

ABSTRACT

The mechanisms of the interactions of HOSO \cdot and CH $_3$ SO \cdot radicals with water, formic acid and sulfuric acid were studied and characterized using extensive molecular modeling based on density functional theory (DFT) and ab initio methods. I have systematically examined structural data and binding energies as well as thermodynamic and spectroscopic properties of the complexes formed in these interactions. Monomers associate in the complexes mainly through hydrogen bonding. The HOSO \cdot radical complexes are generally more stable than the corresponding complexes of the CH $_3$ SO \cdot radical, the increased number of H bonds in the complex, although weak, leads to the greater stability. Complex formations induce a large spectral red-shift and an enhancement of the IR intensity for the H-bonded OH stretching vibrations relative to the modes in the monomers forming the complex. There are a good correlations of the spectral shifts with the OH bonds lengthening. Calculated vertical excitation energies for all HOSO \cdot and CH $_3$ SO \cdot complexes differ insignificantly from the values for free radicals, suggesting that the radicals and complexes would not be easily distinguishable using standard UV/vis absorption spectroscopy. The dominant electronic transitions for the most identified complexes occur at wavelengths below 300 nm, implying that the complexes are expected not to photolyze under sunlight, thus, they are photochemically stable.

Further, the effect of water molecules on the direct hydrogen abstraction from HOSO \cdot by \cdot NO $_2$ were investigated. The potential energy surface for naked reaction and one or two water molecules catalyzed reactions are qualitatively identical but shifted to more negative energies. The results demonstrate that barrier for the direct hydrogen abstraction is low and the barrier for the one water catalyzed reaction decreases practically to zero. The second water molecules have no further effect either on the barrier height nor on the mechanism, thus, already in the presence of a single water molecule the hydrogen abstraction process becomes barrierless. The process is spontaneous and very feasible under atmospheric conditions.

Subsequent studies on the thermodynamic parameters for the deactivation of HOSO \cdot radical and its complexes with water and formic acid molecules in the reactions with the hydrogen atoms and the hydroxy radicals have shown that the complex transformations into the final products are less exothermic compared to the deactivation of the free radical. On the other hand, Gibbs free energy changes remain almost the same due to the increased entropy contributions.

Keywords: hydrogen-bonded complexes, atmospheric concentrations, water-mediated radical reactions, quantum chemical calculations