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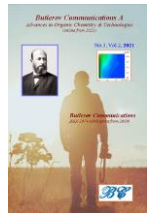

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Characterization of the thermodynamic parameters of the reactions of urea with methanol associates by the quantum-chemical density functional method

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Abstract

The free energies, enthalpies, and entropies of reactions of urea with a monomer, linear dimer, and a trimer of methanol with the sequential formation of *O*-methylcarbamate and dimethylcarbonate were calculated by the quantum-chemical method of the density functional M06/6-311++G(df,p).

The first stage of interaction of urea with methanol monomer is exothermic, the second stage is endothermic. The enthalpies and entropies at each stage of conversion increase with an increase in the degree of association of methanol. The relative changes in free energies are determined by the entropies of the reactions. At the stage of interaction of urea with methanol with the formation of *O*-methyl carbamate, and at the stage of formation of dimethyl carbonate, reactions with methanol associates are thermodynamically more preferable than transformations with the participation of methanol monomer.

The equilibrium constants for the reaction of methanol monomer with urea decrease significantly with increasing temperature. The equilibrium constants of the reaction with the participation of the methanol dimer are large, and they ensure the practical irreversibility of the process. The conversions of the methanol trimer with urea are characterized by even higher equilibrium constants. In this case, the equilibrium constants increase with increasing temperature.

The reactions of *O*-methylcarbamate with methanol dimer and trimer have large equilibrium constants, which increase with increasing temperature. The equilibrium constants for the reactions of *O*-methylcarbamate with a methanol dimer and trimer provide an almost irreversible course of interactions even at moderate temperatures.

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