Abstract

At a temperature of 500 °C vacuum pyrolysis of di-*tert*-butyl sulfoxide (*t*-Bu_2SO) solely leads to *tert*-butylsulfenic acid (*t*-BuSOH) by elimination of 2-methylpropene. At temperatures above 500 °C the intermediate, *tert*-butylsulfenic acid, may decompose via two competing intramolecular reaction pathways forming HSOH or its energetically less stable isomer H_2OS. The latter molecule may either reversibly rearrange into HSOH or decompose into H_2O and sulfur atoms. The pyrolysis products are characterized by means of mass spectrometry and matrix isolation as well as rotational-resolved gas phase IR spectroscopy. Quantum chemical calculations support the experimental results. The decomposition routes of di-*tert*-butyl sulfoxide and of the primary intermediate, *tert*-butylsulfenic acid, are discussed on the basis of a computational study performed at the B3LYP/6-311G* and second-order Møller-Plesset (MP2/6-311G*) levels of theory.

Several new routes to synthesize HSOH by RF-discharge of appropriate starting compounds in the gas phase are investigated. According to the observed rotational-torsional spectra HSOH can be generated by RF-discharge of mixtures of H_2O/H_2S, H_2S/N_2O, CS_2/H_2O as well as S_8/H_2O.

The previously unknown isotopomer HSOD is generated in a RF-discharge of elemental sulfur and HDO (H_2O and D_2O, 1:1) and is characterized by its rotational-torsional spectra.