Mechanistic investigation of the uncatalyzed self-esterification reaction of L-lactic acid: a DFT study

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Abstract: Lactic acid is a bio-based organic acid derived from renewable agricultural resources. It has currently received great interest as an important reactant in many industrial synthetic processes, especially in the synthesis of environmentally friendly solvents and polymers, due to its nontoxic and biodegradable properties. However, the use of lactic acid as reactant is complicated, since the degree of intermolecular esterification of lactic acid to form linear dimer and higher oligomers increases over a concentration range of higher than 20 wt% aqueous lactic acid solutions. In this work, a comprehensive mechanistic investigation of the uncatalyzed self-esterification reaction of L-lactic acid at the molecular level was undertaken to understand the origin of such aforementioned behaviours. Two competing reaction pathways, i.e. a one-step concerted S_N2-like mechanism and a two-step concerted addition-elimination mechanism in the presence of the commonly assumed tetrahedral intermediate, were studied. The effects of the water and lactic acid molecules participating as proton mediators on the free energy barriers for the proton-transfer esterification reactions were also examined. Density functional theory (DFT) calculations at the M06-2X/6-311G(d,p) level establish that the intermolecular esterification of lactic acid is a reversible reaction and favorably proceeds through the two-step concerted mechanism, with the kinetically relevant step involving the reversible elimination of water. The formation of dimer and higher oligomer acids at low and moderate concentrations of aqueous lactic acid solutions is more likely to take place via the water-mediated proton transfer esterification mechanism whereas that at high concentrations should occur more favourably via the lactic acid-mediated proton transfer mechanism. Similar conclusions are also drawn from the intramolecular esterification studies of dimer and trimer of lactic acid.

Keywords: Lactic acid; DFT; Esterification; Proton transfer; Mechanism