AN EXTENSION OF CARBOXYLIC SULFURIC ANHYDRIDE FORMATION CHEMISTRY: THE REACTION OF SO_3 AND THIOBENZOIC ACID, AND THE MICROWAVE SPECTRUM OF THIOBENZOIC SULFURIC ANHYDRIDE

AARON J REYNOLDS, KENNETH J. KOZIOL, KENNETH R. LEOPOLD, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*.

Prior work in our laboratory has characterized the reaction between SO_3 and carboxylic acids to form carboxylic sulfuric anhydrides. In this study, this chemistry is shown to extend to thiocarboxylic acids. Thiobenzoic acid, C_6H_5COSH, was combined with sulfur trioxide in a supersonic jet using an on-the-fly mixing nozzle in which C_6H_5COSH vapor was introduced through a hypodermic needle into an Ar/SO_3 expansion. The product species, $C_6H_5C(=S)OSO_2OH$, was observed by Fourier transform microwave spectroscopy and its identity was confirmed by isotopic substitution as well as agreement with M06-2X/6-311++G(d,p) calculations. The calculations further indicate that the reaction is energetically favorable: the $SO_3 \cdot C_6H_5COSH$ complex is 15.2 kcal/mol lower in energy than C_6H_5COSH + SO_3 at infinite separation, and the anhydride product is 3.6 kcal/mol below that. The barrier to anhydride formation, starting with the complex, is 4.5 kcal/mol. Clearly, the anhydride forms rapidly in the jet, as the collisional phase of the expansion only lasts for several tens of microseconds.