

# COMPUTATIONAL KINETICS STUDY OF ATMOSPHERIC RING-CLOSURE AND DEHYDRATION REACTIONS OF 1,4-HYDROXYCARBONYLS IN THE GAS PHASE<sup>a</sup>

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Several experimental studies have shown that 1,4-hydroxycarbonyls can undergo sequential reactions involving cyclization followed by dehydration to form dihydrofurans.<sup>b</sup> As dihydrofurans contain a double bond, they are highly reactive towards OH, O<sub>3</sub>, and NO<sub>3</sub> in the atmosphere. In this work, we investigate the energetics and kinetics of the cyclization and dehydration reaction steps associated with 4-hydroxybutanal (4-OH-BL), a prototypical 1,4-hydroxycarbonyl molecule using ab initio calculations. The cyclization step transforms 4-OH-BL into 2-hydroxytetrahydrofuran (2-OH-THF), which can subsequently undergo dehydration to form 2,3-dihydrofuran. Since the barriers associated with the cyclization and dehydration steps for 4-OH-BL are respectively 34.8 and 63.0 kcal/mol in the absence of any catalyst, both reaction steps are not feasible under atmospheric conditions. However, the presence of a suitable catalyst can significantly reduce the reaction barriers. Therefore, we investigate the effect of a single molecule of H<sub>2</sub>O, HO<sub>2</sub> radical, HC(O)OH, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> as catalysts on the reaction. We find that H<sub>2</sub>SO<sub>4</sub> lowers the reaction barriers the greatest, with the barrier for the cyclization step being reduced to -13.1 kcal/mol and that for the dehydration step going down to 9.2 kcal/mol, below their respective separated starting reactants. Interestingly, our rate calculations shows that HNO<sub>3</sub> provides the fastest rate due the combined effects of larger atmospheric concentration and reduced barrier. Thus, our study suggests that with acid catalysis the cyclization reaction step can readily occur for 1,4-hydroxycarbonyls in the gas phase. The 2-OH-THF products, once formed, likely undergo reaction with OH radicals in the atmosphere because the dehydration step involves a large barrier even with acid catalysis. The reaction pathways and rate constant for this reaction in the presence of molecular oxygen (<sup>3</sup>O<sub>2</sub>) were also investigated using computational chemistry over the 200-300K temperature range. The main products found from the 2-OH-THF + OH/<sup>3</sup>O<sub>2</sub> reactions are succinaldehyde + HO<sub>2</sub> and 2,3-dihydro-2-furanol + HO<sub>2</sub>.

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<sup>b</sup>Atkinson, R. et al. Atmos. Environ. 2008, 42, 5859; Ranney, A. P.; Ziemann, P. J. J. Phys. Chem. A 2016, 120, 2561.