



Thematic section: Quantum-Chemical Research.

Subsection: Organic Chemistry.

Full Paper

The Reference Object Identifier – ROI-jbc-A/21-2-3-10

The Digital Object Identifier – DOI: 10.37952/ROI-jbc-A/21-2-3-10

Received 10 June 2021; Accepted 13 June 2021

Theoretical study of the mechanism of metathesis of *N*-methylformamide with dimethyl carbonate with the participation of σ -bonds

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Keywords: dimethyl carbonate, isocyanates, carbamates.

Abstract

Using the density functional method B3LYP/6-311++G(*df,p*), the mechanism of metathesis of *N*-methyl-formamide with dimethyl carbonate with the participation of σ -bonds, leading to the formation of *N,O*-dimethylcarbamate, has been considered. The reaction can proceed as a bimolecular interaction, and as a transformation catalyzed by alcohols (monomers and dimers). Methanol catalyzed reactions can develop in two different directions.

Bimolecular metathesis is characterized by a large value of the enthalpy of activation and a small value of the entropy of activation. All this leads to the appearance of a large free energy barrier on the path of transformation. The reactions proceeding by this mechanism must be high-temperature. In the reaction discussed, a hydrogen atom is transferred from the formyl group of the formamide molecule to the carbonyl carbon atom of dimethyl carbonate.

In the first catalytic route, the transfer of a hydrogen atom to the carbonyl carbon atom of dimethyl carbonate occurs from the hydroxyl group of the monomer or dimer of methanol, and the hydrogen atom in the formyl group of *N*-methylformamide is transferred to the monomer or dimer of methanol.

In the second catalytic route, as in the bimolecular reaction, a hydrogen atom at the formyl group of *N*-methylformamide is transferred to the carbonyl carbon atom of dimethyl carbonate. The difference lies in the fact that a new C-O bond is formed due to the attack by the oxygen atom of the monomer or dimer of methanol on the carbonyl carbon atom of *N*-methylformamide.

All reactions proceed through cyclic coordinated transitional states in which the destruction of old and the formation of new chemical bonds occur simultaneously.

For citation: Dmitry N. Khrizanforov, Tanzilya A. Valiullova, Margarita A. Dolgusheva, Alexander Ya. Samuilov, Yakov D. Samuilov. Theoretical study of the mechanism of metathesis of *N*-methylformamide with dimethyl carbonate with the participation of σ -bonds. *Butlerov Communications A*. **2021**. Vol.2. No.3. Id.10. DOI: 10.37952/ROI-jbc-A/21-2-3-10

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