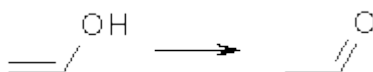


CATALYZING THE KETO-ENOL TAUTOMERIZATION

Proton and hydrogen transfers can be catalyzed by many things. Da Silva shows that carboxylic acids can catalyze the hydrogen shift that converts an enol into a carbonyl species.¹ The specific example is the ethenol to acetaldehyde tautomerization. This reaction has a barrier of 56.6 kcal mol⁻¹ (computed using the composite method G3SX).



With formic acid as the catalyst, the reactant is the hydrogen-bonded complex of ethanol with formic acid and the product is the complex of acetaldehyde with formic acid. The transition state is shown in Figure 1. The barrier is only 5.6 kcal mol⁻¹, a significant reduction. da Silva discusses how carboxylic acids might be catalyzing the enol-keto tautomerization in the troposphere and also in combustion reactions.

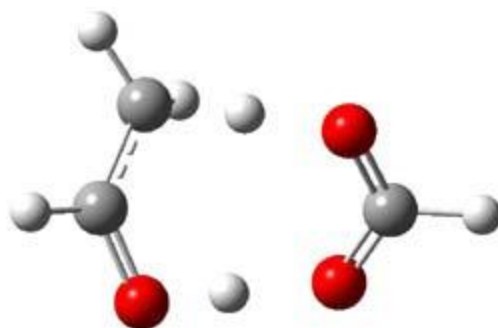


Figure 1. B3LYP/6-31G(2df,p) optimized TS of the formic acid catalyzed enol-keto tautomerization of acetaldehyde.

Source: <http://comporgchem.com/blog/?p=1259>