

## Influence of solvent nature and aliphatic amine structure on the rate of ethylene carbonate aminolysis

© Dmitry A. Gordeev,<sup>1</sup> and Sergey N. Mantrov<sup>2\*†</sup>

<sup>1</sup> SRCHTEOC. Shosse Entuziastov, 38. Moscow, 111123. Russia.

<sup>2</sup> D. Mendeleev University of Chemical Technology of Russia. Miusskaya pl., 9. Moscow, 125047. Russia. Phone: +7 (495) 944-32-73. E-mail: mantrovsn@yandex.ru

\*Supervising author; †Corresponding author

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### Abstract

The reaction of primary aliphatic amines with ethylene carbonate at 30 °C in various solvents were studied. It is shown that studied interaction occurs two parallel paths. One of them is the second order for reacting amine, which suggests the attack of ethylene carbonate by amine dimers. The second route is described as autocatalytic aminolysis process, wherein the reaction product – 2-hydroxyethyl butylcarbamate accelerates of the reaction. Based on the experimental data suggested a theoretical foundation of the established reaction scheme, which is in a good agreement with the results of quantum chemical calculations presented in the literature. The influence of the reaction environment on the process of ethylene carbonate aminolysis by *n*-butylamine was studied by varying the solvent. Both reaction routes was fitted by Palm-Koppel correlation equations. It is shown that parameters of reaction medium polarity and acidity positively influence on the autocatalytic reaction route, while reaction of the ethylene carbonate with amine dimers accelerated by solvents with high basicity and polarizability values. However, the influence of the reaction medium itself has a weak character, as a whole the rate constants for the mixture ethylene carbonate : inert low-polar aprotic solvent (50:50) depend little on the solvent properties. This behavior is explained by the "effect of the cell" that is caused by solvent in homogeneities due to the high polarity of the ethylene carbonate. Under these conditions ethylene carbonate gives self-associates surrounded, by which the interaction occurs. The features of ethylene carbonate aminolysis by various primary aliphatic amines were studied. Based on the experimental data was obtained Taft correlation equations for two routes of ethylene carbonate aminolysis. In both cases for the calculation is proposed to use parameters of the steric substituents considering hyperconjugation component. It is found that the reaction rate of ethylene carbonate with amine dimers much more dependent on the structure of the amine than the rate of the autocatalytic reaction. For both routes, the process speeding up is observed with increasing electron-donating properties of the amine substituent. However, the bulky group in the amine results in interaction slowing.

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