

SYNTHESIS AND PRELIMINARY SPECTROSCOPIC IDENTIFICATION OF HOSH

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Hydrogenthioperoxide or oxadisulfane, H-O-S-H, has been synthesized in two ways.

1. by flash vacuum pyrolysis of di-*tert*-butylsulfoxide
2. by radio frequency (RF) discharge of H₂S and H₂O

(1) The pyrolysis at the temperature of 500°C gave *tert*-butylsulfenic acid, *t*-BuSOH and its S-protonated isomer *t*-BuS(O)H in almost quantitative yield as judged from the mass and IR spectra. These were the steps which provided the precursor which at 1100°C produced the molecule HOSH. The method with which finally confirmed the gas phase existence of HOSH was high resolution rotational spectroscopy.

(2) The transient species oxadisulfane (HSOH) has long been sought due to its extraordinary position between the well known molecules hydrogen peroxide (H₂O₂) and disulfane (H₂S₂). Our investigations into the flash vacuum pyrolysis of di-*tert*-butylsulfoxide led to the first gas phase synthesis of HSOH to yielded spectra with explicit structural information. After optimization of the reaction conditions by mass spectrometry IR spectra of the products were obtained. The ab initio structure (CCSD(T)/cc-pVQZ) of the unbranched structure (skew chain) of HSOH has been calculated. The comparison of the observed vibrational bands to the predicted normal vibrations (CCSD(T)/cc-pVTZ) supplies the evidence for the formation of this catenated isomer of HSOH in the gas phase. Furthermore results of DFT calculations (B3LYP/6-311G+(2d,p)) could confirm the presence of the O- and S- protonated structures of *tert*-butylsulfenic acid by their characteristic IR transitions. It may thus be concluded that the latter isomer plays an important role as a key intermediate in the generation of HSOH via a five-membered cyclic transition state. Recently we succeeded in obtaining the first rotational spectroscopic data of HSOH by recording the characteristic pattern of its ^rQ₁-branch.