

Thermal decomposition of methylene-4,4'-di(ethylphenyl-carbamate) to methylene-4,4'-di(phenylisocyanate)

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Received 17 February 2004; received in revised form 6 November 2004; accepted 6 November 2004

Available online 8 January 2005

Abstract

During thermal decomposition of methylene-4,4'-di(ethylphenylcarbamate) (MDU), methylene-4,4'-di(phenylisocyanate) (MDI) appears to be the main product, provided that the ethanol formed in the reaction is carried away. Polycarbodiimides are the main by-products along with small amounts of 4,4'-di(aminophenyl)methane and its derivatives. Under the reaction conditions used in these studies, the latter compound together with its derivatives, reacts both with MDI and MDU. At 220–310 °C and a reaction time of 80–110 min, the selectivity of the MDU transformation to MDI in relation to consumed MDU is 60–87 mol.%. The selectivity of the transformation to polycarbodiimides is 7–20 mol.%, and that to amines and urea derivatives is about 1–2 mol.%. © 2004 Elsevier B.V. All rights reserved.

Keywords: Methylene-4,4'-di(ethylphenylcarbamate); Methylene-4,4'-di(phenylisocyanate); Thermal decomposition; Polyurethane; Polycarbodiimide

1. Introduction

The need for clean and atom efficient technologies, which is embodied in the Principles of Green Chemistry [1], has increased the interest in the development of methods to reduce the possible impacts associated with production of chemicals [2]. This also concerns the technologies in which the hazardous and arduous chemicals are used, especially on a commercial scale.

In this context, methylene-4,4'-di(phenylisocyanate) (MDI) deserves for a particular attention, beside a mixture 2,4- and 2,6-tolylene diisocyanate since they are produced at a rate of approximately 4 million tonnes per year [3]. These chemicals are the important intermediates used in a wide range of processes to manufacture of the polyurethane polymers and other products.

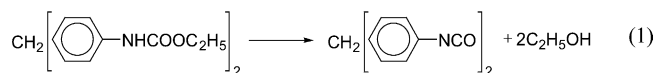
Diisocyanates are produced on a commercial scale from diamine and phosgene [2]. However, the use of phosgene for isocyanate production makes this process arduous for environment taking into consideration a high toxicity as well as

the formation of a stoichiometric amount of HCl as a by-product.

A phosgene-free synthesis of MDI proceeds in three steps [4,5]:

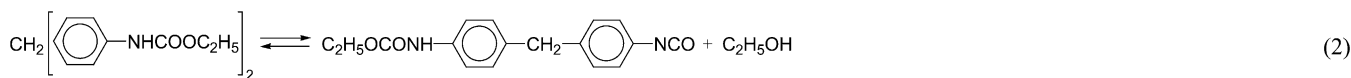
- catalytic oxidative carbonylation of aniline with carbon monoxide, ethanol, and oxygen to prepare ethyl *N*-phenyl carbamate (EPC);
- catalytic condensation of EPC with aqueous formaldehyde to obtain dinuclear methylene-4,4'-di(ethylphenylcarbamate) (MDU);
- thermal decomposition of MDU to obtain MDI and ethanol, which is recycled to the carbonylation step.

In the phosgene-free method of MDI synthesis, the key stage is based on the thermal decomposition of MDU [4,6]. The main product of the thermal decomposition of MDU is MDI:



Methylene-4-phenylisocyanato-4'-ethylphenylcarbamate (ethyl monocarbamate monoisocyanate, MMI) is formed as an intermediate product:

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There is only one report in the literature, describing in detail the thermal decomposition of MDU [7]. The methods of thermal decomposition of MDU to MDI are also discussed in several patents [6,8–11]. However, there is no report dealing with the technological parameters and the reactions occurring during the thermal decomposition of MDU. Such data are very important with regard to an industrial realization of such process and the possible impacts on the environment.

2. Experimental

2.1. Raw materials

MDI, m.p. 40.4 °C, b.p. 174–175 °C/0.133 kPa, was obtained from Chemical Work “Zachem”, Poland.

MDU was prepared in the Institute of Chemical Organic Technology, Technical University of Szczecin according to Gaylord and O’Brien’s method [12]. This compound was purified in the following way: a solution of MDU in nitrobenzene was extracted twice with the mixture of 15 wt.% of ethanol and 85 wt.% hydrochloric acid (30 wt.%) and then rinsed with water up to pH 7. Nitrobenzene was distilled off at 0.666 kPa. The product was recrystallized from ethanol and dried for 38 h at room temperature and 1.333 kPa, m.p. 188 °C.

The 4,4’-di(aminophenyl)methane, m.p. 93–95 °C, purity > 98% was obtained from Fluka.

The 4,4’-di(aminophenyl-*N*-ethyl)methane and (4-aminophenyl-*N*-ethyl-4’-amino-phenyl)methane were obtained in the form of a mixture by alkylation of 4,4’-di(aminophenyl)methane with ethyl bromide, according to the general method [13].

MMI was obtained from MDI and ethanol at 30–50 °C and at the molar ratio of MDI:ethanol of 10:1.

Dodecylbenzene with purity $\geq 97\%$ (GC) was obtained from Fluka.

2.2. Procedure of MDU thermal decomposition

The thermal decomposition of MDU was carried out in the reactor 5 in a form of quartz tube 1.7 cm \times 90 cm (Fig. 1). The reactor was filled with aluminium rods (solid packing or solid catalyst or both) and was equipped with external electric heater. In the upper part of the reactor, there was a reflux condenser 9 with a receiver 10 for ethanol, and in turn, a cold trap 11 cooled down with acetone–carbon dioxide (–40 °C), a drier 12 with molecular sieves 5 Å and anhydrous magnesium sulphate. In the absorption part of the apparatus a bubbling washer 13a filled with a solution of bromide in carbon tetrachloride and a packing scrubber 14, and bubble counter were placed. Ethylene reacted to 1,2-dibromoethane in a washer 13a, and the amount of the product was determined by chro-

matographic method. The amount of separated ethylene is directly associated with the amount of primary amines (reactions 9 and 11), which were formed in the process. A scrubber sprinkled with 10 wt.% NaOH solution was located behind the washer in order to absorb the carbon dioxide. From the amount of carbon dioxide determined as NaHCO₃, an approximate amount of polycarbodiimides and amines (reactions 9–11) was determined.

A stream of dry nitrogen from bottle 1 (12–30 Ndm³/h), heated to 150–250 °C in the electric warming plate 4, was passed through the reactor. A solution of MDU in dodecylbenzene, heated up to 120 °C, was introduced at a rate of 0.3–1.5 g/dm³ min into the reactor filled with dodecylbenzene and heated up to 250–300 °C. The product was collected in receiver 15 as the MDI solution in dodecylbenzene.

2.3. MDI heating

In order to elucidate the formation of polymer heating of the MDI (5 wt.% MDI solution in dodecylbenzene) was carried out under a reflux condenser at 280 °C and atmospheric pressure for 2 h. The heating of MDI resulted in the evolution of carbon dioxide and the formation of the polymer having the same properties as that resulting from MDU thermal decomposition. Both polymers (from pyrolysis and MDI heating) were partially soluble in ethanol during long lasting (36 h) heating under reflux condenser. The heating of polycarbodiimides with ethanol caused the evolution of carbon dioxide and ethylene, identified in the same way as during the decomposition of MDU. Carbodiimide polymers (from both processes) were also partially soluble in *N,N*-dimethylformamide. They did not dissolve in chloroform, carbon tetrachloride, tetrahydrofurane, and dioxane.

2.4. IR spectroscopy

IR spectra of the polymers resulting from thermal decomposition of MDU and pure MDI spectra obtained in this process were performed using Specord IR 71 spectrophotometer. Both kinds of samples showed a sharp absorption peak at 2084–2439 cm^{–1} and poorly defined absorption in the 1449–1613 cm^{–1} and 2564–3330 cm^{–1} regions.

IR spectra of the polymer obtained from MDI heating showed a high absorptivity in the range of 2082–2127 cm^{–1}, characteristic for carbodiimide groups, and a lower absorptivity in the ranges of 1450–1613 cm^{–1}, and 2562–3330 cm^{–1}.

2.5. HPLC method

The determination were performed on Chrom 5001 apparatus with a Separon SGX C18, 5 μ m column, 3.3 mm in

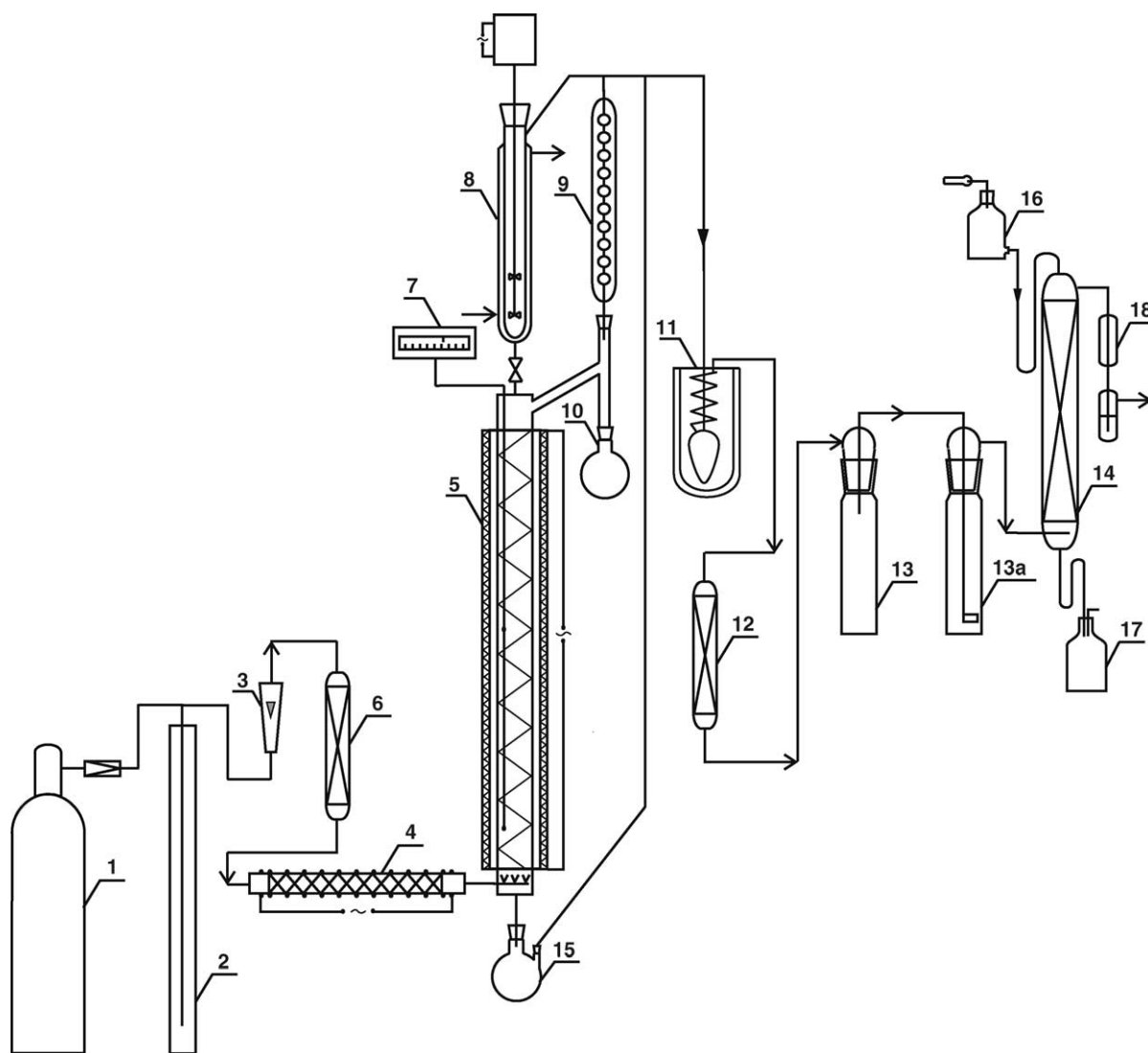
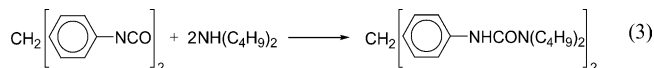


Fig. 1. Scheme of the apparatus for MDU pyrolysis: (1) nitrogen cylinder; (2) manostat; (3) rotameter; (4) nitrogen heater; (5) reactor with heating jacket; (6) and (12) dryers; (7) temperature meter; (8) MDU volume feeder; (9) reflux condenser; (10) ethanol receiver; (11) freezer; (13) washer; (13a) bubbling washer; (14) scrubber; (15) product receiver; (16) container for NaOH solution; (17) container for NaHCO₃ solution; (18) bubble counter.

diameter and 2 cm × 15 cm long. Eluent 75 vol.% of acetonitrile and 25 vol.% of water, flow velocity, 0.3 cm³/min; UV detector, λ = 254 nm; pressure, 10 MPa.

The samples with the isocyanate groups (e.g. MDI, MMI) were converted into derivatives with an excess of *n*-dibutylamine [14] according to the reaction:



A 5 cm³ of acetone and a known amount of dibutylamine were added to 0.2–0.6 g of sample resulting from thermal decomposition of MDU. The reaction was run at room temperature for 4 h with occasional shaking of the mixture. If the sample was only slightly soluble in acetone, *N,N*-dimethylformamide was applied. If the sample contained insoluble polymers, they had to be filtered off on a sintered glass funnel.

2.6. GC method

Both, ethanol and 1,2-dibromoethane (formed from ethylene) were determined on Chrom-5 apparatus. A steel column 0.4 cm × 2 m, filled with Chromosorb 101 was applied. FID detector and nitrogen as carrier gas were used.

3. Results and discussion

Experimental results of decomposition of MDU to MDI under the condition similar to those described in patents [2,4–8] are presented in Table 1. The conversion of MDU is high, 85–99 mol.%, depending on the calculation method. The highest selectivity of the transformation to MDI in relation to consumed MDU was achieved at 285 °C. At the same

Table 1
Analysis of thermal decomposition of MDU in dodecylbenzene

	Decomposition temperature (°C)	Reaction time (min)	Selectivity (mol.%)		MDU conversion (mol.%) ^c	
			MDI ^a	Polycarbodiimides ^b	HPLC determination	From ethanol amount
1	260	110	60.2	17.4	84.8	80.5
2	275	90	82.5	7.1	97.5	85.8
3	285	100	87.2	7.3	98.1	86.1
4	300	80	78.2	18.6	99.5	85.2

Concentration of MDU in dodecylbenzene, 5 wt.%; dropping of MDU solution rate, 8 g/dm³ min; nitrogen flow rate, 12 Ndm³/h.

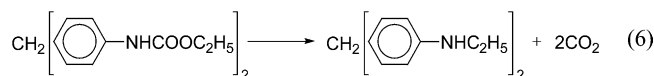
^a From the amount of MDI (mole) in relation to consumed MDU (mole), HPLC determination.

^b From the amount of the polymer remained after thin layer distillation.

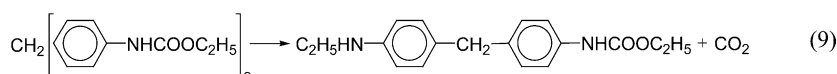
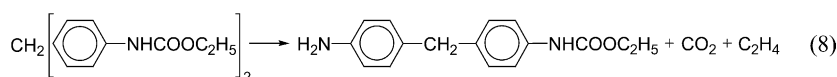
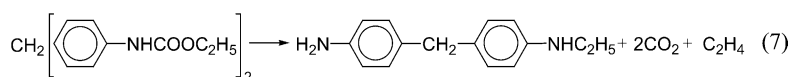
^c From the amount of MDU (moles), before and after the process of thermal decomposition.

time, the lowest selectivity of the transformation to polycarbodiimides was observed.

The presence of Al rods is indispensable, although its role has not been completely elucidated. It was found that the thermal decomposition of MDU proceeds at a high rate when Al

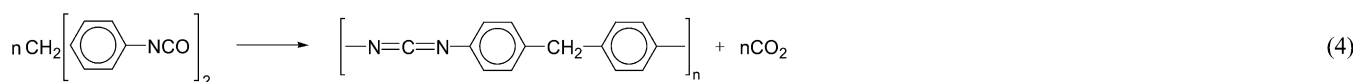


The results of the chromatographic analysis of the tails after MDI, and the solvent had been distilled off show the existence of other amines:



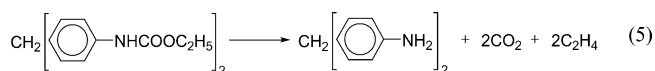
rods are present. They can act as the catalyst or as solid packing, which increase the surface area of the liquid component or serves as a desirable medium for imparting the heat for thermal decomposition of MDU [4].

During thermal decomposition of MDU, beside the main reaction (1), occurs the forming of methylene-4,4'-di(phenylisocyanate)polycarbodiimides (PCDI). This reaction is the result of rearrangement and decarboxylation in MDI molecule:



Their formation was confirmed in some additional experiments (see Section 2.3). A partial solubility of polymers results probably from various degree of cross-linking.

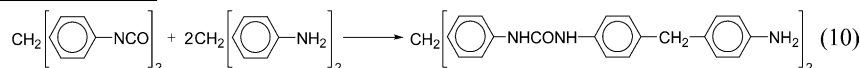
In the test of MDU thermal decomposition carried out in the range of 220–310 °C, the following amines were additionally identified by HPLC method: 4,4'-di(aminophenyl)methane, 4,4'-di(aminophenyl)-*N*-ethylmethane (Fig. 2) [14]. They are formed according to the reactions:



The amount of MDU decomposed to amines, calculated from the amount of evolved ethylene is small. The selectivity of the transformation to primary amines in relation to consumed MDU, calculated from the amount of ethylene equals 0.2–0.5 wt.%. On the basis of HPLC determination, this selectivity equals to 0.6–2.5 wt.% (Table 2). The selectivity of the transformation to polycarbodiimides and amines in relation to consumed MDU, calculated from the amount of carbon dioxide equals 8.5–19.2 wt.% and is higher than that

calculated on the basis of polymer amount 7.1–18.6 wt.% (Table 1).

Other chemical reactions also proceed in this thermal decomposition process. MDI resulting from the main reaction (1) reacts with 4,4'-di(aminophenyl)methane (5) and other amines (6)–(9), forming urea derivatives. Some urea derivatives (10) and (11) were identified by HPLC method in the products of MDU thermal decomposition. These derivatives appeared to have the retention parameters identical to those obtained in the reaction of 2 wt.% MDI solution in dodecylbenzene with an equimolar amount of 4,4'-di(aminophenyl)methane:



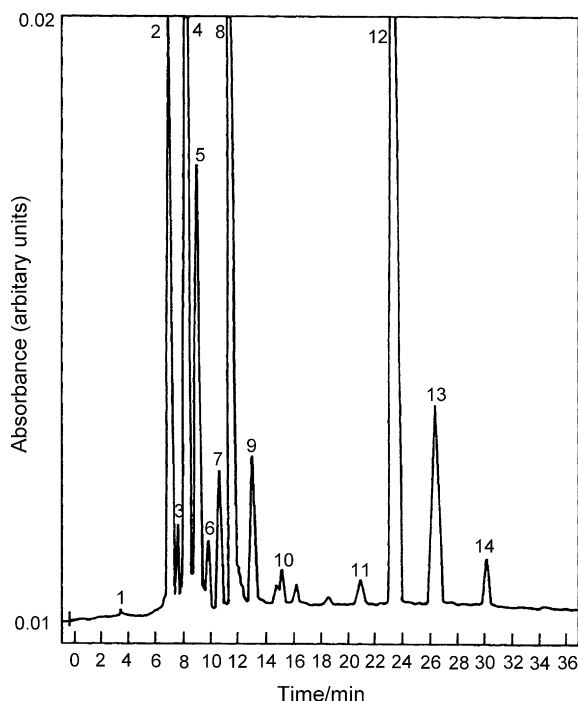
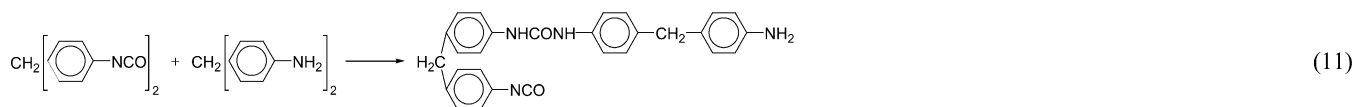


Fig. 2. Chromatogram of MDU thermal decomposition products. Peaks: (1) formaldehyde; (2) acetone; (3) ethyl-*N*-phenylcarbamate (FU); (4) methylene-4,4'-di(ethylphenylcarbamate) (4,4'-MDU); (5) methylene-2,4'-di(ethylphenylcarbamate) (2,4'-MDU); (6) methylene-2,2'-di(ethylphenylcarbamate) (2,2'-MDU); (7) 4,4'-di(aminophenyl)methane; (8) methylene-4-phenylisocyanato-4'-ethylphenylcarbamate (4,4'-MMI); (9) methylene-2-phenylisocyanato-4'-ethylphenylcarbamate (2,4'-MMI); (10) methylene-2-phenylisocyanato-2'-ethylphenylcarbamate (2,2'-MMI); (11) 4,4'-di(aminophenyl-*N*-ethyl)methane; (12) methylene-4,4'-di(phenyl isocyanate) (4,4'-MDI); (13) methylene-2,4'-di(phenyl isocyanate) (2,4'-MDI); (14) methylene-2,2'-di(phenyl isocyanate) (2,2'-MDI).

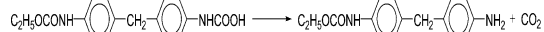
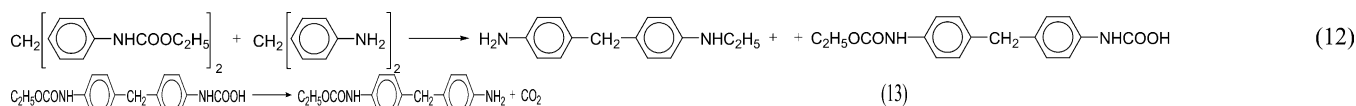
Table 2
By-products of MDU thermal decomposition

	(Amines + carbodiimides) selectivity (on the basis of CO ₂ quantity) (wt.%)	Amines selectivity (wt.%)		MDU decomposed to ureas (HPLC determination) (wt.%)
		On the basis of ethylene quantity	On the basis of HPLC determination	
1	18.2	0.2	0.8	0.3
2	8.5	0.3	0.6	0.4
3	8.9	0.3	1.4	0.7
4	19.2	0.5	2.5	0.9

Conditions as in Table 1.

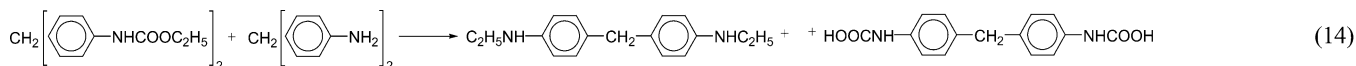


MDU reacts with 4,4'-di(aminophenyl)methane and other amines (5–8) to form new amine derivatives:



In this case, a solution of 5 wt.% MDU and 1 wt.% 4,4'-di(aminophenyl)methane in dodecylbenzene was subjected

to the reaction carried out in the liquid phase at 280 °C. The reaction was run in a tube reactor, which enables the collection of ethanol in nitrogen stream (Fig. 1). In the reaction mixture, the 4,4'-di(aminophenyl)methane appeared beside amine derivatives resulting from the reaction 12 and 13. The presence of the former compound can be accounted for the reaction of both functional groups in MDU and 4,4'-di(aminophenyl)methane:



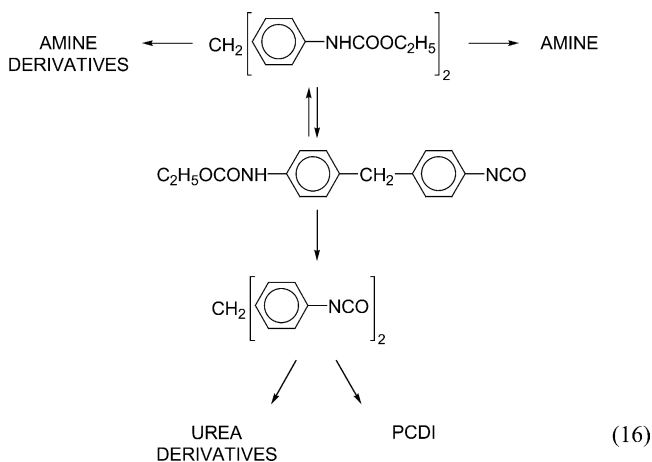
In this reaction 4,4'-di(aminophenyl)methane is reproduced:



Only very small quantities of ethanol were observed in the upper receiver. This confirms that the thermal decomposition of MDU also proceeds during its heating with 4,4'-di(aminophenyl)methane. Moreover, the polymer was formed during this process. Probably, this polymer was a product of the reaction of MDI with 4,4'-di(aminophenyl)methane or polymerisation of MDI.

However, allophanate compounds were not detected in the product of thermal decomposition of MDU. This was confirmed by a negative test reaction of a polymer resulting from MDU decomposition, after MDI and dodecylbenzene had been distilled off, with aniline and *n*-butylamine. The reaction was carried out at 180 °C for 10 h in sealed glass ampoule. Analysis by HPLC method did not confirm the presence of new compounds provided that aminolysis did not occur. In the presence of allophanates, the aminolysis to urethanes and ureas would proceed.

On the basis of our research, the following mechanism of MDU thermal decomposition may be proposed:



4. Conclusions

Although phosgene-free method of MDI production is interesting and much better than phosgene method, it also possesses several disadvantages. Especially, the thermal decomposition of MDU needs attention. This procedure forms abundance of by-products beside the main reaction forming MDI.

The main by-products are polycarbodiimides, with a various degree of cross-linking. During the thermal decomposition of MDU, 4,4'-di(aminophenyl)methane and its derivatives are formed. Under the reaction conditions used in this work, the 4,4'-di(aminophenyl)methane and its derivatives both react with MDU, and MDI forms new amine derivatives.

The thermal decomposition of MDU proceeds most advantageously under the following reaction conditions: time, 100 min; temperature, 285 °C. Under these conditions, the highest selectivity of the transformation to MDI in relation to consumed MDU was achieved. At the same time, the lowest selectivity of the transformation to polycarbodiimides was observed. Depending on the calculation method, the conversion of MDU amounted to 86–98 mol.%.

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