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Communications to the Editor

The Formation of a Surprisingly Stable $HO_2-H_2SO_4$ Complex

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Bimolecular complexes formed between closed-shell species are generally known to have modest binding energies, on the order of 10 kcal mol^{-1}. This Communication reports the results of quantum chemical calculations that reveal an unusually strong bonding in the open-shell complex formed by peroxy radicals (HO_2) and sulfuric acid (H_2SO_4). Figure 1 illustrates that the $HO_2-H_2SO_4$ complex forms a nearly planar seven-membered ring in which the HO_2 acts as both a hydrogen-bond donor and a hydrogen-bond acceptor. The binding energy calculated for the $HO_2-H_2SO_4$ complex, −18.9 kcal mol^{-1}, is ca. 3 kcal mol^{-1} stronger than that calculated for the $H_2O_2-H_2SO_4$ or $H_2O-H_2SO_4$ complexes. Obtaining a detailed understanding of the chemical bonding and energetics of the $HO_2-H_2SO_4$ complex represents the first step toward elucidating the physical mechanism of HO_2 uptake by sulfuric acid aerosols in the atmosphere[1−5] and complements previous studies detailing the strong interactions between HO_2 and hydrogen-bond donor/acceptor molecules.[6]

The importance of heterogeneous chemistry in high-latitude atmospheric ozone depletion is well-documented;[1] however, the impact of heterogeneous interactions on the chemical loss of gas-phase free radicals is less certain. Recent remote sensing experiments indicate that the loss of peroxy radicals caused by aerosol processing may explain the differences between model predictions and measured HO_2 levels.[2−4] The dominant contributions to atmospheric HO_2 aerosol processing are assumed to occur on/in liquid sulfuric acid particles.[7] Laboratory studies demonstrate that the mass accommodation coefficient for HO_2 uptake by sulfuric acid aerosols approaches unity whether the aqueous solutions are concentrated (typical of sulfuric acid aerosols in the lower stratosphere/upper troposphere) or dilute (typical of sulfuric acid aerosols in the lower troposphere).[8] The uptake of gas-phase HO_2 by sulfuric acid aerosols may, therefore, be limited only by the rate of diffusion to the aerosol surface. Heterogeneous HO_2 loss constitutes 5−10% of the homogeneous gas-phase chemical loss for low to moderate aerosol-loading conditions (<300 particles cm^{-3}) and becomes comparable to gas-phase chemical loss for high aerosol loading (300−3000 particles cm^{-3}).[2,4] These estimates assume that HO_2 is irreversibly destroyed upon being accommodated into the aerosol surface, and this assumption remains the principal uncertainty in this process.

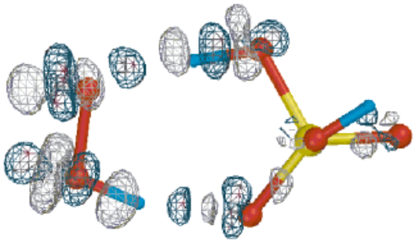

Figure 1. Electron density difference map of the $HO_2-H_2SO_4$ complex. The black areas represent regions of increased electron density, while the gray areas represent regions of decreased electron density.

To investigate the potential role sulfuric acid aerosols in processing atmospheric HO_2, we quantified the energetics of $HO_2-H_2SO_4$ complex formation with a series of quantum chemical calculations. The geometries of monomers and complexes were fully optimized with the unrestricted second-order Møller−Plesset perturbation theory (MP2) method[9] and with the unrestricted density functional Becke's three parameter and Lee−Yang−Parr functional (B3LYP) method.[10] Preliminary optimizations were performed with the 6-31G(d) basis set; subsequent optimizations were performed using the larger 6-311++G(2d,2p), 6-311++G(2df,2p), and 6-311++G(3df,3pd) basis sets. Optimizations with the larger basis sets were necessary to reduce the basis set superposition error (BSSE). The counter poise correction[11] was found to be negligible (<0.3 kcal mol^{-1}) when using the larger basis sets. Vibrational frequency analysis confirmed that all optimized geometries represented stable minima on their respective energy hypersurfaces. The corrections for the zero-point energies (ZPE) were calculated using the harmonic frequencies at the B3LYP/6-311++G(2df,2p) level of theory. The GAUSSIAN 98 program was used in all calculations.[12]

The reliability of the structure optimizations was verified by comparing the theoretical and experimental structures of H_2SO_4 and HO_2. On the basis of the microwave spectrum of gaseous sulfuric acid,[13] H_2SO_4 has C_s symmetry with pairs of equivalent S=O (1.422 Å), S−O′ (1.574 Å), and H−O (0.970 Å) bond lengths. The optimized MP2/6-311++G(3df,3pd) and B3LYP/6-311++G(3df,3pd) structures agree well with the experimental H_2SO_4 structure, although the MP2 level of theory provides slightly better bond lengths: 0.006 Å rms error (MP2) versus 0.014 Å rms error (B3LYP). The experimentally determined HO_2 equilibrium structure[14,15] exhibits C_s symmetry with $R(H-O) = 0.9708$ Å, $R(O-O) = 1.33051$ Å and $\angle HOO = 104.30°$. The

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optimized MP2/6-311++G(3df,3pd) [R(H−O) = 0.9698 Å, R(O−O) = 1.3036 Å, and ∠HOO = 104.95°] and B3LYP/6-311++G(3df,3pd) [R(H−O) = 0.9754 Å, R(O−O) = 1.3239 Å and ∠HOO = 105.51°] structures agree well with the experimental structure, with the MP2 level of theory again providing a slightly better characterization than B3LYP. These results suggest that the $HO_2-H_2SO_4$ structure and, presumably, the associated energetics will be better described at the MP2 level.

The optimized $HO_2-H_2SO_4$ structure forms a nearly planar seven-membered ring with the HO_2 acting as both a hydrogen-bond donor and acceptor. The low deprotonation energy associated with the HO_2 moiety and the formation of two strong hydrogen bonds drive the energy stabilization of this relatively unusual structure. This is reflected in the electron density difference map (Figure 1). In fact, the redistribution of electron density to regions concentrated along the internuclear axes of the hydrogen bonds is consistent with the initial stages of covalent bond formation. The bond strengths inferred by the electron density map are mirrored by the calculated bond lengths: 1.649 Å for the OOH$\cdots$O=S and 1.608 Å for the HOO$\cdots$H−O′S, respectively, at the MP2/6-311++G(3df,3pd) level of theory.

The strength of the hydrogen bonding is further reflected in the significant perturbations that complex formation induces in the HO_2 and H_2SO_4 structures. The formation of the OOH$\cdots$O=S bond causes the OO−H bond to lengthen by 0.028 Å while the S=O bond lengthens by 0.010 Å. Formation of the HOO$\cdots$H−O′S bond entails delocalization of the lone pair electrons from the terminal oxygen atom of the HO_2 radical and even larger structural changes: a 0.042 Å contraction in the H−O′S bond, a 0.056 Å elongation in the HO′−S bond, and a 0.018 Å contraction in the HO−O bond. The unpaired electron in HO_2 resides on the terminal oxygen atom in an orbital perpendicular to the HOO$\cdots$H−O′S bond, and does not participate in the bond formation. These results suggest that stronger bonding occurs in the HOO$\cdots$H−O′S linkage, consistent with its shorter 1.608 Å bond length. It should be noted that the optimized B3LYP structures show similar trends but that the MP2 structures generally predict stronger complex bonding.

The $HO_2-H_2SO_4$ binding energy (D_0) and well depth (D_e) calculated at various levels of theory are presented in Table 1. The MP2 method systematically predicts greater complex stability than the B3LYP method for basis sets larger than 6-31G(d), consistent with the structure optimizations. The calculated value of $D_e(D_0)$ is 18.9(15.6) kcal mol^{-1} at the MP2/6-311++G(3df,3pd) level of theory and 15.7(12.4) kcal mol^{-1} at the B3LYP/6-311++G(3df,3pd) level of theory. The stabilization energy difference is 3.2 kcal mol^{-1}; nevertheless, the results reveal unusual stability in the $HO_2-H_2SO_4$ complex. For comparison, the D_0 value calculated at the MP2/6-311++G(2d,2p) level is 2.1 kcal mol^{-1} larger than the D_0 value of 11.2 kcal mol^{-1} Beichert and Schrems reported for the closed-shell analogue, $H_2O_2-H_2SO_4$ and 3.5 kcal mol^{-1} larger than the D_0 value for $H_2O-H_2SO_4$ at this level of theory.[16] Comparisons of the stabilities of the $HO_2-H_2SO_4$ and $H_2O-H_2SO_4$ complexes calculated using the B3LYP method also show differences of 3−4 kcal mol^{-1}.[17,18]

Table 1. Binding Energies (kcal mol^{-1}) Calculated for $HO_2-H_2SO_4(g) \rightarrow HO_2(g) + H_2SO_4(g)$

level of theory	D_e	D_0
B3LYP/6-31G(d)	18.7	15.4
B3LYP/6-311++G(2d,2p)	15.0	11.7
B3LYP/6-311++G(2df,2p)	15.1	11.8
B3LYP/6-311++G(3df,3pd)	15.7	12.4
UMP2/6-31G(d)	18.1	14.8
UMP2/6-311++G(2d,2p)	16.6	13.3
UMP2/6-311++G(2df,2p)	15.3	12.0
UMP2/6-311++G(3df,3pd)	18.9	15.6

We conclude from this study that HO_2 and H_2SO_4 form an unusually stable complex with hydrogen bond strengths comparable to those of weak covalent bonds. As recognized by Nelander, the partitioning of peroxy radicals between the gas phase and aerosol droplets will be partially determined by their ability to donate and accept hydrogen bonds.[19] The stability of the $HO_2-H_2SO_4$ complex indicates that $HO_2(g)$ bonds irreversibly to $H_2SO_4(g)$ under atmospheric conditions. The binding energetics between HO_2 and H_2SO_4 in the surface monolayer of an aerosol particle are probably not significantly different, explaining the large uptake coefficients observed for HO_2.[5,7,8] The question of whether subsequent HO_2 chemistry occurs on the aerosol surface or in the bulk requires further study. However, the present results imply that sulfuric acid aerosols play a significant role in perturbing atmospheric HO_2 levels.

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