

Research the sulfonation mechanism of urea in oleum by density functional theory calculation

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Abstract

The work investigates the sulfonation mechanism of urea in oleum, which is used in the synthesis of sulfamic acid. In addition to sulfamic acid, carbon dioxide is also released in the process. The method of density functional theory was used to model the sulfonation reaction using cation HSO_3^+ as a true sulfonating agent.

All elementary acts, intermediates, and transition states of the reaction are determined. Six possible complexes of urea and cation HSO_3^+ are identified, of which two are reactive, formed through the bonding of the nitrogen atom of urea and sulfur of the HSO_3^+ . The most stable complex is formed through the bonding of the oxygen atom of urea and sulfur of the HSO_3^+ , from the reactive complexes it is separated by an activation barrier of 149.86 kJ/mol, so its formation inactivates the starting reagents and their return to a reactive state is possible only through interaction with negatively charged particles.

The activation energies and thermal effects of the stages are calculated. The first stable intermediate of the process is isocyanic acid. Subsequently, isocyanic acid reacts with sulfuric by two mechanisms: the formation of urethane-like structures of $\text{NH}_2\text{COOSO}_3\text{H}$ or carbamic acid. The second mechanism is preferred since it requires much milder conditions.

Using the continuum models D-PCM and COSMO, the influence of the solvent on the reaction mechanism was studied. As a solvent, 100% sulfuric acid was taken.

The maximum activation energy of elementary stages according to the first mechanism was: 167.37 (COSMO) kJ/mol, 169.77 (D-PCM), without solvent 180.38 kJ/mol. By the second mechanism: 57.38 (COSMO) kJ/mol, 59.91 (D-PCM), without solvent 91.15 kJ/mol. The number of elementary acts is 6 for the first mechanism and 7 for the second.

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