

THE CATALYTIC EFFECT OF DBU ON URETHANE FORMATION – A COMPUTATIONAL STUDY

HADEER Q. WALEED¹ – MARCELL CSÉCSI² – RACHID HADJADJ³ –
RAVIKUMAR THANGARAJ⁴ – MICHAEL OWEN⁵ – MILÁN SZŐRI⁶ –
ZSOLT FEJES⁷ – BÉLA VISKOLCZ⁸ – BÉLA FISER⁹

Abstract: A theoretical investigation of urethane formation through the reaction of phenyl isocyanate and methanol without and in the presence of a secondary ketimine catalyst (DBU) was carried out by using density functional theory method in gas phase and in organic solvent (THF). The reaction mechanisms have been explored, and the corresponding thermodynamic properties have been computed. The reaction in the presence of the catalyst largely differs from the catalyst-free case. It was found that the activation energy decreased significantly in the presence of DBU in both gas phase and organic solvent by more than 67.0 kJ/mol, compared to the catalyst-free reaction, which proves the importance of catalysts in (poly)urethane synthesis.

Keywords: Polyurethane, DFT, Secondary ketimine, THF, Catalyst-free

INTRODUCTION

The term catalysis was coined by Berzelius in 1835 and comes from the Greek words “kata” meaning down and “lyein” meaning loosen [1], [2]. Catalysts are key in the

¹ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
kemhader@uni-miskolc.hu

² Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
csesci.marcell2@gmail.com

³ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
hrachid.chemeng@gmail.com

⁴ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
ravikumar8019@gmail.com

⁵ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
michaelowen27@gmail.com

⁶ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
kemszori@uni-miskolc.hu

⁷ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
kemfejes@uni-miskolc.hu

⁸ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
bela.viskolcz@uni-miskolc.hu

⁹ Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
Higher Education and Industrial Cooperation Centre, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
Ferenc Rákóczi II. Transcarpathian Hungarian College of Higher Education, 90200 Beregszász, Transcarpathia, Ukraine, kemfiser@uni-miskolc.hu

chemical industry and with their help the environmental impact of chemical processes and the energy required to carry them out are significantly reduced [3]. Catalysts can expedite chemical reactions compared to catalyst-free systems. By applying catalysts, new reaction pathways may become possible [4]. Currently, catalysts are used in more than 90% of chemical and refining processes. The world depends on them, as plastics, artificial fibres, food, and fuel are prepared by using these special chemicals [5]. Also, catalysts are important additives in the process of synthesizing polymers, especially in polyurethane (PU) synthesis [6]. PU is one of the most versatile and unique polymer being a part of our daily life and used in different applications [7]. Therefore, there are various types of catalysts used for polyurethane synthesis. The PU catalyst can increase the reaction rate, the production efficiency, and promote the urethane formation while suppress the side reactions selectively [8]. In the production of polyurethane-based products, although the amount of catalyst is small, but its role is significant. The most important catalysts applied in PU foam production are amine-containing chemicals [8].

The reaction between methyl isocyanate and methanol with and without catalyst addition has been studied at the B3LYP/3-21G level of theory. It was found that the addition of the catalysts has a great influence on the stability of the transition states [9]. However, there are still various aspects of the catalytic urethane formation reactions which has to be understood. There is also an increasing demand to design environmentally friendly polyurethane catalysts. Therefore, additional studies to gain more information about urethane and polyurethane synthesis is inevitable.

In the current work, urethane formation is studied by using computational chemical tools in the presence of a secondary ketimine catalyst, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU). The effect of the catalyst on the phenyl isocyanate – methanol reaction is examined, and the steps of the reaction are described.

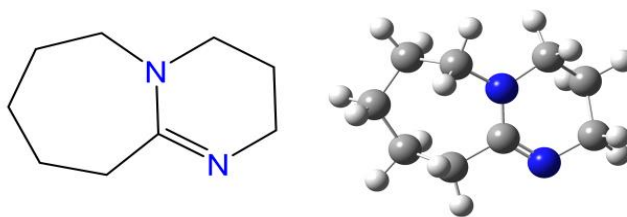


Figure 1
2D and 3D structures of the studied catalyst,
1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)

1. METHODS

All calculations were performed by using the B3LYP (Becke, 3-parameter, Lee-Yang-Parr) [10] DFT method in combination with the 6-31G(d) basis set in gas phase, and in tetrahydrofuran (THF, $\epsilon_r = 7.4257$) by using the SMD implicit solvent model. Opti-

mizations and frequency calculations were carried out to locate the minima and transition states. Intrinsic reaction coordinate (IRC) calculations were also performed starting from the transition states to verify that those connect the right minima. The Gaussian 09 program package was used to carry out the calculations [11].

2. RESULTS AND DISCUSSION

2.1. Catalyst-free Reaction between Phenyl Isocyanate and Methanol

The methanol (MeOH) - phenyl isocyanate (PhNCO) reaction has been used as a model to study urethane formation. For the catalyst-free system, the geometries have been optimized in gas phase and THF, and the corresponding thermodynamic properties have been computed (Table 1), and based on these, the reaction has been characterized (Figure 2).

Table 1

The zero-point corrected relative energies (ΔE_0), enthalpies (ΔH), and Gibbs free energies (ΔG) of the reaction between phenyl isocyanate (PhNCO) and methanol with and without catalyst (DBU), calculated at the B3LYP/6-31G(d) level of theory in gas phase and THF at 298.15 K and 1 atm. R: reactants, RC: reactant complex, TS: transition state, IM: intermediate, PC: product complex, P: product

Catalyst-free	ΔE_0 (kJ/mol)		ΔH (kJ/mol)		ΔG (kJ/mol)	
	Gas	THF	Gas	THF	Gas	THF
R (PhNCO+MeOH)	0.00	0.00	0.00	0.00	0.00	0.00
RC	-15.81	-10.40	-14.15	-8.92	20.85	27.24
TS	107.93	110.22	104.79	106.85	156.35	159.14
P	-100.38	-100.32	-103.70	-103.57	-51.43	-54.37
Catalysed	ΔE_0 (kJ/mol)		ΔH (kJ/mol)		ΔG (kJ/mol)	
	Gas	THF	Gas	THF	Gas	THF
R (PhNCO+MeOH+DBU)	0.00	0.00	0.00	0.00	0.00	0.00
RC	-66.03	-39.66	-62.66	-35.62	18.34	41.53
TS1	-9.69	-8.04	-11.31	-9.09	84.65	85.76
IM	-37.49	-102.89	-39.50	-104.60	63.69	-7.03
TS2	—*	-108.68	—*	-111.17	—*	-10.37
PC	-140.84	-129.74	-142.01	-130.86	-45.86	-36.00
P	-100.38	-100.32	-103.70	-103.57	-51.43	-54.37

* – TS2 were not found in gas phase.

It can be seen from the optimized geometries that the urethane bond formation is going through a concerted mechanism (Figure 2). It starts with the formation of the reactant complex (RC, PhNCO---MeOH). The geometrical properties of the complex in gas phase and THF are slightly differ (2.179 and 2.150 Å, respectively) (Figure 2).

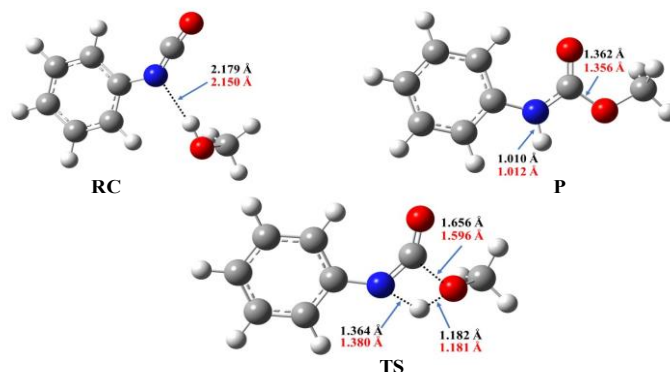


Figure 2

3D structures in the reaction of phenyl isocyanate (PhNCO) and methanol. The optimizations were carried out at the B3LYP/6-31G(d) level of theory in gas and solvent (THF) phase at 298.15 K and 1 atm. RC: reaction complex, TS: transition state, and P: product. The most important distances are also depicted in Å. Black: gas phase. Red: THF.

The corresponding zero-point corrected relative energy, enthalpy and Gibbs free energy values indicates that the complex is more stable in gas phase than in THF. In the next step, the product (P) will be formed through the transition state (TS). In the TS, a proton transfer from the methanol's hydroxyl group to the isocyanate's nitrogen will occur and a bond will be formed between the oxygen of the methanol and the carbon of the isocyanate group. The N-H distance in the TS is 1.364 Å, and 1.380 Å in gas phase and in THF, respectively. The forming C-O bond in the TS between the isocyanate's carbon and methanol's oxygen is 1.656 Å, and 1.596 Å in gas phase and in THF, respectively. The TS has the highest relative energy along the reaction pathway and a significant barrier height has to be overcome to achieve the product (Figure 3).

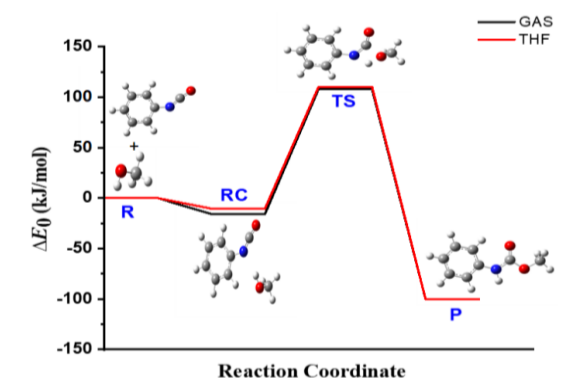


Figure 3

Energy diagram (zero-point corrected) of the phenyl isocyanate (PhNCO) and methanol reaction calculated at the B3LYP/6-31G(d) level of theory in gas phase and THF (using the SMD implicit solvent model) at 298.15 K and 1 atm

The zero-point corrected relative energies indicate that the final urethane product, P is very stable and the corresponding DE_0 is -100.3 kJ/mol (Table 1).

2.2. Reaction between Phenyl Isocyanate and Methanol in the Presence of DBU

The steps of the phenyl isocyanate – methanol reaction in the presence of the DBU catalyst in gas phase and THF has also been computed (Figure 4, Table 1). Additional structures (e.g., IM) have been formed compared to the catalyst-free pathway.

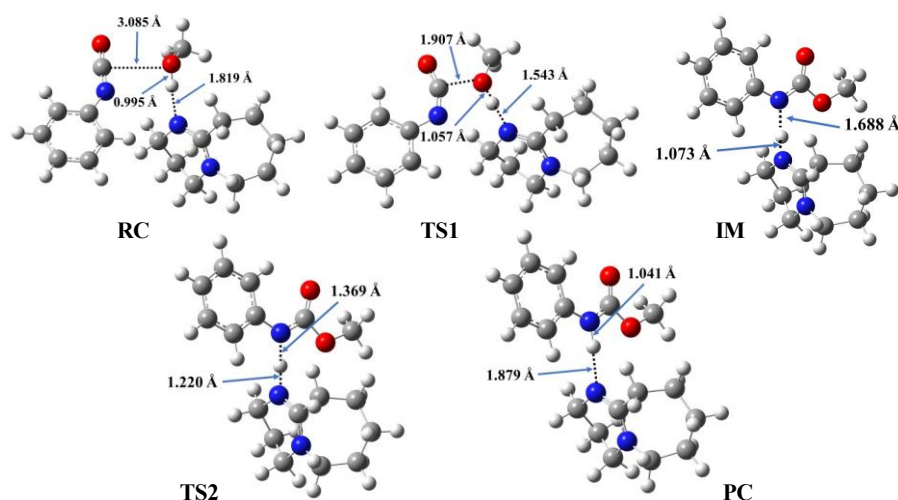


Figure 4

3D structures of the reaction between phenyl isocyanate (PhNCO) and methanol in the presence of DBU. The structures have been optimized at the B3LYP/6-31G(d) level of theory in THF at 298.15 K and 1 atm. RC: reaction complex, TS: transition state, IM: intermediate, PC: product complex. The bond distances are also depicted in Å.

In the first step, a trimolecular reactant complex, RC was formed in this case. A hydrogen bond formed between the hydroxyl group of the methanol and the DBU's nitrogen and the corresponding N-H distance is 1.799 Å, and 1.819 Å in gas phase and THF, respectively (Figure 4). Another interaction established between the isocyanate's carbon and methanol's hydroxyl oxygen. The C-O distance is slightly longer in gas phase (3.183 Å) than in THF (3.085 Å). The reaction is going through two transition states and an intermediate. After the formation of the complex (RC), a proton transfer will occur in TS1 from the hydrogen of the hydroxyl group to the nitrogen of the catalyst and thus, the N-H distance will be reduced ($N-H_{\text{gas}} = 1.410$ Å, and $N-H_{\text{THF}} = 1.543$ Å) compared to that of the reaction complex. Furthermore, a bond is forming between the methanol's oxygen and the isocyanate's carbon. The relative energy of the TS1 is lower than the reactants' level ($\Delta E_{0\text{gas}} = -9.69$ kJ/mol,

and $\Delta E_{0\text{THF}} = -8.04$ kJ/mol) (Table 2, Figure 5). This is a significant decrease compared to the catalyst-free case. On the other hand, the solvent has only a slight effect on the relative energy of TS1 ($\Delta E_{0\text{gas-THF}} = 1.65$ kJ/mol).

Through TS1, an intermediate structure (IM) obtained within which a bond is formed between the isocyanate's carbon and the methanol's oxygen, while the protonated DBU is hydrogen bonded to the nitrogen of the former isocyanate group (Figure 4). The relative stability of the IM in gas and solvent phase differs significantly ($\text{DDE}_{0\text{gas-THF}} = 65.4$ kJ/mol).

The reaction was continued with TS2 within which the proton transfer from the catalyst to the product will occur. It can be seen that in TS2 one N-H distance decreased, while the other increase compared to the IM (Figure 4). The zero-point corrected relative energy of TS2 calculated in THF is -108.68 kJ/mol, which is slightly lower than in the case of IM ($\text{DE}_0 = -102.89$ kJ/mol) (Table 1, Figure 5). Due to the potential limitations of the method, attempts to locate TS2 were not successful in gas phase. The penultimate step in this reaction mechanism is the formation of the product complex (PC). It is a bimolecular complex of the final product methyl phenyl-carbamate and DBU (Figure 4). The final step is the separation of the catalyst from the product. All in all, the solvent has a quite large effect on the energetics of the catalytic reaction (Table 1). The presence of the catalyst changes significantly the reaction mechanism compared to the catalyst-free case. The product will form through a multi-step pathway and the relative energies are also significantly reduced by the presence of DBU (Figure 3 and Figure 5).

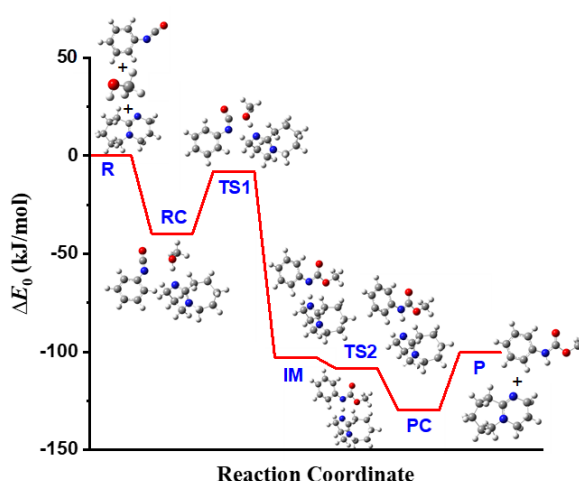


Figure 5

Energy diagram (zero-point corrected) of the phenyl isocyanate (PhNCO) and methanol reaction in the presence of DBU calculated at the B3LYP/6-31G(d) level of theory in THF using the SMD implicit solvent model at 298.15 K and 1 atm. R: reactants+catalyst (PhNCO+MeOH+DBU), RC: reactant complex, TS: transition state, IM: intermediate, PC: product complex, P: product

CONCLUSION

Catalysts play a fundamental role in industrial chemical transformations. Most of the chemicals are made through catalytic processes since catalysts provide energetically more favorable reaction pathways compared to noncatalytic processes. The urethane formation between phenyl isocyanate and methanol as a model system in the presence of a secondary ketimine (DBU) catalyst was investigated. Using DFT calculation at the B3LYP/6-31G(d) level of theory the reaction was investigated in gas phase and in organic solvent (THF). The catalyst-free reaction was also computed and used as a reference. The results showed that the highest energy point along the reaction in the presence of DBU was below the entrance level ($\Delta E_{0\text{gas}} = -9.69$ kJ/mol, and $\Delta E_{0\text{THF}} = -8.04$ kJ/mol), while the corresponding value in the catalyst-free case was above 100 kJ/mol in both gas phase and THF ($\Delta E_{0\text{gas}} = 107.93$ kJ/mol, and $\Delta E_{0\text{THF}} = 110.22$ kJ/mol). Thus, by adding a catalyst to the system, the activation energy is significantly reduced, and urethane formation is promoted. A multi-step catalytic process revealed, and further studies will be carried out to understand other aspects of the reaction. Based on the current and upcoming results, the design of new catalysts will be possible in the near future.

ACKNOWLEDGMENT

This research is supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, which aimed to promote the cooperation between the higher education and the industry. BF thanks the support by the UNKP-20-4 New National Excellence Program of The Ministry for Innovation and Technology from the source of the National Research, Development, and Innovation Fund (Hungary). The GITDA (Governmental Information-Technology Development Agency, Hungary) is gratefully acknowledged for allocating computing resources used in this work.

REFERENCES

- [1] Wisniak, J. (2010). The History of Catalysis. From the Beginning to Nobel Prizes. *Educuation Chimcia*, Vol. 21, No. 1, pp. 60–69, [http://doi.org/10.1016/S0187-893X\(18\)30074-0](http://doi.org/10.1016/S0187-893X(18)30074-0)
- [2] Yanping, Y. (2018). The development of polyurethane. *Mater. Sci. Mater. Rev.*, Vol. 1, No. 1, pp. 1–8, <http://doi.org/10.18063/msmr.v1i1.507>.
- [3] Silva, A. L., Bordado, J. C. (2004). Recent developments in polyurethane catalysis: Catalytic mechanisms review. *Catal. Rev. – Sci. Eng.*, Vol. 46, No. 1, pp. 31–51, <http://doi.org/10.1081/CR-120027049>.
- [4] Gates, B. C., Huber, G. W., Marshall, C. L., Ross, P. N., Siirola, J., Wang, Y. (2008). Catalysts for emerging energy applications. *MRS Bull.*, Vol. 33, No. 4, pp. 429–435, <http://doi.org/10.1557/mrs2008.85>.

-
- [5] Lloyd, L. (2008). *Handbook of industrial catalysts*. New York, NY, USA: Springer.
- [6] Dworakowska, S., Bogdał, D., Zaccheria, F., Ravasio, N. (2014). The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials. *Catal. Today*, Vol. 223, pp. 148–156, <http://doi.org/10.1016/j.cattod.2013.11.054>.
- [7] Cavaco, L. I. (2012). *Polyurethanes properties, structure and applications*. New York: Nova Science Publishers, Inc.
- [8] Ruiduan, L., Ling, L., Yanjie, L., Ben, W., Jia Jun, Y., Jibo, Z. (2018). Research Progress of Amine Catalysts for Polyurethane. Vol. 1, No. 1, pp. 54–57, <http://doi.org/10.26480/icnmim.01.2018.54.57>.
- [9] Hatanaka, M. (1993). DFT Analysis of Catalytic Urethanation. *Bull. Chem. Soc. Jpn.*, Vol. 84, No. 9, pp. 933–935, <http://doi.org/10.1246/bcsj.20110144>.
- [10] Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, Vol. 98, No. 7, pp. 5648–5652, <http://doi.org/10.1063/1.464913>.
- [11] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Menucci, B., Petersson G. A. et al. (2009). *Gaussian 09, Revision, E.01*. Gaussian, Inc.: Wallingford, CT, USA.