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Theoretical study of dimethylcarbonate production by urea alcoholysis

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Abstract

Using the density functional method M06, the mechanisms of non-catalytic reactions of transesterification of urea with methanol with the formation of dimethyl carbonate, as well as in catalysis with zinc oxide and acetate, were studied. The transesterification proceeds stepwise with the intermediate formation of methyl carbamate.

The non-catalytic process of transesterification of urea with methanol proceeds by the mechanism of nucleophilic S_N2 substitution and is accompanied by the formation of pre-reaction complexes, which through synchronous transition states turn into post-reaction complexes, decomposing into ammonia and methyl carbamate in the first stage and dimethyl carbonate in the second. It has been established that methanol associates can take part in these reactions. Their participation is preferable both kinetically and thermodynamically. An analysis of the equilibrium constants of the reaction of urea with methanol at various temperatures showed that in a wide temperature range their values remain large in the first stage – the formation of methyl carbamate and become significantly reversible in the second – the conversion of methyl carbamate to dimethyl carbonate.

Reactions involving acetate and zinc oxide proceed through the same stages as non-catalytic interactions. In the case of zinc acetate catalyzed reactions, if methanol monomer is involved in the reaction, the reaction of formation of methyl carbamate has a lower activation barrier compared to the reaction of conversion of methyl carbamate to dimethyl carbonate. If a methanol dimer is involved in the reaction, both reactions have a practically equal activation barrier. In the case of zinc oxide catalyzed interactions, reactions involving a methanol dimer were not detected.

The participation of the catalyst leads to a significant decrease in activation barriers, and a more significant decrease occurs in the case of catalysis with zinc oxide. The reason for the different catalytic activity, in our opinion, is the difference in the charges on the urea carbon atom in the pre-reaction complexes.

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