SULFUR CHEMISTRY

Gas phase observation and microwave spectroscopic characterization of formic sulfur anhydride

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We report the observation of a covalently bound species, formic sulfur anhydride (FSA), that is produced from formic acid and sulfur trioxide under supersonic jet conditions. FSA has been structurally characterized by means of microwave spectroscopy and further investigated by using density functional theory and ab initio calculations. Theory indicates that a $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ cycloaddition reaction between $\text{SO}_3$ and $\text{HCOO}_2$ is a plausible pathway to FSA formation and that such a mechanism would be effectively barrierless. We speculate on the possible role that FSA may play in the Earth’s atmosphere.

The present work was stimulated by a series of studies concerned with the formation of sulfuric acid in the atmosphere. The acid, which can form via both gas-phase and aqueous-phase processes, is generated in the gas phase by the oxidation of $\text{SO}_3$ to $\text{SO}_4^2-$, which is subsequently hydrated to give $\text{H}_2\text{SO}_4$

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (1)$$

Both theoretical and experimental studies of this reaction indicate that viable mechanisms in the gas phase involve a facilitator molecule. Here is an extensive literature on the chemistry of sulfur oxides and their derivatives. The area is rich in fundamental science and finds applications ranging from industrial chemistry to laboratory synthesis. Sulfur compounds are also active species in the atmosphere (1), and in particular, the oxides and oxycarboxylates are important players in the formation of atmospheric aerosol (2). Here, we present a microwave spectroscopic study of the anhydride derived from formic and sulfuric acids, produced in a supersonic jet containing $\text{HCOOH}$ and $\text{SO}_3$.

REFERENCES AND NOTES

18. Materials and methods are available as supplementary materials on Science Online.
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SUPPLEMENTARY MATERIALS

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Materials and Methods
Table S1
Figs. S1 to S9
References (2E–33)

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As e con dw at e rm o le cu l et o H2O  

\[ \cdots \cdot \cdot \cdot \text{SO}_3 \] substantially lowers the activation barrier for Eq. 1, and indeed, kinetic data show a second-order dependence on water concentration \((4)\). More recently, computational work by Hazra and Sinha has indicated that the conversion is essentially barrierless within the complex HCOOH\(\cdots\)H\(\cdot\)O\(\cdots\)SO\(\cdot\) (5). Upon considering the concentration of formic acid, one of the most common atmospheric volatile organic compounds (VOCs), these authors argued that this pathway may be important for the formation of sulfuric acid. Furthermore, this mechanism terminates in the formation of the hydrogen-bonded complex H\(\text{SO}_4\)\(\cdots\)HCOOH, which may be a preliminary step in a nucleation process. Indeed, the involvement of organic compounds in new particle formation has become a central topic in atmospheric particle research, and it now has been shown that organics participate not only in particle growth \((6-8)\) but in nucleation as well \((9-15)\). Carboxylic acids are abundant in the atmosphere \((16)\), and thus, their primary interactions with sulfur-containing atmospheric species are of great interest.

Previous work in our laboratory has characterized a variety of atmospheric molecular complexes— including SO\(\cdot\)H\(\cdot\)O \((17)\), H\(\text{SO}_4\)\(\cdot\)H\(\cdot\)O \((18)\), and H\(\text{NO}_3\)\(\cdot\)(H\(\cdot\)O\(\cdot\))\(\text{H}_2\) \(\cdot\)—in a supersonic jet by using microwave spectroscopy. Such systems, in general, are important to study because of the roles they play as intermediates in chemical reactions and precursors to atmospheric aerosol. Although conditions in the jet do not mimic those in the atmosphere, they can produce the same species, albeit under conditions amenable to microwave spectroscopy (in a collisionless

**Table 1. Comparison of experimental and theoretical intermolecular distances.**

<table>
<thead>
<tr>
<th>Distance</th>
<th>M06-2X†</th>
<th>MP2†</th>
<th>Experiment‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-S5</td>
<td>2.589</td>
<td>2.593</td>
<td>2.594(5)</td>
</tr>
<tr>
<td>C1-H2</td>
<td>1.092</td>
<td>1.091</td>
<td>1.11(1)</td>
</tr>
<tr>
<td>C1-H9</td>
<td>2.634</td>
<td>2.572</td>
<td>2.62(1)</td>
</tr>
<tr>
<td>S5-H9</td>
<td>2.085</td>
<td>2.069</td>
<td>2.025(3)</td>
</tr>
<tr>
<td>S5-H2</td>
<td>3.514</td>
<td>3.520</td>
<td>3.513(2)</td>
</tr>
</tbody>
</table>

*All distances are in angstroms. †M06-2X and MP2 calculations were done with 6-311++G(3df,3pd) basis set. ‡Determined from Kraitchman’s equations.
environment that is cold enough to ensure population of only the lowest rotational energy levels). Spectral analysis yields accurate information about gas-phase molecular and electronic structure, which in turn provides an important touchstone for computational studies. Therefore, inspired by Hazra and Sinha, and by the recent research suggesting the involvement of organic acids in aerosol formation, we set out to investigate the complexes such as H$_2$SO$_4$–HCOOH and SO$_3$–HCOOH by means of microwave spectroscopy in a supersonically expanded mixture of SO$_3$, H$_2$O, and HCOOH seeded in argon (Ar). What we found was entirely unexpected.

Rotational spectra were observed by means of Fourier transform microwave (FTMW) spectroscopy. Two methods were used: conventional cavity-type FTMW spectroscopy and the newer broadband, chirped-pulse FTMW technique. The cavity spectrometer in our laboratory has been described elsewhere (20). Briefly, molecules enter a tuned microwave cavity and are coherently excited by a 1- to 2-μs pulse of radiation. The resulting free induction decay is heterodyne-detected, digitized, and Fourier transformed so as to produce a signal in the frequency domain. Uncertainties in spectral transition frequencies are typically on the order of 2 to 3 kHz. In our broadband spectrometer (21), which applies the methods developed by Fate and coworkers (22), the cavity is eliminated, and the radiation for sample excitation is generated by up-conversion of a 0.2- to 3.2-GHz chirped pulse to the microwave spectral region of interest. A 20-W amplifier boosts the power before irradiation of the molecular sample, which is accomplished via a microwave horn. The resulting free induction decay is received by an identical companion microwave horn, down-converted for digitization, and Fourier transformed so as to produce a 3-GHz-wide segment of the microwave spectrum. Linewidths are typically ~90 kHz, and the apparatus is less sensitive than that of the cavity spectrometer but it allows for rapid location and identification of spectra. In this work, spectra were initially recorded with the broadband spectrometer and subsequently remeasured at high resolution by using the cavity system.

A key feature of this experiment was the molecular source (23), which consisted of a supersonic expansion of SO$_3$ in Ar, to which a flowing stream of formic acid and water vapor was added. The Ar carrier gas was seeded with SO$_3$ by means of entrainment upon passage over solid, polymerized SO$_3$. A gaseous mixture of HCOOH and H$_2$O was added by bubbling Ar through 88% aqueous formic acid and injecting it into the expansion (Fig. 1A). This configuration provides “on-the-fly” mixing of reactive reagents during the first few tens of microseconds of the supersonic expansion.

Transitions from a variety of known species—including Ar–SO$_3$, H$_2$O–SO$_3$, H$_2$SO$_4$ (formed from SO$_3$ + H$_2$O), H$_2$SO$_4$–H$_2$O, Ar–HCOOH, and H$_2$O–HCOOH—were observable, as were numerous lines of unknown origin (Fig. 1B). Among these was a set of strong transitions whose pattern made them readily identifiable as the a-type spectrum of an asymmetric rotor, and a preliminary least-squares fit to a Watson A-reduced Hamiltonian gave residuals of ~5 kHz. The appearance of these transitions required the presence of HCOOH, and our initial hypothesis was that they were due either to the H$_2$SO$_4$–HCOOH or SO$_3$–HCOOH weakly bound complex. However, theoretical predictions of the rotational constants for both species by using the density functional M06-2X (table S1) clearly indicated that neither is the carrier of the observed spectrum. Indeed, the computed rotational constants of H$_2$SO$_4$–HCOOH as well as those of several weakly bound isomers of SO$_3$–HCOOH (table S1 and fig. S3) differ by up to ~1 GHz and ~200 MHz, respectively, from those fitted from experimental data.

We performed additional calculations near the global minimum energy configuration of SO$_3$–HCOOH with starting configurations at progressively shorter intermolecular separations. These eventually revealed a new chemically bonded species in which the acidic proton of the formic acid transfers to the SO$_3$ and a new sulfur-oxygen bond is formed (tables S2 and S3). We performed frequency calculations in order to verify the authenticity of the potential energy minimum, and the density functional theory (DFT) results were confirmed with MP2 calculations. The structure of this molecule, formic sulfuric anhydride (FSA), is shown in Table 1. This structure has substantial dipole moment components along each of its three inertial axes ($μ_a$, $μ_b$, and $μ_c$ = 3.19, 0.48, and 0.97 D, respectively; $μ_{total}$ = 3.37 D), and with this information, b-type and c-type transitions were easily predicted and located. With a, b, and c-type transitions recorded, we performed a final fit, which yielded

![Table 2. Comparison of experimental and calculated rotational constants for FSA.](http://science.sciencemag.org/)
the rotational constants listed in Table 2. As indicated in the table, the predicted rotational constants of FSA match the experimental values to within 0.7% (32 MHz for A and 14 MHz for B and C).

As a final test, we predicted and observed spectra of the $^{32}$S, $^{13}$C, and both monodeuterated isotopologues. We recorded $^{35}$S- and $^{15}$C-isotopologue spectra in natural abundance and used isotopically enriched HCOOD or DCOOH in experiments on the deuterated species. Transition frequencies and fitted spectroscopic constants for the observed isotopologues are provided in tables S4 to S9. All observed isotopic shifts were in excellent agreement with those predicted from the theoretical structure. When we used HCOOD, the deuteron was found in the H9 position, confirming the occurrence (direct or indirect) of proton transfer (23); isotopic substitutions allowed determination of several interatomic distances by using Kraitchman’s equations (24). These results are given and compared with the theoretical values in Table 1, where agreement is again seen to be excellent. The agreement between experimental and theoretical rotational constants, their isotope shifts, and the computed interatomic distances unambiguously establishes that the observed species is FSA.

The literature on compounds related to FSA appears sparse, although a few prior condensed phase studies are noteworthy. The sodium salt of acetic sulfuric anhydride has been described (25), but the parent acid (CH$_2$COOSO$_2$H) is reportedly unstable with respect to rearrangement or decomposition (26, 27). Dissolved salts of form[M$^{+}$][SO$_3$OCHO]$^{-}$ have also been described in a patent concerning the preparation of isoflavones in a variety of nonaqueous solvents (28). We are unaware, however, of any previous gas-phase observations of FSA or its analogs. To better understand the pathway for the formation of FSA in the gas phase, we performed calculations (27) to locate the transition state connecting it with the SO$_3$⋯HCOOH van der Waals complex (table S10). For these calculations, using the optimized MP2 geometries, single-point coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)] calculations were done by using the complete basis set extrapolation scheme of Neshe and Valeev with the ANO-pVDZ to ANO-pVTZ basis sets (29). The transition state (TS in Fig. 2A) was found and corresponds to a concerted $\pi_1 + \pi_2 + \sigma_2$ cycloaddition (Fig. 2B), in which the acidic proton is transferred to form the new S–O bond is formed. A similar reaction has been proposed for SO$_2$⋯HCOOH, but the formation of the resulting monomer, formic sulfurous anhydride, from SO$_3$ and HCOOH is endothermic (30). In the current case, however, FSA is 4.4 (4.2) kcal/mol lower in energy than the SO$_3$⋯HCOOH van der Waals complex, where the value in parentheses is zero-point corrected. The energy of the transition state is 2.2 (0.2) kcal/mol higher than that of SO$_3$⋯HCOOH, indicating that its conversion to FSA, with zero-point corrections, is essentially barrierless. In this light, it is not surprising that transitions of FSA were among the most prominent features in the observed spectrum. A second conformer of FSA, with the OH bound rotated 180°, was also identified from the MO6-2X calculations (fig. S5). However, this local minimum lies 4.0 (3.6) kcal/mol above the global minimum of Table 1, and no spectra corresponding to this structure were identified, presumably because of insufficient population in the supersonic jet. We also sought to establish the stability of the putative FSA precursor, SO$_3$⋯HCOOH, relative to that of other bimolecular complexes with potential roles as sulfuric acid and/or aerosol precursors. Computed energies of the complex formed from SO$_3$, H$_2$O, and HCOOH are included in Fig. 2A, fig. S4, and table S10. With zero-point corrections, the SO$_3$⋯HCOOH complex is 3.6 and 4.4 kcal/mol more stable than H$_2$O⋯HCOOH and H$_2$O⋯SO$_3$, respectively. Similar calculations for H$_2$O⋯HCOOH and H$_2$O⋯SO$_3$ have been given elsewhere (31, 32) but are reproduced here in order to ensure comparisons at a uniform level of theory. Both carboxylic and sulfonic acid anhydrides hydrolyze in water, and the hydrolysis of acetic sulfuric anhydride has been studied (27, 31). Thus, it is reasonable to hypothesize that the formation of SO$_3$⋯HCOOH with a barrierless conversion to FSA, followed by reaction with water and/or uptake into liquid droplets, may constitute an alternate pathway for H$_2$SO$_4$ production in the atmosphere. The computed energy for the process is -25.5 kcal/mol (table S10).

As a final test, we predicted and observed spectra with possible intermediates. Because formic acid inevitably contains water, experiments do not definitively establish whether the transformation of SO$_3$⋯HCOOH occurs directly or whether an additional water molecule participates. However, the theoretical results of this work suggest that the reaction is possible without such assistance. We are unaware of any previous gas-phase observations of FSA or its analogs. To better understand the pathway for the formation of FSA in the gas phase, we performed calculations (27) to locate the transition state connecting it with the SO$_3$⋯HCOOH van der Waals complex (table S10). For these calculations, using the optimized MP2 geometries, single-point coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)] calculations were done by using the complete basis set extrapolation scheme of Neshe and Valeev with the ANO-pVDZ to ANO-pVTZ basis sets (29). The transition state (TS in Fig. 2A) was found and corresponds to a concerted $\pi_1 + \pi_2 + \sigma_2$ cycloaddition (Fig. 2B), in which the acidic proton is transferred to form the new S–O bond is formed. A similar reaction has been proposed for SO$_2$⋯HCOOH, but the formation of the resulting monomer, formic sulfurous anhydride, from SO$_3$ and HCOOH is endothermic (30). In the current case, however, FSA is 4.4 (4.2) kcal/mol lower in energy than the SO$_3$⋯HCOOH van der Waals complex, where the value in parentheses is zero-point corrected. The energy of the transition state is 2.2 (0.2) kcal/mol higher than that of SO$_3$⋯HCOOH, indicating that its conversion to FSA, with zero-point corrections, is essentially barrierless. In this light, it is not surprising that transitions of FSA were among the most prominent features in the observed spectrum. A second conformer of FSA, with the OH bound rotated 180°, was also identified from the MO6-2X calculations (fig. S5). However, this local minimum lies 4.0 (3.6) kcal/mol above the global minimum of Table 1, and no spectra corresponding to this structure were identified, presumably because of insufficient population in the supersonic jet. We also sought to establish the stability of the putative FSA precursor, SO$_3$⋯HCOOH, relative to that of other bimolecular complexes with potential roles as sulfuric acid and/or aerosol precursors. Computed energies of the complex formed from SO$_3$, H$_2$O, and HCOOH are included in Fig. 2A, fig. S4, and table S10. With zero-point corrections, the SO$_3$⋯HCOOH complex is 3.6 and 4.4 kcal/mol more stable than H$_2$O⋯HCOOH and H$_2$O⋯SO$_3$, respectively. Similar calculations for H$_2$O⋯HCOOH and H$_2$O⋯SO$_3$ have been given elsewhere (31, 32) but are reproduced here in order to ensure comparisons at a uniform level of theory. Both carboxylic and sulfonic acid anhydrides hydrolyze in water, and the hydrolysis of acetic sulfuric anhydride has been studied (27, 31). Thus, it is reasonable to hypothesize that the formation of SO$_3$⋯HCOOH with a barrierless conversion to FSA, followed by reaction with water and/or uptake into liquid droplets, may constitute an alternate pathway for H$_2$SO$_4$ production in the atmosphere. The computed energy for the process is -25.5 kcal/mol (table S10).
An unexpected gaseous sulfur species

Sulfuric acid plays a central role in both industrial and atmospheric contexts. As such, the behavior of SO$_3$ mixtures in gas phases has been studied for over a century. In gas-phase experiments on wet SO$_3$ and formic acid, Mackenzie et al. discovered a previously unrecognized covalent adduct: formic sulfuric anhydride, or HC(O)OSO$_2$H. The combination of microwave spectroscopy and theoretical calculations reveals its structural properties. The compound may play a role in the nucleation of atmospheric aerosols by serving as an intermediate to H$_2$SO$_4$ formation. Science, this issue p. 58