



**MISKOLCI**  
EGYETEM  
UNIVERSITY OF MISKOLC

***Theses of Ph.D. Dissertation***

titled as

***A Study of Elementary Reactions of  
Isocyanate Production***

*presented by*

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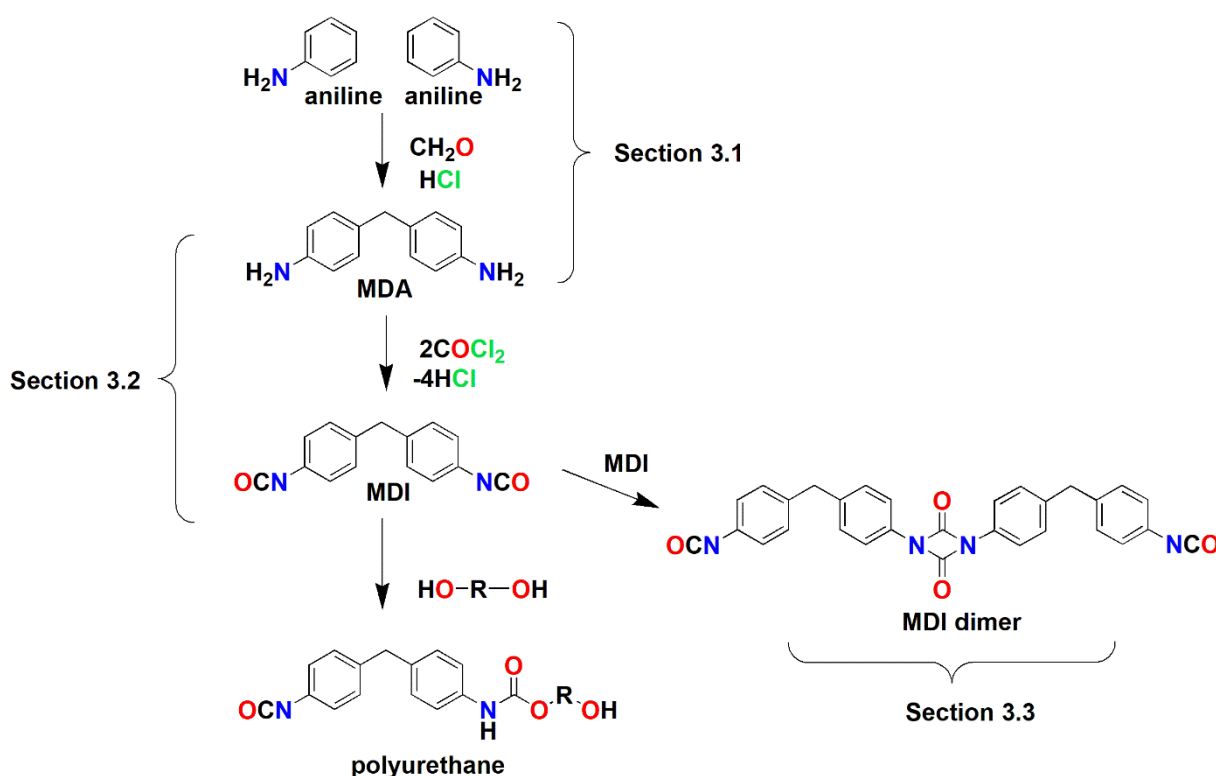
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## 1 INTRODUCTION

Polyurethanes (PUs) are the most versatile, extensively used and progressive materials in the world. Those applied for shoe soles are significantly different than those utilized for mattresses or applied in car industry<sup>1,2</sup>. The worldwide demand for PUs was about 5% of the total plastic consumption<sup>3</sup> in 2010, but this number is still growing. The most common synthesis of PUs is based on the reaction of di- or polyisocyanates with di- or polyalcohols<sup>1</sup> (see bottom of *Figure 1*).



**Figure 1:** Schematic representation of industrial polyurethane production and indication of the sections describing each reaction steps.

Methylene diphenyl diisocyanate (MDI) is one of the main diisocyanate used as raw material for industrial PU production<sup>4</sup>. The global MDI market is predicted to reach 8.7 Mt by 2023 due to the unique features of the product and increasing utilization of MDI based polyurethanes<sup>5</sup>.

MDI is mostly produced via phosgenation of the appropriate amine, methylene diphenyl diamine (MDA) (*Figure 1*). The MDA is produced from aniline and formalin in the presence of hydrochloric acid as catalyst in the first step. The second step of the MDI synthesis involves the phosgenation of the MDA via an addition-elimination type mechanism. The product MDI can undergo a dimerization process with the reaction of free isocyanate

groups. This side reaction causes several problems during the applications<sup>4</sup>.

Despite the fact that, MDI is one of the most important raw material of polyurethane industry the reaction mechanism of its synthesis is poorly characterized in the literature. The purpose of this research was to study the reactions at the molecular level to understand the industrial MDI production mechanism and support further technological developments.

## **2 AIMS AND CONCEPTIONS**

The aim of this thesis is to provide a coherent, quantum chemistry-based reaction mechanism of MDI production started from aniline and formaldehyde. Although there are several competing mechanisms established in the literature<sup>3,6,7</sup> based on detection of few intermediate species, they are not coherent at the atomistic level and the reaction bottlenecks and the competing side reactions had not yet been explored in detail. Therefore, our intent was to provide structural and thermodynamic characterization of the missing intermediates as well as to identify those transition states which may be kinetically accessible at industrial condition.

To shed some lights on the temperature, pressure and solvent effects on the Gibbs free energy profile of the reaction studied calculations systematically were performed at different conditions. In addition, some of these reactions are carried out in solvents, but their roles cannot be easily distinguished in experimental condition.

Due to the large number of missing thermochemical data of the participated species, an accurate prediction of the thermochemical properties was also an important aim of this work.

Finally, to verify the proposed reaction mechanism and to show further directions for future research, the investigation of the possible competing side reactions had also been in our focus of research.

### 3 NEW SCIENTIFIC RESULTS

#### Reaction Mechanism of MDA Synthesis<sup>8</sup>

##### 1<sup>st</sup> Thesis

A new reaction mechanism of MDA synthesis has been found at molecular level consisting of eight steps and including condensations and rearrangements. In the initial reaction step a non-covalent aniline dimer is proposed to react with formaldehyde. This hypothetical aniline dimer is based on experimental observation (*e.g.* high viscosity of aniline, scattering experiments).

- The global minimum of the potential energy surface of the studied reaction was found to be the *N*-(*p*-aminobenzyl)anilinium (protonated PABA, PABAH<sup>+</sup>), which is in good agreement with the experimental observation of PABA during MDA production. Two rearrangement steps of aniline resulted the protonated MDA isomers (MDAH<sup>+</sup>). The species in the proposed mechanism are proton activated. They got more acidic in aniline (basic) environment which can then deactivate the intermediates.
- Solvent effect (water and aniline) was found to be significant and thus, the difference was big between gas phase and liquid phase energetics. The highest transition (*N*-hydroxymethylaniline) state was by 12.7 kJ/mol.

##### 2<sup>nd</sup> Thesis

Side reactions were also examined computationally. Our results confirmed that the aminal formation (protonated *N,N'*-Diphenylmethylenediamine, AMH<sup>+</sup>), is both thermodynamically and kinetically preferable than the formation of PABAH<sup>+</sup>, but it is a kinetic dead-end at the same time. The aniline addition in ortho position (formation of 2,4'-MDA) is competitive with that of in the para position (formation of 4,4'-MDA) from both kinetic and thermodynamic points of view. The preference of the formation of 4,4'-MDA can be hypothesized over MDA oligomer formation as intermediate.

### **Reaction mechanism of MDI synthesis<sup>9</sup>**

Phosgenation mechanism of MDA was studied by computational calculations. We assumed two possible reaction mechanisms: 'Phosgenations first' and 'Stepwise phosgenations'.

#### **3<sup>rd</sup> Thesis**

'Phosgenations first': both amino groups transformed to carbamoyl chloride groups giving [methylenebis(4,1-phenylene)]dicarbamic chloride and then two endothermic HCl-elimination steps occurs. 'Stepwise phosgenations': One of the amino groups of MDA turns into isocyanate by phosgene and then the other amine does. The 'Phosgenation first' mechanism is the energetically more favourable pathway.

#### **4<sup>th</sup> Thesis**

The activation barriers for both phosgenation mechanisms were determined and found to be high in the gas phase, while all the reaction barriers are dramatically reduced in o-dichloro benzene (ODCB) making the incorporation of the first phosgene occurred in ODCB via submerge transition state. The reaction with the second phosgene has also a low-lying transition state in this case. Further findings are the following:

- Accurate standard enthalpy of formation was determined for MDI (14.8 kJ/mol) with the uncertainty of 5.2 kJ/mol. This value was compared with the uncertain literature standard enthalpies of formation for MDI.
- The ionic complex ( $\text{IM1H}^+ \times \text{Cl}^-$ ) has relatively high stability at industrial conditions which might inhibit the second phosgene to incorporate both sterically and energetically. MDA can also form such charge separated complex with HCl (when there is a large excess of HCl in the reactor) due to such thermodynamically preference. This may decrease the reactivity of MDA towards phosgene.
- Only moderate effect on the relative enthalpies and Gibbs free energies found by changing the temperature and pressure range of the industrial operation ( $90^\circ\text{C} < T < 160^\circ\text{C}$  and  $6 \text{ bar} < p < 11 \text{ bar}$ ).

## **Thermodynamic investigation of MDI dimerization<sup>10</sup>**

Inappropriate storage or transport of MDI facilitates its dimerization. Ten different MDI dimer structures were assumed.

### **5<sup>th</sup> Thesis**

The 4,4'-MDI dimer with four-membered ring is the most stable among the studied dimers due to the aromatic electronic structure of the uretidione ring.

- The relative stability of the dimers is influenced by the steric effects and the relative positions of isocyanate groups.
- Among the MDI monomers, the 2,2'-MDI was found to be the most thermodynamically stable, while the industrially preferred isomer is the 4,4'-MDI.

### **6<sup>th</sup> Thesis**

The most thermodynamically stable dimer is turned out to be 4,4'-4,4'-MDI dimer.

- Considering equilibrium for the MDI dimerization, the reaction Gibbs free energy is the lowest for the 4,4'-4,2'-MDI ( $\Delta_r G^\circ = -12.6$  kJ/mol), but the formation of 4,4'-4,4'-MDI is just slightly smaller ( $\Delta_r G^\circ = -12.2$  kJ/mol).

## **4 COMPUTATIONAL METHODS**

The reaction mechanism of the MDI production and its selected side reactions was investigated by means of computational chemistry methods. As a part of the G3MP2B3 computational protocol<sup>11</sup>, B3LYP/6-31G(d) level of theory<sup>12,13</sup> was applied to explore the reaction mechanisms including the calculation of geometries, and harmonic wavenumbers. Normal mode analysis was carried out on each vacuum and solvent optimized structure. The transition state (TS) structures were confirmed to locate at first order saddle points using GaussView 5<sup>14</sup>. Intrinsic reaction coordinate (IRC) calculations<sup>15</sup> were also carried out to find the minimal energy pathways (MEP). In this study, SMD<sup>16</sup> implicit solvent model was used to mimic the surrounding media. Due to the computationally demanding QCISD(T)/6-31G(d) calculation in G3MP2B3, the geometries, harmonic frequencies and thermodynamic properties of MDI dimer were computed using Truhlar's M06-2X functional<sup>17</sup> with the 6-31G(d,p) basis set<sup>18</sup>. For verification purposes, G4<sup>19</sup>, G4MP2<sup>19</sup> and CBS-QB3<sup>20</sup> model chemistries were used to estimate the accuracy of G3MP2B3 for the smaller systems. All quantum chemistry calculations were carried out using the Gaussian09<sup>21</sup> program package.

## 5 SUMMARY

In this research the reaction mechanism pathway of methylene diphenyl diisocyanate (MDI) synthesis was explored using G3MP2B3 quantum chemical method in gas phase and in industrially relevant solvents applying the SMD solvation model. The first step of the MDI synthesis is the methylene diphenyl diamine (MDA) formation from aniline and formaldehyde in the presence of hydrochloric-acid as catalyst. The proposed mechanism was critically evaluated, considering the possible side reactions as well as the acid strength of the key intermediates. The most stable intermediate *N*-(*p*-aminobenzyl)aniline (PABA) was confirmed by gas chromatography analysis. Gas phase and solvent phase calculations were compared and it was found that the solvent had a positive effect and reduced the barrier heights. The biggest decrease in relative energy was observed in the case of the last step, that is the deprotonation of the MDAH<sup>+</sup> which is the last step of the MDA synthesis. The possible reaction mechanisms of the MDA phosgenation were also investigated. The formation of MDI is possible via two different mechanisms: 'Phosgenations first' and 'Stepwise phosgenations'. The 'Phosgenation first' mechanism was found to be more energetically favourable. The activation barriers for both phosgenation mechanisms are high in the gas phase, while all the reaction barriers are dramatically reduced making the incorporation of the first phosgene occurred in ODCB via submerge transition state. We found that the thermodynamically stable charge separated amine hydrochloride intermediate can mask the amine toward phosgene. Based on the gas phase G3MP2B3 calculations standard enthalpy of formation, entropy and heat capacity values were calculated for intermediates, reactants and products by using the atomization scheme. Group additivity increments for NCO and NHCOCI groups linked to phenyl ring were proposed ( $\Delta_{f,i}H^\circ(-NCO) = -61.2$  kJ/mol and  $\Delta_{f,i}H^\circ(-NHCOCI) = -195.0$  kJ/mol). These data can be used in industrial predictions which could become more precise. Besides the study of MDI synthesis route an important side-reaction, the dimerization of MDI was also examined, which cause several difficulties during the application. These dimers are formed via a four-membered ring (uretidione) influenced by the steric effects and the relative positions of isocyanate groups. The most thermodynamically stable dimer was found to be the 4,4'-4,4'-MDI dimer.

## 6 ÖSSZEFOGLALÁS

Munkánk során a metilén difenil diizocianát (MDI) szintézis reakciómechanizmusát vizsgáltuk G3MP2B3 kvantumkémiai módszert alkalmazva, gázfázisban és ipari szempontból fontos oldószerekben SMD oldószermoddell segítségével. Az MDI szintézis első lépése a metilén difenil diamin (MDA) előállítása anilin és formaldehid reakciójával sósav katalizátor jelenlétében. Az irodalomban felvázolt reakciómechanizmust módosítottuk, figyelembe véve a legvalószínűbb mellékreakciókat, illetve a kulcsfontosságú köztitermékek savi erősségét. A legstabilisabb köztiterméket (para-amino-benzil anilin, PABA) sikerült analitikai úton detektálnunk. Az oldószerekben (víz és anilin) számolt eredményeket összevetettük a gázfázisú mechanizmussal, ahol azt tapasztaltuk, hogy a formaldehid addíciójához tartozó legmagasabb relatív energiájú átmeneti állapot energiája csökkent oldószerekben. A legnagyobb relatív energia csökkenést a reakció utolsó lépésénél tapasztaltunk, a protonált metilén difenil diamin (MDAH<sup>+</sup>) deprotonálódásánál. Az MDI gyártás következő lépésének, az MDA foszgézésének reakciómechanizmusát is tanulmányoztuk, melynek két reakcióútja lehet a „foszgézés először” illetve a „lépcsőzetes foszgézés”. A „foszgézés először” típusú mechanizmus energetikailag kedvezőbbnek bizonyult. Az aktiválási gátak magassága mindkét reakció esetében gázfázisban jelentős, míg az összes reakciónál drasztikusan lecsökken már az első foszgén beépülésekor o-diklór benzol (ODCB) oldószerekben ún. „süllyesztett” átmeneti állapoton keresztül. Azt tapasztaltuk, hogy a termodinamikailag stabil töltésszeparált amin-hidroklorid köztitermék jelenléte gátolja a foszgén molekula útját az aminhoz. A G3MP2B3 elméleti módszerrel kivitelezett gázfázisú számolások segítségével meghatároztuk az egyes köztitermékek, reaktánsok és termékek standard képződési entalpiáját, entrópiáját és hőkapacitását az atomizációs séma szerint. Javaslatot tettünk csoportadditív hozzájárulások kiszámolására a fenil gyűrűhöz kapcsolódó NCO és NHCOCl funkciós csoportok esetében ( $\Delta_{f,i}H^\circ(-NCO)=-61.2$  kJ/mol és  $\Delta_{f,i}H^\circ(-NHCOCl)=-195.0$  kJ/mol. Ezeket az adatokat javasoltuk ipari használatra, a hőtani számításokhoz. Az MDI szintézis reakcióútjának feltérképezése mellett tanulmányoztunk egy nem kívánt mellékreakciót: az MDI dimerizációját, amely számos felhasználástechnikai nehézséget okoz. Az MDI dimerek egy négytagú gyűrű (uretídon) létrejöttével keletkeznek. Szerkezetük kialakulására befolyással van az izocianát csoportok szterikus hatása és relatív helyzete. A termodinamikailag legstabilisabb dimer a 4,4'-4,4'-MDI.



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## 8 LIST OF PUBLICATIONS

### 8.1 Bibliometrics

Number of papers and abstracts published and accepted:	7
Cumulative impact factor:	9.047
Cumulative impact factor (related to the thesis):	6.136
Total number of citations:	1
Number of independent citations:	0

### 8.2 Publications Related to the Subject of the Dissertation

1. R. Zsanett Boros, Anita Ragyanszki, Imre G. Csizmadia, Bela Fiser, Andrea Guljas, Laszlo Farkas, Bela Viskolcz, Industrial Application of Molecular Computations on the Dimerization of Methylene Diphenyl Diisocyanate, *Reaction Kinetics and Catalysis Letters*, **2018**, 124, 1-14., **IF(2017): 1.515**
2. R. Zsanett Boros, Tamás Koós, Wafaa Cheikh, Károly Nehéz, László Farkas, Béla Viskolcz, Milán Szőri, A Theoretical Study on the Phosgenation of Methylene Diphenyl Diamine (MDA), *Chemical Physical Letters*, **2018**, 706, 568-576, **IF(2017): 1.686**
3. R. Boros, László Farkas, Károly Nehéz, Béla Viskolcz, Milán Szőri, An Ab Initio Investigation of the 4,4'-Methylene Diphenyl Diamine (4,4'-MDA) Formation from the Reaction of Aniline with Formaldehyde, *Polymers*, **2019**, 11, 398., **IF(2017): 2.935**
4. R. Zsanett Boros, István Varga, Barnabás Buzellák, Márta Harangozó, Milán Szőri, Béla Viskolcz, László Farkas, An Approach for Eliminating Phenyl Isocyanate from Solvent Used in Isocyanate Production, *Materials Science and Engineering: A Publication of the University of Miskolc*, **2018**, 43, 11-16., **IF: -**

### 8.3 Further Publications

1. Anett Juhász, Attila Timkó, Renáta Zsanett Boros, Synthesis and Industrial Application of Aminopyrimidines, *Materials Science and Engineering: A Publication of the University of Miskolc*, **2016**, 41, 51-61., **IF(2017): -**

2. Ákos Korbács, R. Zsanett Boros, Angelica Rodriguez, László Farkas, Reducing of DNT Content in Red Water Formed During TDI Production, *Materials Science and Engineering: A Publication of the University of Miskolc*, **2018**, 43, 71-78., **IF(2017): -**
3. Vanyorek László, Bánhidi Olivér, Muránszky Gábor, Sikora Emőke, Prekob Ádám, Boros Zsanett, Farkas László, Viskolcz Béla, Chlorate Elimination by Catalytically Hydrogenation, Catalyst Development and Characterization, *Catalysis Letters*, **2018**, 149, 196–202, **IF(2017):2.911**

#### **8.4 Presentations Related to the Dissertation**

1. Chemistry Conference for Young Scientists (ChemCYS2016)  
16-18, 03.2016, Blankenberge, Belgium  
*Empirical and Theoretical Study on Molecules of Isocyanate Synthesis*
2. KeMoMo Workshop  
01-02.06.2017, Szeged, Hungary  
*Theoretical Investigation of Methylene Diphenyl Diamine Synthesis*

#### **8.5 Further Presentations**

1. UTECH Europe (The leading international exhibition and conference for the Global Polyurethanes Industry)  
29-31.05.2018, Maastricht, Netherlands  
*A Transition from Synthetic to Biodegradable Polyurethanes*

#### **8.6 Posters Related to the Dissertation**

1. XI. Országos Anyagtudományi Konferencia (OAK)  
15-17.10.2017, Balatonkenese, Hungary  
*Poliuretán gyártás egyik legfontosabb alapanyagának vizsgálata elméleti kémaiai úton*
2. XXI. Nemzetközi Vegyészkonferencia  
24-16.09.2015, Erdély, Csíksomlyó, Románia  
*Izocianát gyártásban legfontosabb alapanyagok előállításának vizsgálata*
3. XXIV. Nemzetközi Vegyészkonferencia  
24-26.10.2018, Szovátafürdő, Románia  
*MDA gyártás előállítási lépéseinek tanulmányozása laboratóriumi körülmények között*

## 8.7 Further Posters

1. X. Országos Anyagtudományi Konferencia (OAK)  
11-13.10.2015, Balatonalmádi, Hungary  
*Vegyszerálló kármentők anyagának összehasonlító vizsgálata*
2. 6<sup>th</sup> Visegrad Symposium on Structural Systems Biology  
18-19.06, 2016, Warsaw, Poland  
*Computational Study on Isocyanate-peptide Adduct as Potential Biocompatible Polymers*
3. 7<sup>th</sup> Visegrad Symposium on Structural Systems Biology  
21-24.06.2017, Nove Hradý, Czech Republic  
*Study the Reactivity of Methylene Diphenyl Diisocyanate with Biological Motifs*

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