

**SOLVENT EFFECTS ON THE KETO-ENOL TAUTOMERIC
EQUILIBRIUM OF TETRONIC AND ETHYL ACETOACETATE
CARBON ACIDS: A THEORETICAL STUDY**

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Abstract :

The solvent effects on the keto-enol tautomeric equilibriums of ethyl acetoacetate (EAA) and tetronic acid (TA) are theoretically investigated. The present study shows that the most stable keto tautomer of EAA corresponds to the trans diketo, E, Z form; while the most stable enol tautomer corresponds to the structure in which the enolization takes place at the carbonyl group. Our calculations also put in evidence that the keto tautomer of TA prefers the trans diketo, E, E form, while the most stable enol tautomer corresponds to the structure in which the enolization takes place at the carbonyl group. The calculated free energies indicate that, in polar solvents, the keto-enol equilibrium of EAA is shifted towards the keto tautomer, whereas the keto-enol equilibrium of TA is shifted toward the enol tautomer. The trends of the change of equilibrium constants with respect to the change of solvent polarity are well reproduced by both B3LYP and MP2 calculations. The present study shows that the enthalpic term is predominant in the determination of the calculated equilibrium constants and the entropic effect on the calculated Gibbs free energies is found to be very small and has little influence on the studied keto-enol tautomeric equilibriums.

Keywords : Ethyl acetoacetate; tetronic acid; solvent effects; keto-enol equilibrium; theoretical calculations.

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