

Ab Initio Molecular Orbital Study of the Mechanism of the Gas Phase Reaction $\text{SO}_3 + \text{H}_2\text{O}$: Importance of the Second Water Molecule

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The reaction of SO_3 with H_2O to form H_2SO_4 in the gas phase is considered to be the final step of the chain reactions of oxidation of sulfur oxide and is important in connection with the acid rain problem.¹ In experimental studies, though Castleman et al.² reported a very fast rate of $9 \times 10^{-13} \text{ cm}^3/\text{s}$ obtained using mass spectrometry, this value has been challenged with much smaller rates of $(5.7 \pm 0.9) \times 10^{-15} \text{ cm}^3/\text{s}$ by Lee et al.³ and $2 \times 10^{-15} \text{ cm}^3/\text{s}$ by Kolb et al.⁴ Shriver et al. found in matrix isolation photolysis evidence only for the 1:1 $(\text{H}_2\text{O})(\text{SO}_3)$ complex.⁵ On the theoretical side, a justification of a fast rate with a small activation barrier of 3.3 kcal/mol by Castleman et al.'s earlier semiempirical molecular orbital (MO) calculation⁶ was contradicted with the ab initio barrier of 23 kcal/mol at the MP2/3-21G(*)//HF/3-21G(*) level by Chen and Moore Plummer^{7,8} and 19.4 kcal/mol at the RMP4SDQ/6-311+G(2df,p)//RMP2/6-31+G* + ZPE(RMP2/6-31G*) level by Hofmann and Schleyer.⁹ If the 1:1 reaction of $\text{H}_2\text{O} + \text{SO}_3$ has a high barrier, one may ask how many water molecules are needed for the reaction to take place.

In the present communication, we report results obtained using the ab initio MO method: while the barrier for the 1:1 reaction is indeed very high, two water molecules can react with SO_3 very easily to convert it to sulfuric acid. The transition state for this easy reaction is six-centered, with transfer of two protons taking place simultaneously.

All the geometries of the reactants, intermediates, and transition states were optimized at the MP2/6-311+G(d,p) level, i.e., with the frozen core second-order Møller–Plesset perturbation method with the 6-311+G(d,p) basis set.¹⁰ The energies reported were calculated at the the fourth-order MP4SDQ level with the same basis set and include the zero-point energy correction, which was obtained with the analytical second derivative at the Hartree–Fock (HF)/6-311+G(d,p) level for the optimized geometries at the same level and scaled by an empirical factor of 0.8929.¹¹

As shown in Figure 1, the transition state TS1 for the reaction $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ is four-centered and has a high activation barrier relative to those of the isolated reactants (23.8 kcal/mol) or the 1:1 $(\text{H}_2\text{O})(\text{SO}_3)$ complex (32.2 kcal/mol), as shown in

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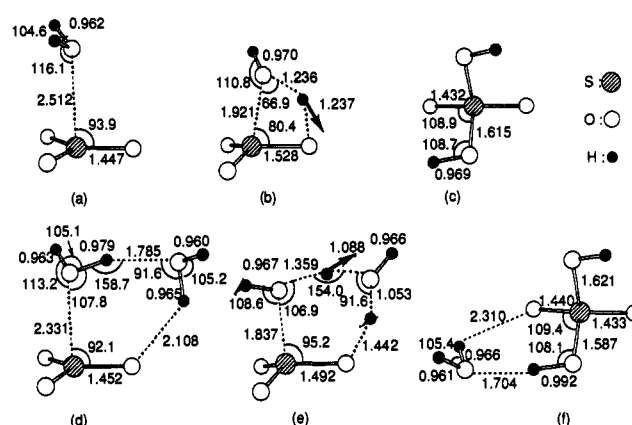


Figure 1. Optimized geometries, in angstroms and degrees, at the MP2/6-311+G(d,p) level for (a) the complex $(\text{H}_2\text{O})(\text{SO}_3)$, (b) the transition state TS1 for $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$, (c) the product H_2SO_4 , (d) the complex $(\text{H}_2\text{O})_2(\text{SO}_3)$, (e) the transition state TS2 for $2\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4$, and (f) the product complex $(\text{H}_2\text{O})(\text{H}_2\text{SO}_4)$. The arrows at the TSs are the reaction coordinate vectors calculated at the HF/6-311+G(d,p) level.

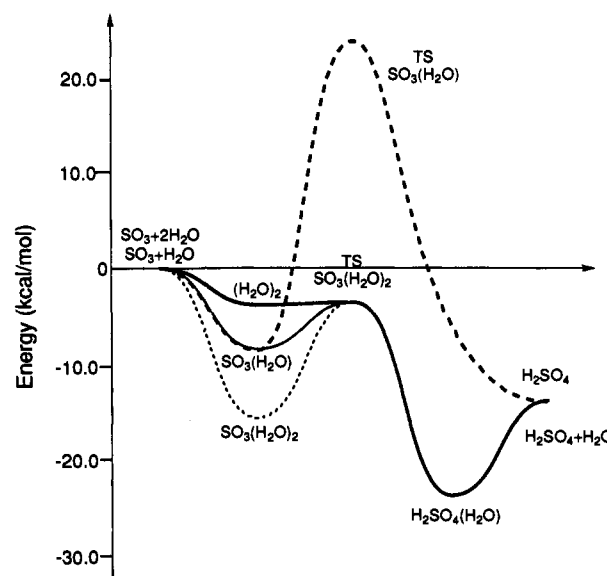


Figure 2. Potential energy profiles at the MP4SDQ/6-311+G(d,p) level, including the zero-point correction obtained at the scaled HF/6-311+G(d,p) level.

Figure 2, and in qualitative agreement with the previous ab initio results.^{7,9} This reaction is not likely to contribute significantly at room temperature or below.

When the second H_2O molecule is brought into the system, several transition states leading to sulfuric acid have been found. The energetically most favorable one, TS2, shown also in Figure 1, is totally different from TS1 discussed above and is a six-centered cyclic transition state. As shown by the arrows representing the reaction coordinate vector, the normal coordinate having an imaginary frequency, two water molecules are concertedly transferring their hydrogen-bonding protons to the proton acceptor oxygen atoms, while a new S–O bond is being formed between the newly generated hydroxyl group and SO_3 . The structures of the $(\text{H}_2\text{O})_2$ and the $(\text{H}_2\text{O})(\text{SO}_3)$ fragment in TS2 are similar to the equilibrium structures of the water dimer and the 1:1 complex, respectively, and TS2 seems to be easily reachable starting from either complex without invoking a substantial structural reorganization. Transition states in which a solvent (often water) molecule becomes a positive participant of a reaction have long been recognized in theoretical calculations,¹² and this is a dramatic example of such a case. Other transition states

found are essentially similar to TS1, on which the second water molecule has hydrated either at the sulfur atom of SO_3 or at both the SO_3 oxygen and the hydroxyl proton. All of them are less stable at least by 20 kcal/mol than, and therefore cannot compete with, TS2.

As shown in Figure 2, the energy of TS2 is below that of the isolated reactants, $2(\text{H}_2\text{O}) + \text{SO}_3$, and only 0.7 kcal/mol higher than that of the water dimer + SO_3 . The reaction should proceed easily from either the isolated reactants or $(\text{H}_2\text{O})_2$ at lower temperature, where the entropy factor is not important. The reaction of the prepared 1:1 $(\text{H}_2\text{O})(\text{SO}_3)$ complex + free H_2O should be slower than that of $(\text{H}_2\text{O})_2 + \text{SO}_3$ but should take place because of a still small barrier of 5.3 kcal/mol. The reaction of the 2:1 complex $(\text{H}_2\text{O})_2(\text{SO}_3)$ would be more difficult due to the high barrier, even if a large concentration of the complex is produced. The present potential energy profile suggests that the

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rate of formation of H_2SO_4 should be second order with respect to the water pressure. This prediction is in qualitative agreement with the recent experimental finding by Kolb et al.⁴

For more quantitative evaluation of the energetics of the potential energy surface, one would have to perform higher level calculations including triple excitations. Such a study is in progress. For quantitative explanation of the experimentally observed temperature dependency of the rate in the range of -30 to 60 °C,⁴ one will have to take into account the contribution of entropy, which differs substantially among different channels. Such an analysis based on ab initio calculated partition functions is in progress and will be reported elsewhere, together with a detailed account of calculated structures and energies.

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