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Stabilization of metastable hydrogen trioxide (HOOOH) and the hydrotrioxyl radical (HOOO$^\cdot$) by complexation with sulfuric acid. A theoretical study

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ABSTRACT

The formation of bimolecular complexes of HOOOH and the HOOO$^\cdot$ radical with sulfuric acid (H_2SO_4–HOOOH, H_2SO_4–HOOO$^\cdot$) has been investigated by using DFT (B3LYP/6-311++G(3df,3pd)) and CCSD(T)-F12 methods. For the first time the structures and the binding energies (BEs) for the various isomeric hydrogen-bonded complexes have been reported. The results reveal an unusually stable H_2SO_4–HOOOH eight-membered ring structure with two relatively strong hydrogen bonds, and with a calculated BE (CCSD(T)-F12) of 12.7 kcal mol^{-1}. This is equivalent to the BE in the H_2SO_4–HOOH complex investigated at the same theoretical level. The complexation of HOOO$^\cdot$ with H_2SO_4 stabilizes this metastable polyoxide intermediate by about 10.0 kcal mol^{-1}.

1. Introduction

The existence of hydrogen trioxide (HOOOH) [1–13] and its radical HOOO$^\cdot$ [8,14–28] has been unambiguously verified by experiment [2,3,5–7,11,15,16,18,20,22,23] and theory [1,4,8,10,12–14,17,19,21,24–28] in recent years. These polyoxide species were found to be key intermediates in the low-temperature ozonation of various saturated organic compounds [2,5,29] and hydrogen peroxide [30], and are also believed to be involved in the oxidation processes that span atmospheric [20,22,23,31,32], environmental [33–36], and biological [37] systems.

The purpose of the present theoretical study is to investigate the possible existence of the gas-phase complexes of HOOOH and HOOO$^\cdot$ with sulfuric acid and, for comparison, acetone. Gaseous H_2SO_4 plays an important role in aerosol formation in both troposphere and stratosphere. At the same time, recent evidence indicates that both hydrogen polyoxide species are most likely present in significant amounts in the atmosphere. Although, several studies on the H_2SO_4–HOH [38,39], H_2SO_4–HOOH [38], and H_2SO_4–HOO$^\cdot$ [40,41] complexes have been reported, this is to the best of our knowledge, the first investigation of the possible nucleation processes of H_2SO_4 with HOOOH and the HOOO$^\cdot$ radical, respectively.

2. Computational methods

Structures were optimized using DFT [42,43], utilizing the B3LYP [44–46] functional and the 6-311++G(3df,3pd) [47–50] basis set in the Gaussian 09 [51] program. CCSD(T)-F12a [52–55] single point calculations were carried out on the optimized structures with the aug-cc-pVDZ [56,57] (AVDZ) basis set developed for the CCSD(T)-F12-a method, in the Molpro 2010 [58] program. Systems with radicals, utilized unrestricted coupled-cluster with Single and Double and perturbative Triple excitations, UCCSD(T) [59,60]. Systems containing sulfur used an AVDZ + d [61] basis set on the sulfur atom. All binding energies have been corrected for basis set superposition error (BSSE) [62–64] using the counterpoise correction.

3. Results and discussion

3.1. Monomers

The monomers of H_2SO_4, HOOOH and the HOOO$^\cdot$ radical can exist in either a *cis* or *trans* configuration and we therefore optimized each of these possible arrangements to determine their relative stability (Fig. 1). The H_2SO_4 [65,66] and HOOOH [67] monomers both show a preference for the *trans* configuration over their *cis* counterparts by −1.26 kcal mol^{-1} and −2.39 kcal mol^{-1}, respectively at the B3LYP level of theory, which is consistent with the CCSD(T)-F12 single point energies (−1.25 kcal mol^{-1} and

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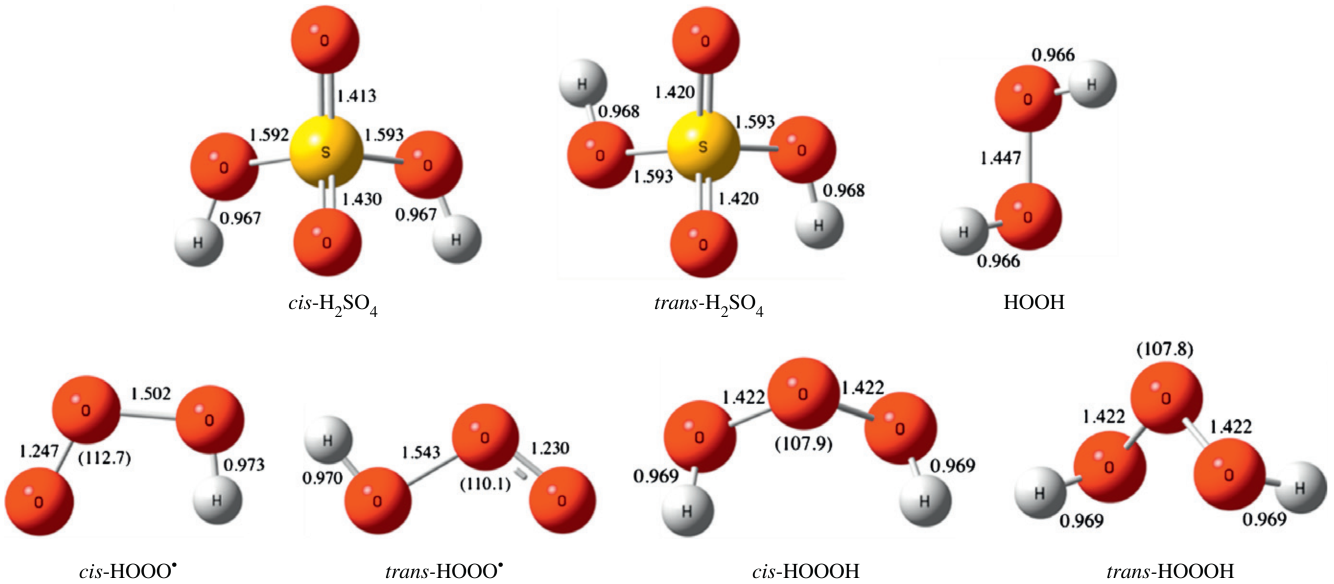

cis-H_2SO_4 *trans*-H_2SO_4 HOOH

cis-HOOO$^{\bullet}$ *trans*-HOOO$^{\bullet}$ *cis*-HOOOH *trans*-HOOOH

Fig. 1. Structures of the B3LYP optimized compounds used in forming the complexes. Distances in Å, angles in degrees.

-2.37 kcal mol^{-1}) of these structures. Conversely, there is no clear preferred conformation (*cis* or *trans*) of the HOOO$^{\cdot}$ radical with both levels of theory showing the structures to be energetically equivalent ($\Delta E_{\text{trans-cis}}$(B3LYP) = -0.07 kcal mol^{-1}, $\Delta E_{\text{trans-cis}}$(CCSD(T)-F12) = 0.20 kcal mol^{-1}) [8,17,21,24–28], [68]. Therefore, the more stable *trans* forms of H_2SO_4 and HOOOH were used to construct each of the complexes (*vide infra*). In the case of the HOOO$^{\cdot}$ radical, the negligible difference in the energy between the two structures suggests that they will both be present; therefore, we constructed complexes based on both the *cis* and *trans* forms. The observation that the B3LYP functional is able to produce results that agree with the higher level of theory is consistent with our previous work on related complexes [9].

3.2. H_2SO_4–HOOH

The complex between H_2SO_4 and HOOH was found to be stabilized by two medium strength hydrogen bonds (**1A**: 1.687 Å and 1.879 Å, Fig. 2), which account for a binding energy of 11.00 kcal mol^{-1} at the B3LYP level of theory (Table 1). The single-point energy calculation of this complex at the CCSD(T)-F12 level of theory reveals that B3LYP slightly underestimates the binding energy of the complex by 1.72 kcal mol^{-1} (Table 1). All binding energies reported have been corrected for basis set superposition error (BSSE) using the counterpoise correction method. The BSSE for each complex is *ca.* 1 kcal mol^{-1} in each case and is similar for both the DFT and CCSD(T)-F12 methods used (see Supporting Information).

3.3. H_2SO_4–HOOOH

The complexes formed between H_2SO_4 and HOOOH were found to have four different configurations based on (a) the nature of the H_2SO_4 oxygen atoms involved in the hydrogen bonds; and (b) the conformation of the 8-membered ring formed through hydrogen bonding. The use of both of the H_2SO_4 hydroxyl groups in hydrogen bonding results in a destabilization of the complex (compare **2A** ($\Delta E = -10.71$ kcal mol^{-1}) and **2B** ($\Delta E = -6.76$ kcal mol^{-1})), which is reflected in the elongation of both O–H hydrogen bond distances (Fig. 2). This destabilization is also reproduced when the more accurate CCSD(T)-F12 method is employed, although the complexes are found to be more strongly bound at this level of theory by *ca.* 2 kcal mol^{-1} ($\Delta\Delta E$, Table 1). The near linear hydrogen bonds that form between the H_2SO_4 and HOOOH allow for a pseudo-boat (**2A**, **2B**, Fig. 2) or pseudo-chair (**2C**, **2D**, Fig. 2) conformation for the 8-membered ring. However, the difference in the relative conformation of the 8-membered ring has little effect on the overall stability of the complex (e.g.; **2A**: $\Delta E = -10.71$ kcal mol^{-1}; **2C**: $\Delta E = -10.47$ kcal mol^{-1}; Table 1). In the chair conformation of the complex (**2C** and **2D**), the destabilization between the two hydrogen bonding arrangements is also seen, although to a lesser extent (**2C**: $\Delta E = -10.47$ kcal mol^{-1}; **2D**: $\Delta E = -7.56$ kcal mol^{-1}, Table 1). Both methods (B3LYP and CCSD(T)-F12) predict the same order of stability, **2A** > **2C** > **2D** > **2B**, suggesting that the use of both hydroxyl groups from the H_2SO_4 moiety destabilizes the boat structure to a greater extent than the chair, hence the greater elongation of the key hydrogen bonds (Fig. 2).

The vibrational modes of the complexes and monomers were also calculated to allow comparison with experimental values. The major shifts occur for those O–H stretching vibrations where the H atom is involved in forming a hydrogen bond. In the case of the most strongly bound species involving HOOOH (**2A**), the HOO(O–H) stretch is red-shifted by *ca.* 215 cm^{-1} from *ca.* 3720 cm^{-1} in the unbound *trans* monomer of HOOOH to 3505 cm^{-1} in the complex (see Supporting Information). This is reminiscent of the behavior previously observed for the binding of HOOOH to acetone (see Supporting Information) and dimethyl ether, although in these cases a larger red-shift, up to 315 cm^{-1}, was observed. Similarly, the H atom from H_2SO_4 involved in forming a hydrogen bond in **2A** also experiences a red-shift by *ca.* 506 cm^{-1} from the unbound state upon complexation (from 3767 cm^{-1} to 3261 cm^{-1}).

The inclusion of thermal corrections and the zero-point energy to yield ΔH results in a destabilization of the complexes. This destabilization is fairly consistent across the different conformations and amounts to 1.28–1.53 kcal mol^{-1}. The equilibria between the free and complexed HOOOH will depend on the corresponding Gibbs' free enthalpies ($\Delta G = \Delta H - T\Delta S$). We have computed the entropic contributions by applying the harmonic oscillator/rigid rotor approximation. The resulting ΔG values are listed in Table 1, but should be viewed with caution as the harmonic oscillator/rigid rotor approximation is known to be problematic in the case of