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Prediction of the reactivity of oleum sulfonating agents upon carbamide sulfonation

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Abstract

In this work, a research of the reactivity of sulfonating agents of oleum during sulfonation of carbamide was carried out. Cation HSO_3^+ and sulfur trioxide in monomeric, dimeric, and trimeric forms were chosen as sulfonating agents. The modeling was carried out by the density functional theory (B3LYP5/aug-cc-pVDZ) and the second-order Möller-Plesset perturbation theory (MP2/aug-cc-pVDZ). Simulation was carried out in a vacuum and a polar solvent, which was taken as 100% sulfuric acid. The solvent was taken into account using the COSMO model.

The evaluation of the reactivity of sulfonating agents was carried out on the basis of molecular modeling of sulfonating agents and carbamide. The reactivity descriptors were chosen as the reactivity criteria, such as: energies and the location of the highest occupied molecular orbital and lowest unoccupied molecular orbital, charges on atoms, molecular electrostatic potential, absolute hardness and electrophilicity index.

It was determined that carbamide is a fairly hard Lewis base, the absolute hardness in vacuum is 6.072, and in a solvent it is 6.635, so charge control is preferable for its sulfonation reaction.

Based on this, the greatest preference in the analysis of reactivity indices was given to atomic charges and molecular electrostatic potential.

According to the results of the analysis, it was revealed that the highest activity of the studied sulfonating agents is possessed by cation HSO_3^+, as it has the highest partial charges on atoms (+3.29 in vacuum, +3.38 in a solvent), has the highest electrophilicity (13.45 in a vacuum, 5.35 in a solvent) and does not have steric hindrance factor in contact with the carbamide molecule. Among the forms of sulfur trioxide, preference can be given to both monomeric (highest activity, but there are steric hindrance factor) and trimeric (least steric hindrance factor).

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