

A MICROWAVE AND COMPUTATIONAL STUDY OF PIVALIC SULFURIC ANHYDRIDE AND THE PIVALIC ACID MONOMER: MECHANISTIC INSIGHTS INTO THE RCOOH + SO₃ REACTION

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Recent microwave studies in our laboratory have explored a series of carboxylic sulfuric anhydrides (RCOOSO₂OH, CSAs) that are formed from a cyclic reaction between carboxylic acids and SO₃. These studies have shown that the reaction occurs readily with a wide range of carboxylic acids. Moreover, the zero-point corrected activation energies are typically small and, in some cases even negative, but there remains uncertainty as to the factors which control the size and sign of the barrier. In this talk we present chirped-pulse and cavity microwave spectra of pivalic sulfuric anhydride, (CH₃)₃CCOOSO₂OH (PivSA), and explore the reaction pathway for its formation using computational chemistry. The reaction is found to be best described as a pericyclic heteroene reaction coupled with a 60 degree rotation of the t-butyl group. The process can occur through either a sequential (two-step) or a concerted (one-step) pathway. Based on zero-point corrected single-point CCSD(T) calculations, the sequential pathway has the lowest energy transition state, with a value of -0.52 kcal/mol relative to that of a pivalic acid - SO₃ precursor complex. This value represents the lowest barrier for SO₃ + carboxylic acid reactions studied to date. When compared with CF₃COOSO₂OH, which has the highest barrier among the systems previously studied, the results provide insight into the relative influence of the electronic and mass effects on the reaction energetics. Additional computational studies further explore the effects of the R group of the RCOOH reactants. Finally, as a precursor to the experimental work on PivSA, the microwave spectrum of the pivalic acid monomer was also recorded and is reported here as well.