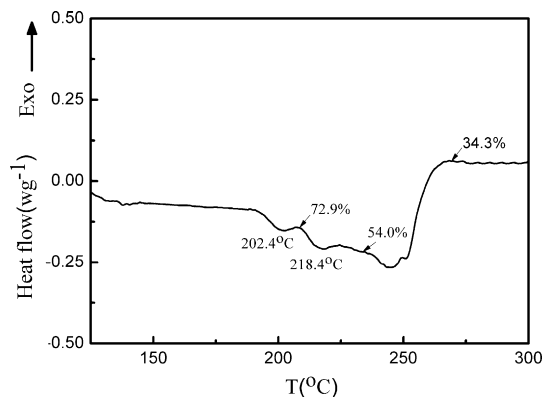


Fig. 2. DSC curve for HDC at a heating rate of 5 °C min<sup>-1</sup>.

sample weight, about 8 mg; heating rates, 4, 5, 7 and 8 °C min<sup>-1</sup>; flow rate of N<sub>2</sub>, 60 ml min<sup>-1</sup>; reference sample, α-Al<sub>2</sub>O<sub>3</sub>.

FT-IR measurements were conducted with Model 60SXR FT-IR. The temperature range is 40–400 °C. The conditions of FT-IR were as follows:

sample weight, 4.418 mg; heating rate, 10 °C min<sup>-1</sup>; flow rate of N<sub>2</sub> 50 ml min<sup>-1</sup>. IR spectra in the 800–4000 cm<sup>-1</sup> were detected at 2 scans s<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. The thermal decomposition mechanism of HDC

##### 3.1.1. TG/DTG

Typical TG/DTG curve and TG–DTG data for HDC are shown in Fig. 1 and Table 1, respectively. It is indicated that the decomposition process can be divided into 3 main stages in the DTG curve. The first mass loss stage ranges from 154.8 °C to 215.5 °C with a mass loss of 29.8%, which is in agreement with the mass loss for the thermal decomposition of HDC to HDI (27.6%). The second stage ranges from 215.5 °C to 237.2 °C with a mass loss of 48.0%, which is in agreement with the mass loss for the polymerization of HDI to carbodiimide (19.4%). And the third stage ranges from 237.2 °C to 292.1 °C, with a mass loss of 66.6%.

##### 3.1.2. DSC

The DSC curve of HDC is shown in Fig. 2. There are 3 endothermic peaks in the DSC curve of HDC thermal decomposition. The first peak ranges from 182.1 °C to 208.9 °C with a peak at 202.4 °C. The mass loss of this stage is 27.1%. The second peak ranges from 208.9 °C to 234.3 °C with a mass loss of 46.0%. The third peak ranges from 234.3 °C to 268.9 °C with mass loss of 65.7%.

##### 3.1.3. FT-IR

FT-IR was used to measure the phase products of the thermal decomposition of HDC at a heating rate of 10 °C min<sup>-1</sup>. The infrared

spectra of gas products of HDC decomposition at different temperatures are shown in Fig. 3.

It is shown that the peaks of methanol are merged in 2947 cm<sup>-1</sup>, 1061 cm<sup>-1</sup> and 1006 cm<sup>-1</sup> at 200 °C. The peak of CO<sub>2</sub> IR absorption in 2270 cm<sup>-1</sup> comes out at 230 °C, which indicate the polymerization process of HDI to carbodiimide. These data help to confirm that the first stage of thermal decomposition process is for HDC to HDI, which release methanol. The second stage should be the polymerization process of HDI to carbodiimide with releasing CO<sub>2</sub>. With the temperature rose, no other obvious peak comes out in the IR spectra. The possible reason is that the gas phase produced in this stage is very little, which is submerged in the background of the peak.

#### 3.1.4. The thermal decomposition mechanism of HDC

According to the results above, the thermal decomposition mechanism of HDC is supposed to 3 stages as Scheme 1.

The first stage is the process for the thermal decomposition of HDC to HDI with a mass loss of 27.6%, which would be studied deeply as follows. The second and third stages are about the further reaction of HDI, which is complicated and would not be discussed in this paper any more.

#### 3.2. The thermal decomposition kinetics of HDC to HDI

In order to obtain the kinetic parameters [apparent activation energy (*E*) and pre-exponential factor (*A*)] of the first endothermic decomposition reaction for HDC, the Kissinger's method and Ozama's method were employed. These methods are as follows:

Table 1

TG–DTG data of HDC ( $\beta = 5 \text{ } ^\circ\text{C min}^{-1}$ ).

The first stage of mass loss	$T_{p1}$ (°C)	$T_{p2}$ (°C)	Mass loss (%)
	179.3	212.9	29.8
The second stage of mass loss	$T_{p3}$		Mass loss (%)
	230.5		18.2
The third stage of mass loss	$T_{p4}$		Mass loss (%)
	245.3		18.6

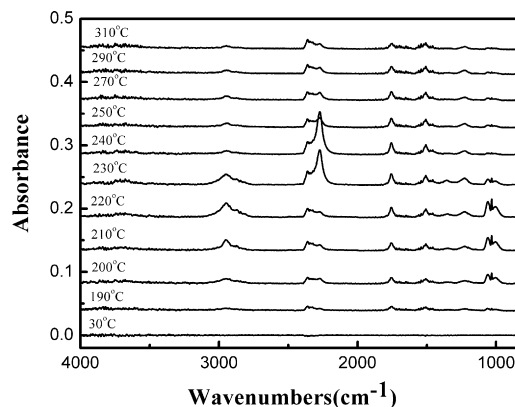
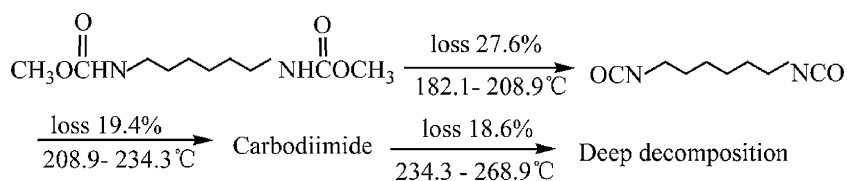


Fig. 3. Infrared spectra of gas products of HDC decomposition at different temperatures.



**Scheme 1.** Proposed thermal decomposition mechanism of HDC.

**Table 2**  
Calculated values of the kinetic parameters for the first stage endothermic decomposition reaction of HDC determined from the DSC curve at different heating rates and a  $N_2$  flow rate of  $60 \text{ ml min}^{-1}$ .

$\beta$ ( $^{\circ}\text{C min}^{-1}$ )	$T_p$ ( $^{\circ}\text{C}$ )	Kissinger method			FWO method	
		$E_k$ ( $\text{kJ mol}^{-1}$ )	$\log A_k$ ( $\text{s}^{-1}$ )	$r_k$	$E_o$ ( $\text{kJ mol}^{-1}$ )	$r_o$
4	198.99	115.66	12.20	0.9951	117.55	0.9986
5	202.38					
7	207.12					
8	209.83					

Kissinger equation [12]:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{A_k R}{E} - \frac{E_k}{RT_p} \quad (1)$$

Flynn–Wall–Ozawa (FWO) equation [13]:

$$\lg \beta = \lg \left( \frac{AE_o}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E_o}{RT} \quad (2)$$

where  $\alpha$  is the conversion degree,  $G(\alpha)$  is the integral mechanism function,  $T$  is the absolute temperature,  $E_k$  is the activation energy calculated by Kissinger method,  $E_o$  is the activation energy calculated by FWO method,  $\beta$  is the heating rate,  $R$  is the gas constant,  $T_p$  is the peak temperature of DSC curve,  $A$  is the pre-exponential factor, subscript  $k$  is data obtained by Kissinger's method and subscript  $o$  is data obtained by FWO method.

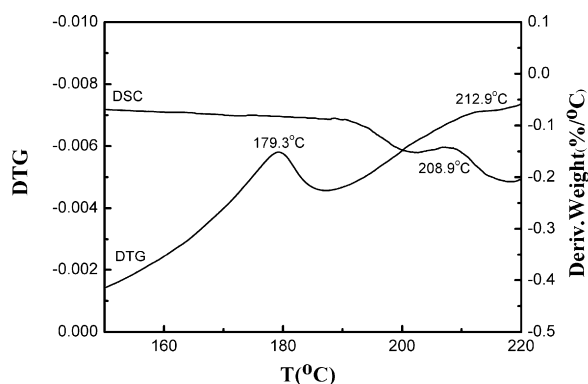
From the original data in Table 2,  $E_k$  obtained by the Kissinger's method is  $115.66 \text{ kJ mol}^{-1}$  and  $A_k$  is  $10^{12.20} \text{ s}^{-1}$  with the lineal

**Table 3**  
Data of HDC determined by TG at different heating rates.

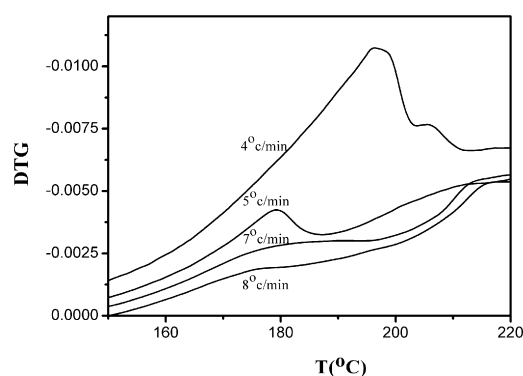
Data point	$\alpha$	$\beta = 4^{\circ}\text{C min}^{-1}$	$\beta = 5^{\circ}\text{C min}^{-1}$	$\beta = 7^{\circ}\text{C min}^{-1}$	$\beta = 8^{\circ}\text{C min}^{-1}$
1	0.025	137.12	139.93	144.97	142.10
2	0.050	145.50	148.66	150.98	150.74
3	0.075	150.84	154.08	155.07	156.29
4	0.100	154.98	158.20	158.42	160.18
5	0.125	158.38	161.27	161.61	163.84
6	0.150	161.18	163.76	164.44	166.65
7	0.175	163.65	166.02	167.03	169.36
8	0.200	165.85	168.03	169.26	171.79
9	0.225	167.77	169.78	171.26	173.95
10	0.250	169.60	171.54	173.26	175.98
11	0.275	171.27	173.05	175.03	177.99
12	0.300	172.74	174.47	176.79	180.15
13	0.325	174.14	175.88	178.44	182.03
14	0.350	175.47	177.15	180.09	184.07
15	0.375	176.75	178.41	181.73	185.95
16	0.400	177.94	179.56	183.37	187.98
17	0.425	179.08	180.75	184.91	189.72
18	0.450	180.22	182.00	186.45	191.49
19	0.475	181.22	183.41	188.10	193.23
20	0.500	182.29	184.85	189.62	194.98
21	0.525	183.24	186.34	191.14	196.47
22	0.550	184.23	187.86	192.80	198.23
23	0.575	185.11	189.37	194.33	199.71
24	0.600	186.02	190.90	195.87	201.19
25	0.625	186.90	192.31	197.39	202.68
26	0.650	187.71	193.72	199.04	204.03
27	0.675	188.51	195.06	200.46	205.36
28	0.700	189.30	196.41	201.86	206.71
29	0.725	190.12	197.66	203.27	207.92
30	0.750	190.85	198.93	204.68	209.00
31	0.775	191.58	200.10	205.86	210.22
32	0.800	192.30	201.26	207.16	211.29
33	0.825	192.98	202.36	208.33	212.36
34	0.850	193.71	203.53	209.52	213.31
35	0.875	194.40	204.62	210.58	214.24
36	0.900	195.07	205.71	211.62	215.18
37	0.925	195.72	206.72	212.45	216.12
38	0.950	196.33	207.80	213.38	216.90
39	0.975	197.00	208.81	214.33	217.86
40	1.000	197.66	209.82	215.26	218.80

**Table 4**  
Kinetic parameters for the thermal decomposition of HDC by different methods.

Equation	$\beta$ ( $^{\circ}\text{C min}^{-1}$ )	$E$ ( $\text{kJ mol}^{-1}$ )	$\lg(A/s^{-1})$	$r$	$Q$
Coats–Redfern	5	129.61	16.11	0.9972	0.0904
	7	113.88	14.14	0.9955	0.1117
	8	107.34	13.25	0.9859	0.1938
Satava–Sestak	5	130.49	16.23	0.9975	0.0394
	7	115.6	14.37	0.9960	0.0489
	8	109.4	13.54	0.9876	0.0846
Mean		119.51	14.82		
Kissinger		115.66	12.20	0.9951	1.4032
Flynn–Wall–Ozawa		117.55		0.9986	0.9366



**Fig. 4.** The DTG and DSC curves of the first stage decomposition.



**Fig. 5.** The DTG curve of the first stage decomposition at different heating rates.

correlation coefficient ( $r_k$ ) being 0.9951. The values of  $E_o$  and  $r_o$  obtained by FWO's method are  $117.55 \text{ kJ mol}^{-1}$  and 0.9986, respectively.

The integral Eqs. (3) and (4) were cited to obtain the values of  $E_\alpha$ ,  $A$  and the most probable kinetic model function  $f(\alpha)$

Coats–Redfern equation [14]:

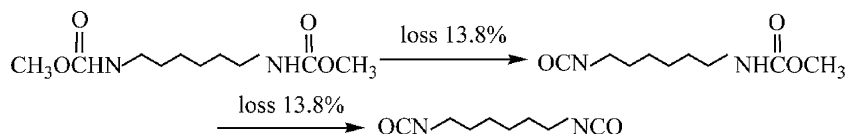
$$\ln \left[ \frac{G(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (3)$$

Satava–Sestak equation [15]:

$$\lg G(\alpha) = \lg \frac{A_s E_s}{R\beta} - 2.315 - 0.4567 \frac{E_s}{RT} \quad (4)$$

According to Eqs. (3) and (4), the original data in Table 3 are calculated, respectively, with the 41 types of kinetic models reported in Ref. [16]. The values of  $E_a$ ,  $A$ , lineal correlation coefficient ( $r$ ), standard mean squared deviation ( $Q$ ) were obtained by the linear least-squares.

The most probable mechanism function was selected by the best values of  $\gamma$ , and  $Q$  based on the following conditions: (1) the selected values of  $E_a$  ( $\text{kJ mol}^{-1}$ ) and  $\lg(A/s^{-1})$  are in the ordinary range of the thermal decomposition kinetic parameters for solid materials [ $E_a$  ( $\text{kJ mol}^{-1}$ ) = 80–50 and  $\lg(A/s^{-1})$  = 7–30]; (2) linear correlation coefficient ( $r$ ) is greater than 0.98; (3) the values of  $E_a$  ( $\text{kJ mol}^{-1}$ ) and  $\lg(A/s^{-1})$  obtained with different integral methods are approximately the same; (4) the mechanism function selected must be in agreement with the tested sample state. The results satisfied with the conditions mentioned above are listed in Table 4.



**Scheme 2.** Proposed reaction mechanism for the first stage thermal decomposition.

According to Tables 2 and 4, when  $f(\alpha) = 2(1-\alpha)^{3/2}$  and  $G(\alpha) = (1-\alpha)^{-1/2}$ , the values (Table 3) obtained from Eqs. (3) and (4) are in good agreement with the calculated values obtained by the Kissinger's and Ozawa's methods.

So it is reasonable that the most probable mechanism function of the first endothermic decomposition process for HDC is  $f(\alpha) = 2(1-\alpha)^{3/2}$  and its integral form is  $G(\alpha) = (1-\alpha)^{-1/2}$ . The apparent activation energy  $E_a$  and the pre-exponential factor  $A$  is  $119.51 \text{ kJ mol}^{-1}$  and  $10^{14.82} \text{ s}^{-1}$ , respectively. Substituting  $f(\alpha)$  with  $2(1-\alpha)^{3/2}$ ,  $E_a/\text{kJ mol}^{-1}$  with 119.51 and  $\lg(A/s^{-1})$  with 14.82 into the non-isothermal kinetics equation, we can infer that the kinetic equation of the first thermal decomposition process for HDC as follows:

$$\frac{d(\alpha)}{d(t)} = 10^{15.12} (1-\alpha)^{3/2} e^{-1.4375 \times 10^4 / T} \quad (5)$$

### 3.3. Proposed reaction mechanism for the first stage thermal decomposition

As shown in Section 3.1.3, the thermal decomposition could be divided into 3 stages, and the first stage is the decomposition for HDC to HDI, with a mass loss of 27.6%.

The TG/DTG and DSC curves of the first process are shown in Fig. 4. Two peaks (179.3  $^{\circ}\text{C}$  and 212.9  $^{\circ}\text{C}$ ) come out in the decomposition process of HDC to HDI from the DTG curve. The mass loss at the first peak is 12.4%, which is in agreement with the mass loss (13.8%) of one end decomposition of HDC. So the reaction mechanism of the first stage can be proposed as Scheme 2.

However, there is only one obvious endothermic peak in the DSC curve at the first stage. The possible reason is that the reaction of the first end decomposition of HDC occurs easily and need little heat. The first and the second end decomposition of HDC cannot be separated completely, which could be proved by the decrease of the first peak at DTG curve at other heating rates (Fig. 5). In the DSC curve, the decomposition of the two ends of HDC is overlapped, so there is only one peak in the first stage of the decomposition. So it is appropriate to combine the two reactions together as the first stage, with a temperature range from 182.1 °C to 208.9 °C.

#### 4. Conclusions

The mechanism of the thermal decomposition reaction of HDC has been investigated. The most probable kinetic model function in integral, apparent activation energy and pre-exponential constant for the first stage thermal decomposition of HDC to HDI in flow N<sub>2</sub> gas are  $(1 - a)^{1/2}$ , 119.51 kJ mol<sup>-1</sup> and 10<sup>14.82</sup> s<sup>-1</sup>, respectively. The kinetic equation of this process can be expressed as

$$\frac{d(\alpha)}{d(t)} = 10^{15.12}(1 - \alpha)^{3/2} e^{-1.4375 \times 10^4/T}$$

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