Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Physical Organic Chemistry. *Reference Object Identifier* – ROI: jbc-01/18-55-7-1
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/18-55-7-1
Submitted on June 18, 2018.

Quantum-chemical study methanolysis of diethyl carbonate catalyzed by bases and Lewis acids

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Keywords: polycarbonates, alcoholysis, catalysis, mechanism.

Abstract

Mechanism of diethylcarbonate transesterification with methanol using sodium methylate and zinc acetate as catalysts resulting in dimethylcarbonate by means of density functional method has been investigated. Transesterification proceeds gradually and leads to methylethylcarbonate intermediate formation.

Reaction between methylethylcarbonate and sodium methylate proceeds according to "addition-elimination" mechanism and formation of prereaction complexes occurs. Sodium atom in these complexes is hold near carbonate fragment by Van der Waals and electrostatical forces. In these fragments, increase in nucleophilic and electron-donating properties of methoxy fragment and increase in electron-acceptor properties of carbonate fragment are observed. Prereaction complexes via low free energy barriers show transition to bipolar ions. In these ions, carbon's carbonyl atom of carbonates obtains tetraedrical structure. These intermediates due to beta-transformation result either in methylethylcarbonate or diethylcarbonate formation. When reaction catalyzes by sodium methylate, rate-limiting step is bipolar intermediate formation stage. Free energy barrier of this stage is fully depended on entropic part. Activation enthalpies of this stage has negative values.

Methanolysis reactions of diethyl- and methylethylcarbonates using zinc acetate as catalyst proceed according to mechanism of nucleophilic substitution near carbon's carbonyl atom. Reactions are accompanied by prereaction triple complexes formation; they show transition to methylethyl- or dimethylcarbonate through approved transition states. Comparison of thermodynamic parameters of activation shows that transesterification using sodium methylate as catalyst is more preferable than using zinc acetate as catalyst.

References

[1] E. Feghali, T. Cantat. Room Temperature Organocatalyzed Reductive Depolymerization of Waste Polyethers, Polyesters, and Polycarbonates. *Chem Sus Chem.* **2015**. Vol.8. No.6. P.980-984.
[2] I.A. Ignatyev, W. Thielemans, B.V. Bake. Recycling of Polymers: A Review. *Chem Sus Chem*. **2014**. Vol.7. No.6. P.1579-1593.
[3] E.V. Antonakou, D.S. Achilias. Recent Advances in Polycarbonate Recycling: A Review of Degradation Methods and Their Mechanisms. *Waste Biomass Valor.* **2013**. Vol.4. Iss.1. P.9-21
[4] D.S. Achilias, E.V. Antonakou, E. Koutsokosta, A.A. Lappas. Chemical recycling of polymers from Waste Electric and Electronic Equipment. *J. Appl. Polymer Sci.* **2009**. Vol.114. No.1. P.212-221.
[5] L. Méndez-Liñán, F.J. López-Garzón, M. Domingo-García, M. Pérez-Mendoza. Carbon Adsorbents from Polycarbonate Pyrolysis Char Residue: Hydrogen and Methane Storage Capacities. *Energy Fuels*. **2010**. Vol.24. No.6. P.3394-3400.
[6] S.-J. Chiu, S.-H. Chen, C.-T. Tsai. Effect of metal chlorides on thermal degradation of (waste) polycarbonate. *Waste Management*. **2006**. Vol.26. No.3. P.252-259.
[7] R. Arai, K. Zenda, K. Hatakeyama, K. Yui, T. Funazukuri. Reaction kinetics of hydrothermal depolymerization of poly(ethylene naphthalate), poly(ethylene terephthalate), and polycarbonate with aqueous ammonia solution. *Chem. Eng. Sci.* **2010**. Vol.65. No.1. P.36-41.
[8] Z. Pan, I.-M. Chou, R. C. Burrus. Hydrolysis of polycarbonate in sub-critical water in fused silica capillary reactor with in situRaman spectroscopy. *Green Chemistry*. **2009**. Vol.11. P.1105-1107.
[9] M. Watanabe, Y. Matsuo, T. Matsushita, H. Inomata, T. Miyake, K. Hironaka. Chemical recycling of polycarbonate in high pressure high temperature steam at 573 K. *Polymer Degradation and Stability*. **2009**. Vol.94. No.12. P.2157-2162.

[10] Y. Huang, S. Liu, Z. Pan. Effects of plastic additives on depolymerization of polycarbonate in sub-critical water. *Polymer Degradation and Stability*. **2011**. Vol.96. No.8. P.1405-1410.
[11] Z. Pan, Z. Hu, Y. Shi, Y. Shen, J. Wang, I.-M. Chou. Depolymerization of polycarbonate with catalyst in hot compressed water in fused silica capillary and autoclave reactors. *RSC Advances*. **2014**. Vol.4. No.38. P.19992-19998.
[12] F.-S. Liu, Z. Li, S.-T. Yu, X. Cui, C.-X. Xie, X.-P. Ge. Methanolysis and Hydrolysis of Polycarbonate Under Moderate Conditions. *J. Polym. Envir.* **2009**. Vol.17. No.3. P.208-211.
[13] G. Grause, N. Tsukada, W. J. Hall, T. Kameda, P. T. Williams, T. Yoshioka. High-Value Products from the Catalytic Hydrolysis of Polycarbonate Waste. *Polymer Journal.* **2010**. Vol.42. P.438-442.
[14] G. Grause, K. Sugawara, T. Mizoguchi, T. Yoshioka. Pyrolytic hydrolysis of polycarbonate in the presence of earth-alkali oxides and hydroxides. *Polymer Degradation and Stability*. **2009**. Vol.94. No.7. P.1119-1124.
[15] H. Tagaya, K. Katoh, J. Kadokawa, K. Chiba. Decomposition of polycarbonate in subcritical and supercritical water. *Polymer Degradation and Stability*. **1999**. Vol.64. No.2. P.289-292.
[16] T. Yoshioka, K. Sugawara, T. Mizoguchi, A. Okuwaki. Chemical Recycling of Polycarbonate to Raw Materials by Thermal Decomposition with Calcium Hydroxide/Steam. *Chem. Lett*. **2005**. Vol.34. No.3. P.282-283.
[17] K. Hatakeyama, T. Kojima, T. Funakuzuri. Chemical recycling of polycarbonate in dilute aqueous ammonia solution under hydrothermal conditions. *J. Mater. Cycles and Waste Management*. **2014.** Vol.16. No.1. P.124-130.
[18] S. Hata, H. Goto, E. Yamada, A. Oku. Chemical conversion of poly(carbonate) to 1,3-dimethyl-2-imidazolidinone (DMI) and bisphenol A: a practical approach to the chemical recycling of plastic wastes. *Polymer*. **2002**. Vol.43. No.7. P.2109-2116.
[19] S. Hata, H. Goto, S. Tanaka, A. Oku. Viable utilization of polycarbonate as a phosgene equivalent illustrated by reactions with alkanedithiols, mercaptoethanol, aminoethanethiol, and aminoethanol: A solution for the issue of carbon resource conservation. *J. Appl. Polymer*. **2003**. Vol. 90. No.11. P.2959-2968.
[20] L.-C. Hu, A. Oku, E. Yamada. Alkali-catalyzed methanolysis of polycarbonate. A study on recycling of bisphenol A and dimethyl carbonate. *Polymer*. **1998**. Vol.39. No.16. P.3841-3845.
[21] H. Jie, H. Ke, Z. Qing, C. Lei, W. Yongqiang, Z. Zibin. Study on depolymerization of polycarbonate in supercritical ethanol. *Polymer Degradation Stability*. **2006**. Vol.91. No.10. P.2307-2314.
[22] F. Liu, Z. Li, S. Yu, X. Cui, X. Ge. Environmentally benign methanolysis of polycarbonate to recover bisphenol A and dimethyl carbonate in ionic liquids. *J. Hazar. Mater*. **2010**. Vol.174. No.1-3. P.872-875.
[23] F. Liu, L. Li, S. Yu, Z. Li, X. Ge. Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]. *J. Hazar. Mater*. **2011**. Vol.189. No.1-2. P. 249-254.
[24] R. Piñero, R. Piñero, J. García, M. J. Cicero. Chemical recycling of polycarbonate in a semi-continuous lab-plant. A green route with methanol and methanol–water mixtures. *Green Chemistry*. **2005**. Vol.7. No.5. P.380-387.
[25] L. Rosi, M. Bartoli, A. Undria, M. Frediani, P. Frediani. Synthesis of dianols or BPA through catalytic hydrolyisis/glycolysis of waste polycarbonates using a microwave heating. *J. Molec. Catal. A: Chemical*. **2015**. Vol.408. P.278-286.
[26] A. Oku, S. Tanaka, S. Hata. Chemical conversion of poly(carbonate) to bis(hydroxyethyl) ether of bisphenol A. An approach to the chemical recycling of plastic wastes as monomers. *Polymer*. **2000**. Vol.41. No.18. P.6749-6753.
[27] C.-H. Lin, H.-Y. Lin, W.-Z. Liao, S. A. Dai. Novel chemical recycling of polycarbonate (PC) waste into bis-hydroxyalkyl ethers of bisphenol A for use as PU raw materials. *Green Chemistry*. **2007**. Vol.9. P.38-43.
[28] M.M.A. Nikje. Glycolysis of polycarbonate wastes with microwave irradiation. *Polimery*. **2011**. Vol.56. P.381-384.
[29] D. Kim, B. Kim, Y. Cho, M. Han, B.-S. Kim. Kinetics of Polycarbonate Glycolysis in Ethylene Glycol. *Ind. Eng. Chem. Res.* **2009**. Vol.48. No.2. P.685-691.
[30] M.V. Korshunov, N.I. Kurshev, A.Ya. Samuilov, E.D. Prokhorova, and Ya.D. Samuilov. Quantum-chemical studying of noncatalytic methanolysis of diethyl carbonate. *Butlerov Communications.* **2018**. Vol.54. No.4. P.1-12. DOI: 10.37952/ROI-jbc-01/18-54-4-1
[31] M. Taguchi, Y. Ishikawa, S. Kataoka, T. Naka, T. Funazukuri. CeO2 nanocatalysts for the chemical recycling of polycarbonate. *Catal. Commun.* **2016**. Vol.34. P.93-97.

[32] A.D. Becke, Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. *J. Chem. Phys.* **1992**. Vol.96. P.2155-2160.
[33] A.D. Becke, Density-functional thermochemistry. II. The effect of the Perdew–Wang generalized-gradient correlation correction. *J. Chem. Phys.* **1992**. Vol.97. P.9173-9177.
[34] A.D. Becke. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**.Vol.98. P.5648-5652.
[35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.1, Gaussian, *Inc.,Wallingford CT,* **2009**.
[36] The chemistry of the hydroxyl group. Ed. S. Patai. *London: Wiley.* **1971**. 1236p.
[37] J.F.O. Granjo, N.M.C. Oliveira. Process Simulation and Techno-Economic Analysis of the Production of Sodium Methoxide. *Ind. Eng. Chem. Res.* **2016. Vol.55**. No.1. P.156-167.
[38] S. Gryglewicz. Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresource Technology*. **1999**. Vol.70. No.3. P.249-253.
[39] L.C. Meher, D.Vidya, S.S.N. Naik. Technical aspects of biodiesel production by transesterification – a review. *Renew. Sustain. Ener. Rev.* **2006**. Vol.10. No.3. P.248-268.
[40] M. Shakourian-Fard, G. Kamath, K. Smith, H. Xiong, S.K.R.S. Sankaranarayanan. Trends in Na-Ion Solvation with Alkyl-Carbonate Electrolytes for Sodium-Ion Batteries: Insights from First-Principles Calculations. *J. Phys. Chem. C.* **2015**. Vol.119. No.40. P.22747-22759.
[41] A.V. Cresce, S.M. Russell, O. Borodin, J.A. Allen, M.A. Schroeder, M. Dai, J. Peng, M.P. Gobet, S.G. Greenbaum, R.E. Rogers, K. Xu. Solvation behavior of carbonate-based electrolytes in sodium ion batteries. *Phys. Chem. Chem. Phys.* **2017**. Vol.19. No.1. P.574-586.
[42] B.B. Snider, E. Ron. The mechanism of Lewis acid catalyzed ene reactions. *J. Am. Chem. Soc.* **1985**. Vol.107. No.26. P.8160-8164.
[43] Lewis Acids in Organic Synthesis. Ed. H. Yamamoto. *Weinheim: Wiley-VCH.* **2002**. 522p.
[44] A.Ch. Shekhar, A.R. Kumar, G. Sathaiah, V.L. Paul, M. Sridhar, P.Sh. Rao. Facile *N*-formylation of amines using Lewis acids as novel catalysts. *Tetrahedron Lett.* **2009**. Vol.50. No.50. P.7099-7101.
[45] E. Quaranta, D. Sgherza, G. Tartaro. Depolymerization of poly(bisphenol A carbonate) under mild conditions by solvent-free alcoholysis catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene as a recyclable organocatalyst: a route to chemical recycling of waste polycarbonate. *Green Chemistry.* **2017**. Vol.19. No.22. P.5422-5434.
[46] T. Do, E.R. Baral, J.G. Kim. Chemical recycling of poly(bisphenol A carbonate): 1,5,7-Triazabicyclo[4.4.0]-dec-5-ene catalyzed alcoholysis for highly efficient bisphenol A and organic carbonate recovery. *Polymer.* **2018**. Vol.143. P.106-114.
[47] Y. Zhao, X. Zhang, X. Song, F. Liu. Highly Active and Recyclable Mesoporous Molecular Sieves CaO(SrO,BaO)/SBA-15 with Base Sites as Heterogeneous Catalysts for Methanolysis of Polycarbonate. *Catal. Lett.* **2017**. Vol.147. No.12. P.2940-2949.