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Computational Chemistry Modelling of Kinetics and Mechanism of the Esterification Reaction of Acetic Acid with Methanol

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Abstract

Esterification is an important reaction in various industrial and commercial processes such as biofuels, pharmaceuticals, solvents, and polymer synthesis [1,2]. The reaction involves heating a mixture of carboxylic acids and an excess of alcohols, but with an acid catalyst's presence, the equilibrium is reached in a shorter time. Therefore, kinetic and thermodynamic parameters affect the reaction. In the reaction study, the computational chemistry calculations based on Density Functional Theory (DFT) provide powerful tools to model and predict molecular properties [3]. This work uses DFT calculations to identify the critical elementary reaction pathways, to determine molecular geometries of reactants, products, transition state (TS) and intermediates. The simulation of the reaction mechanism was performed using the NEB-TS method (from Nudged Elastic Band with TS optimization) with the B3LYP functional and the 6-31G* basis set implemented in the ORCA 5.0 program package. The calculations (Fig.1 (a –d)) show that using an acid catalyst and changing the molar ratio of acetic acid to methanol affect the reaction, kinetic and thermodynamically. From this relative energy diagram, it can be seen that the non-catalytic reaction with acetic acid/methanol molar ratio (1:1) occurs in two steps (TS_1 and TS_2, Fig. 1(a)) with activation energy (Ea_2) of 200.06 kJ/mol. Adding the acid catalyst reduces the reaction pathway to a single step (TS1, Fig. 1 (b)). It forms the tetrahedral intermediate with lower activation energy (Ea_1 =192.85 kJ/mol). The simulation with a lower molar ratio of acetic acid/methanol (1:3) suggests the reaction mechanism with three steps (TS_1, TS_2, and TS_3), with an activation energy of 245.18 kJ/mol attributed to the hydrogen transfer from methanol to the hydroxyl group of the acetic acid (TS1, Fig. 1 (c)). The introduction of the acid catalyst (Fig.1 (d)) leads to a new mechanism in which the reaction takes place in two steps (TS_1 and TS_2), with the second being the determinant step (Ea_2 = 203.35 kJ/mol).

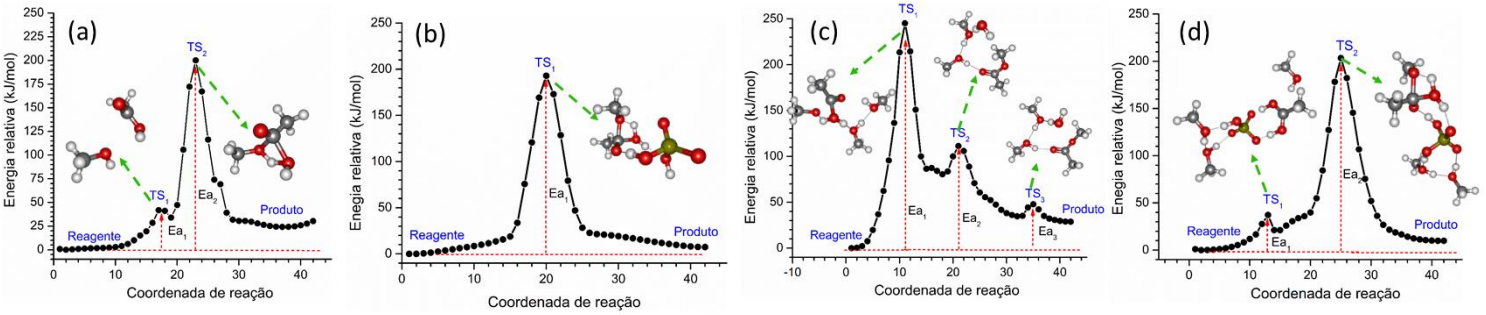

Figure 1. Relative energy profiles for the esterification reaction between acetic acid and methanol: (a) and (b) 1:1 molar ratio, (c) and (d) 1:3 molar ratio. (a) and (c) without (H_2SO_4) catalyst, (b) and (d) with (H_2SO_4) catalyst.

Keywords: Molecular modelling, Esterification mechanism, Acetic acid, Methanol

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