

Acid Rain: *Ab Initio* Investigation of the H₂O·SO₃ Complex and Its Conversion into H₂SO₄

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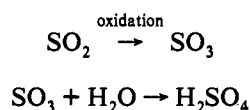
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Abstract: The important gas-phase reaction of H₂O and SO₃ to give H₂SO₄ was investigated at the RMP4SDQ/6-311+G(2df,p)//RMP2(fu)/6-31+G* + ZPE(RMP2(fu)/6-31G*) level. While the computed overall reaction energy of -20.5 kcal/mol agrees with the experimentally derived value for $\Delta H_R^\circ = -22.1 \pm 2.3$ kcal/mol, both the computed complexation energy (-7.9 kcal/mol to give the SO₃·H₂O adduct) and the reaction activation energy (19.4 kcal/mol) are very different from earlier results. For $T = 298$ K, free enthalpies of 0.0 (SO₃·H₂O), +28.6 (TS), and -10.7 kcal/mol (H₂SO₄) relative to isolated H₂O and SO₃ are derived. A new energy decomposition procedure based on a simple point charge model was used together with NBO analysis to examine the bonding in the SO₃·H₂O complex. Electrostatic attraction of the water dipole to SO₃ is as important as charge transfer interaction. However, the changes in electron distribution between the SO₃·H₂O complex and separated SO₃ and H₂O are due mainly to polarization, e.g. dipole induction. The calculated and measured frequencies for the complex compare reasonably well.

Introduction

Atmospheric sulfuric acid is an important constituent of acid rain.¹ H₂SO₄ is formed from sulfur dioxide in the following steps:



Both homogeneous and heterogeneous² processes have been proposed for the addition of H₂O to SO₃. The first experimental investigations in 1934 claimed that the reaction of sulfur trioxide and water was very fast.³ Castleman et al.⁴ supported this finding by a molecular beam experiment, but the possibility that their observations involved the formation of a SO₃·H₂O complex instead of sulfuric acid also was considered: The reaction rate of $(9.1 \pm 2.0) \times 10^{-13}$ cm³ s⁻¹ was anomalously high and the product dissociated easily on moderate heating to about 200 °C.⁵ Holland and Castleman therefore investigated the SO₃·H₂O complex theoretically.⁵ Semiempirical CNDO/2 calculations characterized it as a bound adduct of moderate stability with an estimated barrier of 3.3 kcal/mol for isomerization to H₂SO₄. The first *ab initio* calculations⁶ at the RMP2(fc)/3-21G(*)//RHF/3-21G(*) level disagreed and gave complexation energy of 21.4 kcal/mol and a barrier from the complex of 23.2 kcal/mol. From separated SO₃ + H₂O, the barrier was only 1.8 kcal/mol. The experimental results are contradictory as well. Using a molecular beam reaction technique combined with an electrical deflecting field and a mass spectrometer analyzer-detector, Hofmann-Sievert and Castleman⁷ concluded that the H₂O·SO₃ adduct isomerizes quickly to sulfuric

acid. But Wang et al.⁸ attributed this to heterogeneous reactions and determined an upper limit for the gas-phase reaction rate of $(5.9 \pm 0.9) \times 10^{-15}$ cm³ s⁻¹.

Three groups have achieved matrix isolation of the SO₃·H₂O complex.^{9,10} But their vibrational spectra are not in full agreement, either.

We have now used modern *ab initio* methods to investigate the binding in the SO₃·H₂O intermediate complex, to compare its calculated frequencies with experimental data, and to ascertain the isomerization barrier and reaction energy to H₂SO₄. The relative energies of the stationary points investigated are substantially different from literature values. This is not surprising because much more sophisticated methods can be applied now than in the earlier days of computational chemistry.

Methods

Structures of H₂O (*C*_{2v}), SO₃ (*D*_{3h}), SO₃·H₂O (*C*₂), H₂SO₄ (*C*₂), and the reaction transition state TS (*C*₁) were optimized using the spin-restricted Hartree-Fock (RHF)¹¹ theory as well as the correlated second-order Møller-Plesset (RMP2)¹¹ level. Standard 6-31G* and 6-31+G* basis sets were used for optimizations.¹¹ Two different sets of single-point calculations were carried out using the RMP2(fu)/6-31+G* geometries: first using the quadratic configuration interaction method with single and double excitations and perturbative estimation of triples in the frozen core approximation (RQCISD(T)(fc)/6-31+G**) and second using fourth-order Møller-Plesset theory including single, double, and quadruple excitations with a much larger basis set (RMP4SDQ/6-311+G(2df,p)). Stationary points were characterized by frequency calculations at RHF/6-31G* and RMP2(fu)/6-31G*. All relative energies were corrected by scaled zero vibrational energies (ZPE/RMP2(fu)/6-31G*). The scaling factor for frequencies or vibrational energy was 0.93 for MP2 values.¹¹ The calculations were carried out with the GAUSSIAN 90¹² or GAUSSIAN 92¹³ program package on the Cray-Y-MP/464 at the Leibnitz Rechenzentrum München or the Convex C220-256S in Erlangen.

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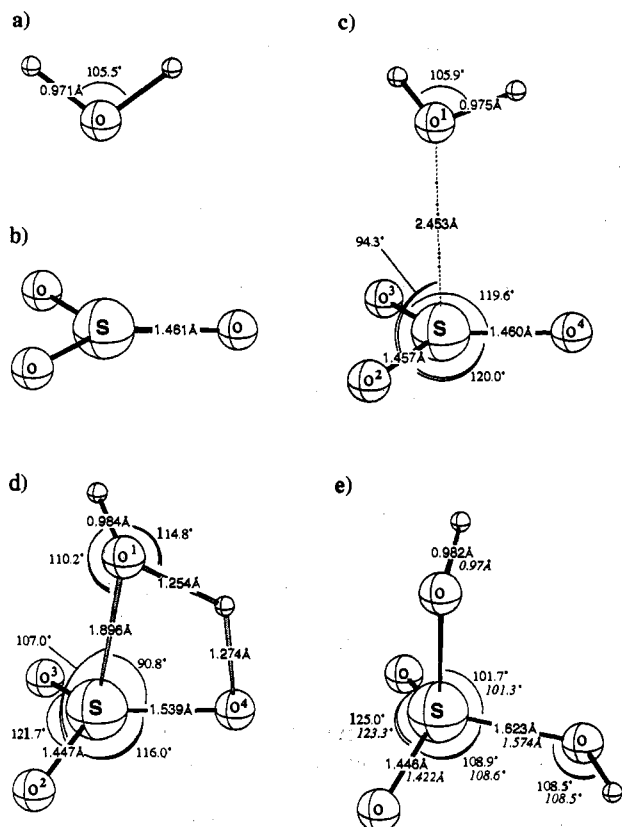
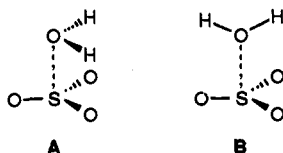


Figure 1. RMP2(fu)/6-31+G* geometries of (a) H₂O (*C*_{2v}), (b) SO₃ (*D*_{3h}), (c) the H₂O-SO₃ minimum energy complex (*C*₄), (d) the transition structure TS for addition (*C*₁), and (e) H₂SO₄ (*C*₂) (italic numbers reflect the GED structure from ref 14).

Results

As was found earlier,⁶ the SO₃·H₂O complex prefers an S-O interaction rather than OH...O hydrogen bonding. Two *C*₂ structures (A and B) are possible:



The second structure (B), in which the H₂O molecule lies in the mirror plane, was found to be a transition state (one imaginary frequency, -290 cm⁻¹). It is 0.79 kcal/mol higher in energy than the corresponding minimum (A) in which H₂O bisects the mirror plane. The MP2(fu)/6-31G* geometry is shown in Figure 1c.

The reaction transition structure TS (Figure 1d) was optimized first at RHF/3-21G*⁶ and refined at higher levels (one imaginary frequency, -1647 cm⁻¹ at RMP2(fu)/6-31G*). Isolated H₂SO₄ is known to have *C*₂ symmetry from experimental microwave spectra¹⁴ as well as from earlier theoretical investigations.¹⁵

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Absolute and relative energies for SO₃ + H₂O, SO₃·H₂O, TS, and H₂SO₄ at various levels of theory are listed in Table 1. RMP2-(fu)/6-31+G* optimized structural parameters are shown in Figure 1. Harmonic frequencies, calculated at RMP2(fu)/6-31G*, corrected by the scaling factor 0.93,¹¹ are listed in Table 2. The data for H₂O, SO₃, and SO₃·H₂O are compared with the experimental results.

Discussion

Hobza and Zahradník¹⁶ pointed out that polarization and diffuse functions as well as methods considering correlation including triple excitations are necessary for a correct description of complexes of neutral molecules. In contrast to prior investigations,^{5,6} our calculations fulfill these requirements. Our results differ remarkably from the earlier reports (see Figure 2). We find a smaller thermodynamic stabilization of the complex (-7.9 kcal/mol) but a much higher barrier for isomerization to sulfuric acid (+19.1 kcal/mol relative to the separated educts). The convergence of our relative energies, based on the single-point calculations at different levels, suggests that it is unlikely that still better treatments would give significantly different results. This should be true at least for the energies of the complex and the transition structure TS relative to isolated SO₃ and H₂O. The overall reaction energy to give sulfuric acid seems to be more difficult to compute accurately! The changes from level to level are much larger than the changes of the other relative energies (Table 1). MP2 does not account for electron correlation sufficiently. With all basis sets employed, the MP2 reaction energy relative to water and sulfur trioxide is underestimated. The most reliable value, -20.5 kcal/mol at RMP4SDQ(fc)/6-311+G(2df,p)//RMP2(fu)/6-31+G*, compares well with the experimental ΔH_R° value of 22.1 ± 2.3 kcal/mol at *T* = 0 K.¹⁷ Unfortunately a CI treatment with the larger basis set is beyond our present computational possibilities, but this should also give a reaction energy close to -20 kcal/mol (the variations among MP4SDQ, QCISD, and QCISD(T) levels with the smaller 6-31+G** basis are insignificant). Note that the CNDO/2 relative energy of H₂SO₄ reported in ref 5 was scaled to the experimental value (see Figure 2). The directly computed results give relative energies of -86.0, -110.4, and -167.4 kcal/mol for SO₃·H₂O, TS, and H₂SO₄, respectively!

While the complexation of SO₃ and H₂O is exothermic, it becomes unfavorable at temperatures *T* > 0 K ($-R \ln K = \Delta H/T - \Delta S$). At room temperature the enthalpy differences ΔH_{298}° are not much different from those at 0 K (see Table 6). But the formation of one particle (SO₃·H₂O) out of two (H₂O + SO₃) leads to a loss of entropy. With $\Delta G_{298}^\circ = 0.0$ kcal/mol the equilibrium constant *K* for the equilibrium between water plus sulfur dioxide and their complex becomes $K = \exp(-\Delta G_{298}^\circ/RT) = 1$. In addition the barrier for isomerization ΔG_{298}^\ddagger (relative to H₂O + SO₃) increases to 28.6 kcal/mol.

The basis set superposition error (BSSE) for SO₃·H₂O can be estimated by counterpoise calculations:¹⁸ at RMP2/6-31+G* we found a 1.7 kcal/mol lowering of the total energy of SO₃ by including the H₂O non-core orbitals. Analogously a value of 2.2 kcal/mol was obtained for H₂O with the SO₃ orbitals. The corresponding SCF values were 1.0 and 1.1 kcal/mol, respectively. While these values are small our complexation energy may be overestimated somewhat.

Our geometries should be satisfactory. The parameters of H₂O and SO₃ are almost unchanged in their complex. The water

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Table 1. Absolute^a and Relative^b Energies for SO₃ + H₂O, SO₃·H₂O, TS, and H₂SO₄

method	SO ₃ + H ₂ O	H ₂ O·SO ₃	TS	H ₂ SO ₄
//RMP2(fu)/6-31G*	-698.89201 (0.0)	-698.91381 (-11.3)	-698.86935 (+14.9)	-698.92386 (-16.3)
//RMP2(fu)/6-31+G*	-698.92624 (0.0)	-698.94448 (-9.1)	-698.89554 (+19.9)	-698.95162 (-12.2)
single points ^c 6-31+G**//				
RMP2(fu)/6-31+G*				
RMP2(fc)	-698.92385 (0.0)	-698.94001 (-7.8)	-698.89185 (+20.7)	-698.94684 (-10.7)
RMP3(fc)	-698.89707 (0.0)	-698.91461 (-9.0)	-698.86590 (+20.2)	-698.93340 (-19.4)
RMP4D(fc)	-698.92229 (0.0)	-698.93871 (-8.3)	-698.88922 (+21.4)	-698.95322 (-16.2)
RMP4DQ(fc)	-698.90632 (0.0)	-698.92319 (-8.5)	-698.87337 (+21.3)	-698.94022 (-18.1)
RMP4SDQ(fc)	-698.92481 (0.0)	-698.94124 (-8.3)	-698.89114 (+21.8)	-698.95478 (-15.6)
RQCISD	-698.92415 (0.0)	-698.94078 (-8.4)	-698.89102 (+21.4)	-698.95532 (-16.4)
RQCISD(T)	-698.95433 (0.0)	-698.97089 (-8.3)	-698.92237 (+20.7)	-698.98164 (-13.9)
single points ^c 6-311+G(2df,p)//				
RMP2(fu)/6-31+G*				
RMP2(fc)	-699.33152 (0.0)	-699.34752 (-8.0)	-699.30563 (+16.9)	-699.36331 (-16.7)
RMP3(fc)	-699.30295 (0.0)	-699.31963 (-8.6)	-699.27617 (+17.5)	-699.34653 (-24.1)
RMP4SDQ(fc)	-699.32597 (0.0)	-699.34174 (-7.9)	-699.29668 (+19.1)	-699.36368 (-20.5)

^a In au. ^b Relative energies in parentheses (in kcal/mol) are ZPE corrected (0.93 scaled RMP(fu)/6-31G* values, see Table 6). ^c Single-point calculations were carried out employing the 6-31+G** or 6-311+G(2df,p) basis set and the RMP2(fu)/6-31+G* geometries.

Table 2. Calculated and Measured Vibrational Frequencies of SO₃·H₂O (in cm⁻¹)

vibration	H ₂ O and SO ₃		SO ₃ ·H ₂ O			
	RMP2 ^a	exptl	RMP2 ^a	ref 2 ^b	ref 9 ^c	ref 10 ^d
ν_3 (H ₂ O) ^e	3643	3726.9 ^f	3592 (-51)	3648.8 (-78.1)	3612.9 (-114.0)	3678.2 (-48.7)
ν_1 (H ₂ O)	3512	3634.5 ^f	3468 (-44)	3562.7 (-71.8)		3562.8 (-71.7)
						3558.6 (-75.9)
ν_2 (H ₂ O)	1614	1597.6 ^f	1588 (-26)		1591.4 (-6.2)	
ν_3 (SO ₃)	1303	1397.7 ^g	1320 (+17)	1399.1 (+1.4)	1401.3 (+3.6)	
		1395.3 ^g	1307 (+4)	1390.3 (-5.0)		1397.0 (-0.7)
ν_{sym} (SO ₃)	953	IR forbidden	972 (+19)	1079.3		
ν_4 (SO ₃)	464	532.1, 531.5 ^g	519 (+55)			549.4 (+17.3)
			496 (+32)			545.8 (+14.3)
ν_2 (SO ₃)	428	488.1 ^g	448 (+20)		490.9 (-9.1)	488.5 (+0.4)
			435 ^h			

^a Using 6-31G*, scaling factor 0.93. ^b Codeposition of H₂O, SO₃, and N₂ (1:1:1500). ^c SO₃·H₂O in Ne matrix at 5 K. ^d By photooxidation of H₂S in O₂ at 15 K. ^e Where possible the vibrations are assigned as motions of the isolated entities. ^f H₂O in N₂ matrix (20 K), ref 31. ^g SO₃ in N₂ matrix, ref 9. ^h The remaining five calculated frequencies for SO₃·H₂O are 427, 178 (ν (H₂O·SO₃)), 146, 143, and 79.

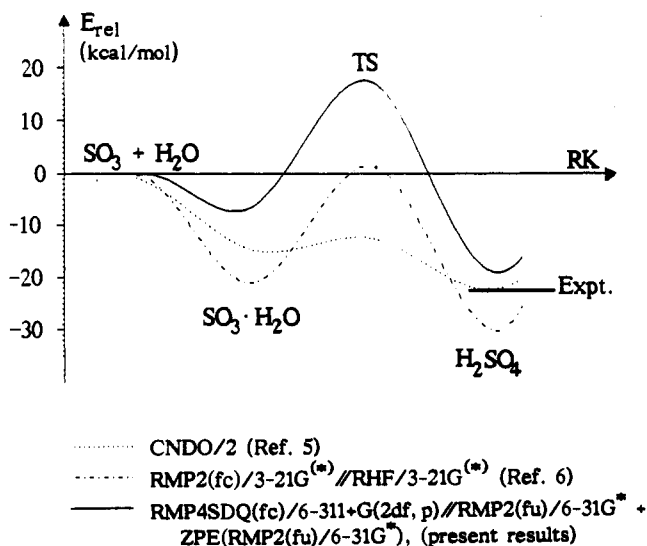


Figure 2. Comparison of the present results with previous computations. Also note the experimental (JANAF) reaction data.

molecule is located above an SO₃ unit in A with an 22° angle between their planes. A starting geometry with a staggered orientation (corresponding to an angle of 90°) also led to the same 22° arrangement. This preference can be rationalized on electrostatic grounds: unlike charged centers attract each other, so that A is preferred over B.

Ab initio calculations normally describe isolated species and thus give equilibrium structures. The geometries of weakly bound

complexes such as BH₃·NH₃¹⁹ or NH₃·SO₃²⁰ are especially sensitive to environmental influences. We could show that this also is true for SO₃·H₂O by SCRF computations. The S...OH₂ distance d (S...O) was partially optimized by calculating SCRF/6-31G* single points using water parameters.²¹ The SCRF/6-31G* d (S...O) minimum is 1.825 Å and the "total energy in the solvent" is 11.9 kcal/mol lower than that computed with the RMP2(fu)/6-31G* vacuum distance d (S...O) = 2.453 Å. Although these results depend on the SCRF model and solvent parameters employed, the contraction in the separation between the components of the complex in a polarizable medium is shown clearly.

In the gas-phase transition structure (TS), d (S...O) is only 1.896 Å and the migrating H is placed almost symmetrically between two oxygens. The dihedral angle is 2.8° in the four-membered cyclic O¹-S-O⁴-H arrangement. The S-O⁴ bond

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Table 3. Charge Transfer Interactions in H₂O-SO₃ Calculated by a Deletion Analysis at RHF/6-31+G*/RMP2(fu)/6-31+G*

$\sigma^*(\text{H}_2\text{O})^a \leftarrow \sigma(\text{SO}_3)$	16.5 kcal/mol
$\sigma(\text{H}_2\text{O}) \rightarrow \sigma^*(\text{SO}_3)$	
$\sigma^*(\text{H}_2\text{O}) \leftarrow \sigma(\text{SO}_3)$	2.5 kcal/mol
$\sigma(\text{H}_2\text{O}) \rightarrow \sigma^*(\text{SO}_3)$	14.1 kcal/mol
lp(O) ^b → 3s,3p _r (S)	11.3 kcal/mol
lp(O) → 3s(S)	2.4 kcal/mol
lp(O) → 3p _r (S)	9.0 kcal/mol

^a σ and σ^* stand for all formally occupied and unoccupied orbitals of a molecule, respectively. ^b lp stands for the oxygen lone pair in water, directed to the sulfur atom of SO₃.

length is near the average of the corresponding separations in the complex and in the acid.

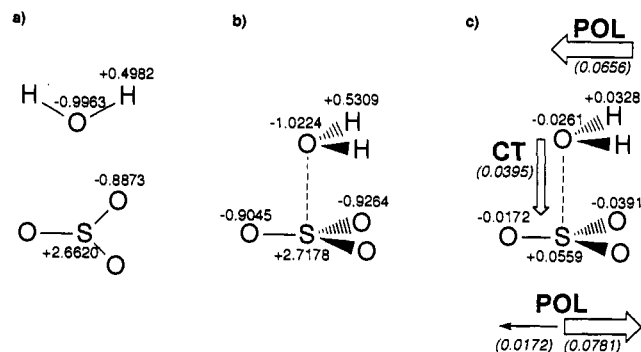
Our computed structural parameters of the acid (Figure 1e) are in good agreement with the GED values of Kuczowski et al.,¹⁴ with the exception of the two S–O distances. The deviations are 2.4 and 4.9 pm for the oxo and hydroxo oxygen, respectively. A RMP2(fc)/6-31+G** single-point calculation on the GED structure gave an energy only 3.8 kcal/mol higher than for the computed minimum. It is not clear which is more accurate, the GED or the theoretical structure. Recent calculations on the isoelectronic H₂PO₄⁻ are in line with our results.^{22,23} They give bond distances of 1.486 Å for P–O⁻ and 1.646 Å for P–OH (at CISD/DZP+diff). Analogously to H₂SO₄ the C₂ symmetric structure was found to be the lowest minimum. The C_s and C_{2v} alternatives are higher in energy by about 1 and 4 kcal/mol and correspond to a minimum and a second-order saddle point (at SCF level), respectively.¹⁵

The situation for the complexes is different: While SO₃ binds H₂O by ca. 8 kcal/mol by an electrophilic attachment to the oxygen (see Figure 1c), PO₃⁻ prefers to form two hydrogen bonds (C_{2v}) resulting in about 12 kcal/mol stabilization.²⁴ The activation barrier (based on the separated reactants) for the addition of water to PO₃⁻ to form H₂PO₄⁻ is only +5 kcal/mol,^{22,23} but around +20 kcal/mol (see Table 1) for the H₂SO₄ system investigated here.

Interactions in the SO₃-H₂O Complex

Sulfur trioxide can act as a Lewis acid and water as a Lewis base. Their complex can be described as a charge transfer (CT) complex with H₂O donating electron density to SO₃. Natural population analysis (NPA)²⁵ shows charge transfer of 0.0395 e from H₂O to SO₃ (RHF/6-31+G*/RMP2(fu)/6-31+G*). In order to quantify this interaction, an NBO deletion analysis for the complex was performed: The orbital interaction energy can be deduced by deleting the corresponding off-diagonal elements from the NLMO (natural localized molecular orbitals) Fock matrix symmetrically and recalculating the new energy.²⁶ Some deletion results are given in Table 3. Note that the energies turn out to be additive although this is not an implicit requirement.

As expected, the most important charge transfer energetically is due to donation of electron density from an oxygen lone pair of the water unit to the sulfur atom in sulfur trioxide. However, the atomic NBO charges show that this is not the only charge redistribution which occurs in the adduct: the water oxygen becomes more negative and the sulfur more positive than in the isolated molecules (see Figure 3, a and b). We ascribe this to polarization (dipole induction) of one molecule in the complex by the other. The changes in atomic charges of H₂O hydrogen

**Figure 3.** NPA charges (RHF/6-31+G*/RMP2(fu)/6-31+G*) for (a) H₂O, SO₃ (b) H₂O-SO₃, and (c) the changes which are ascribed to polarization (POL) and charge transfer (CT).**Table 4.** RHF/6-31+G*/RMP2(fu)6-31+G* NPA Charges for H₂O and SO₃

		molecules in their complex geometry				polarization
		free molecules	in the complex	without charges	with charges ^a	
H ₂ O	O	-0.9963	-1.0224	-0.9990	-1.0826	-0.0836
	H	+0.4982	+0.5309	+0.4995	+0.5413	+0.0418
SO ₃	S	+2.6620	+2.7178	+2.6642	+2.7281	+0.0639
	O ²	-0.8873	-0.9045	-0.8879	-0.8919	-0.0040
	O ^{3,4}	-0.8873	-0.9264	-0.8881	-0.9181	-0.0300

^a NPA/6-31+G* for SO₃: S, +2.72; O², -0.90; O^{3,4}, -0.93, NPA/6-31+G* for H₂O: O, -1.02; H, +0.53.

and SO₃ oxygen, which do not take part in charge transfer directly, provide an estimate of polarization effects (0.0656 e H₂O; 0.0781 e and 0.0172 e in SO₃, see Figure 3). The amount of charge transfer is given directly by the sum of atomic charges of the molecules (0.0395 e). Polarization may thus be more important for the electron density redistribution than the charge transfer (see Figure 3c).

In order to check this conclusion and to obtain quantities for polarization we employed a simple point charge model. The nuclei of one molecule were substituted by point charges derived from NPA and the effect on the other molecule was studied. Of course, contracting the atom charge to a single point models its real continuous charge distribution very crudely. Nevertheless, electrostatic and covalent effects may be estimated separately in this manner. Data in Table 4 show that the change in the electron distribution of one molecule is the same whether it is induced by an second molecule or by the computed charges. Thus, it should be possible to model the electrostatic effect of one molecule in a complex by its NPA point charges.

When the SO₃ molecule is replaced by the corresponding natural charges on O and S, electron shifts relative to unperturbed H₂O also are found (Table 4). However, these are larger than those produced by SO₃ itself. In the SO₃-H₂O complex, electron density is donated from the water oxygen to SO₃. The data in Table 4 also provide details of the effect of H₂O and of the H₂O charges on SO₃. In this case, polarization is the main effect responsible for the changes in charges of the two types of oxygens in the SO₃-H₂O complex. Hence, both polarization and charge transfer are important for the electron distribution in the SO₃-H₂O complex. However, we show below that polarization is not the main effect contributing to the binding energy.

The Morokuma procedure²⁷ has been used to carry out energy decompositions for some SO₂ and SO₃ complexes.²⁸ The results showed electrostatic interaction to be more important than

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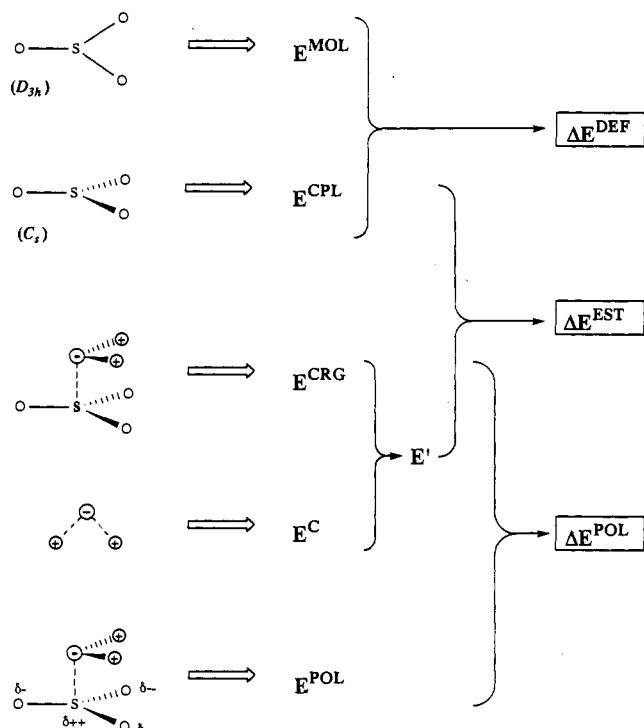


Figure 4. Scheme of the energy decomposition based on a simple NBO/point charge model for SO_3 in $\text{H}_2\text{O}\text{-SO}_3$: E^{MOL} = energy of the isolated molecule; E^{CPL} = energy for the molecule in its complex geometry; E^{CRG} = energy of the unrelaxed wave function (obtained for calculation of E^{MOL}) of one molecule in the presence of the NBO point charges of the other; E^{C} = coulomb energy for the point charges representing one molecule; E^{POL} = energy for the relaxed (polarized) wave function for one molecule in the presence of the point charges.

polarization, charge transfer, and exchange repulsion energy. However, it is claimed that electrostatics are overestimated and charge transfer is underestimated by this decomposition procedure because of an implicit orthogonalization of the occupied orbital space of one molecule to the virtual orbitals of the other.²⁹ We tried an energy decomposition as sketched in Figure 4 employing the NBO method together with the simple point charge model mentioned above. The following data are based on RHF/6-31+G*//RMP2(fu)/6-31+G* results.

First we established that the geometries changed on complexation only slightly. The deformation energies were computed by using the geometries of SO_3 and H_2O in the $\text{SO}_3\text{-H}_2\text{O}$ complex and comparing the single point energies with those of the relaxed species. These deformation energies ($\Delta E^{\text{DEF}}(\text{H}_2\text{O}) = +0.3$ kcal/mol, $\Delta E^{\text{DEF}}(\text{SO}_3) = \pm 0.0$ kcal/mol) are very small.

Absolute energies for one molecule in the presence of point charges were calculated for the undisturbed wave function of the free molecule (E^{CRG}) and for the "relaxed", polarized wave function (E^{POL}). The difference is termed the polarization energy ΔE^{POL} .

E^{CRG} can be decomposed into the energy of the free molecule in its complex geometry (E^{CPL}), the coulomb energy of the point charge arrangement (E^{C}), and the electrostatic interaction energy between the charges and the molecule (ΔE^{EST}). As E^{C} is easily available by simple computation,³⁰ the electrostatic term can be derived by $\Delta E^{\text{EST}} = E^{\text{CRG}} - E^{\text{CPL}} - E^{\text{C}}$. The final electrostatic stabilization of the complex is the average of the two values for water and sulfur trioxide. These calculations were performed with the charges calculated for the free molecules and repeated

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(30) $E^{\text{C}} = \sum_{i,j} Q_i Q_j / 4\pi\epsilon_0 d_{ij}$; $\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$; d_{ij} = distance between charges Q_i and Q_j .

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Table 5. Energy Decomposition^a for $\text{H}_2\text{O}\text{-SO}_3$ at the RHF/6-31+G*//RMP2(fu)/6-31+G* Level

absolute energies ^b		relative energies ^c
(A) H_2O		
$E^{\text{MOL}} = -76.01665$		
$E^{\text{CPL}} = -76.01625$		$\Delta E^{\text{DEF}} = +0.3$
With NPA/RHF/6-31+G* Charges of the SO_3 Molecule ^d		
$E^{\text{CRG}} = -78.13006$		$\Delta E^{\text{CRG}} = -1326.4$
$E^{\text{C}} = -2.07835$		$\Delta E^{\text{EST}} = -22.3$
$E^{\text{POL}} = -78.13784$		$\Delta E^{\text{POL}} = -4.9$
With NPA/RHF/6-31+G* Charges of SO_3 in the Complex ^e		
$E^{\text{CRG}} = -78.24208$		$\Delta E^{\text{CRG}} = -1396.7$
$E^{\text{C}} = -2.19115$		$\Delta E^{\text{EST}} = -21.8$
$E^{\text{POL}} = -78.24985$		$\Delta E^{\text{POL}} = -4.9$
(B) SO_3		
$E^{\text{MOL}} = -621.97531$		
$E^{\text{CPL}} = -621.97536$		$\Delta E^{\text{DEF}} = +0.0$
With NPA/RHF/6-31+G* Charges of the H_2O Molecule ^f		
$E^{\text{CRG}} = -622.46017$		$\Delta E^{\text{CRG}} = -304.2$
$E^{\text{C}} = -0.45780$		$\Delta E^{\text{EST}} = -16.9$
$E^{\text{POL}} = -622.46234$		$\Delta E^{\text{POL}} = -1.3$
With NPA/RHF/6-31+G* Charges of H_2O in the Complex ^g		
$E^{\text{CRG}} = -622.49521$		$\Delta E^{\text{CRG}} = -326.2$
$E^{\text{C}} = -0.49137$		$\Delta E^{\text{EST}} = -17.9$
$E^{\text{POL}} = -622.49726$		$\Delta E^{\text{POL}} = -1.3$

^a For definition of energy contributions see text. ^b Absolute energies in au. ^c Relative energies in kcal/mol. ^d S, +2.66; O, -0.89. ^e S, +2.72; O, -0.90; O, -0.93 (see Figure 1 for numbering). ^f O, -1.00; H, +0.50. ^g O, -1.02; H, +0.53.

with those calculated for the complex in order to ascertain the influence of dipole induction on the electrostatic interaction. The results are presented in Table 5.

The different charges of the free and complexed molecules lead to almost identical results. The electrostatic stabilization $\Delta E^{\text{EST}} = 0.5[\Delta E^{\text{EST}}(\text{H}_2\text{O}) + \Delta E^{\text{EST}}(\text{SO}_3)] = -19.9$ kcal/mol is about the same as the above calculated charge transfer energy ΔE^{CT} (-16.5 kcal/mol). In comparison, the polarization terms ΔE^{POL} are small (-4.9 kcal/mol for H_2O and -1.3 kcal/mol for SO_3), although we did find a major influence on the charge distribution (see above). To rationalize the ΔE^{EST} values, the coulomb energy between the two sets of point charges employed also was calculated. This is -24.3 kcal/mol based on the molecule charges and -24.0 kcal/mol for the complex charges. Hence, our model indicates that charge transfer and electrostatic interaction are equally important for the complex stability. The calculated energy contributions total -42.4 kcal/mol. But as the complex is only -11.1 kcal/mol more stable (at the level of energy decomposition), the repulsion term ΔE^{REP} must be +31.1 kcal/mol. It is obvious that a repulsion term exists, because all the contributions evaluated (besides ΔE^{DEF}) are stabilizing and become even larger at shorter $d(\text{S}\cdots\text{O})$ distances. But the fragments only approach the equilibrium distance where the net sum of all interactions is a minimum. We ascribe ΔE^{REP} to the repulsion of the penetrating electron clouds and to increasing nuclear-nuclear repulsion.

However, charge transfer has a major influence on the geometry of the complex: partial optimization of the $d(\text{S}\cdots\text{O})$ distance in $\text{H}_2\text{O}\text{-SO}_3$ without allowing charge transfer leads to an equilibrium separation of 3.15 Å (RHF/6-31+G*//RMP2(fu)/6-31+G*). We repeated the energy decomposition described above at this geometry and found $\Delta E^{\text{EST}} = -10.4$ kcal/mol and $\Delta E^{\text{POL}} = -0.3$ kcal/mol for H_2O . $\Delta E^{\text{EST}} = -7.0$ kcal/mol and $\Delta E^{\text{POL}} = -0.3$ kcal/mol for SO_3 . Hence, at this large distance without any charge transfer, the electrostatic attraction is only half and the polarization energy is negligible. The total stabilization vs infinite separation is 4.3 kcal/mol, and the repulsion energy is only +4.7 kcal/mol. A closer approach results in charge transfer. At closer distances, mutual polarization of SO_3 and H_2O becomes effective,

Table 6. Thermodynamic Data for SO₃, H₂O, SO₃·H₂O, TS, and H₂SO₄^{a,b}

	SO ₃	H ₂ O	SO ₃ ·H ₂ O	TS	H ₂ SO ₄
C_p° (cal mol ⁻¹ K ⁻¹)	12.4 (12.1)	8.0 (8.0)	22.4	17.9	19.79 (20.02)
S° (cal mol ⁻¹ K ⁻¹)	61.7 (61.3)	45.1 (45.1)	80.3	71.0	71.19 (71.41)
ZPE (kcal mol ⁻¹) ^c	7.1	12.6	21.6	20.2	24.5
rel ΔH_0° (kcal mol ⁻¹) ^d		0.0	-7.9	+19.5	-20.5 (-22.1)
rel ΔH_{298}° (kcal mol ⁻¹) ^e		0.0	-7.9	+17.9	-21.3 (-23.3)
rel ΔG_{298}° (kcal mol ⁻¹) ^f		0.0	0.0	+28.6	-10.7 (-12.9)

^a Theoretical values are derived from the RMP2(fu)/6-31G* frequencies. ^b Experimental values are taken from ref 17 and are given in parentheses. ^c Zero point vibrational energies scaled by 0.93. ^d Relative enthalpies at 0 K: $\text{rel } \Delta H_0^{\circ} = \Delta(\text{MP4}/\text{MP2}) + \Delta\text{ZPE}(\text{MP2})$, see Table 1. ^e $\Delta H_{298}^{\circ} = \Delta H_0^{\circ} + \Delta E_{298}^{\text{vib}} + \Delta E_{298}^{\text{rot}} + \Delta E_{298}^{\text{trans}}$. ^f $\Delta G_{298}^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}$; $T = 298.15$ K.

and the resulting increase in atomic charges led to additional electrostatic attraction.

Frequency Calculations

Ab initio frequencies are calculated with the harmonic approximation and thus they are about 10% larger than those experimentally derived.¹¹ The deviations between calculated and measured values are much larger than the changes caused by complexation. For this reason, we compare these changes rather than absolute values for the complex in Table 2.³²

According to the experimental results,^{2,9,10} all water vibrations are lowered by complexation. This is also found theoretically at MP2(fu)/6-31G*. The SO₃ modes are all shifted to higher wave numbers with the exception of the degenerate ν_3 . One of these vibrations is lowered, but the opposite is given by MP2. The symmetrical SO₃ stretch cannot be compared with experiment, because this vibration is IR forbidden for the free molecule. Calculations for $\nu_2(\text{SO}_3)$ agree better with those of ref 10 than those of ref 9. Experimental and theoretical vibration shifts do not agree well, but note that the largest changes are computed for those frequencies for which the biggest influence of complexation was found experimentally.

Thermodynamic data such as heat capacity (C_p°) and entropy (S°) can be derived from vibrational data. The values obtained for SO₃, H₂O, and H₂SO₄ compare well with experiment¹⁷ (Table 6).

(32) A referee questioned the frequency calculation on H₂O·SO₃ because the magnitude of the frequency shifts is always overestimated for the SO₃ unit and underestimated on the water side. As he points out a possible reason for the discrepancy between calculation and experiment is that the calculated shifts refer to an isolated complex whereas the experimental data were obtained in matrix isolation. The geometry of the complex may be distorted by the matrix in several ways. The experimental signals are dispersed much more than the accuracy of the spectrometers. In agreement with these comments, our SCRF calculations (see Discussion earlier) show a remarkable influence of the medium. Hence, the frequency shifts from the isolated molecules to their complex computed in the gas phase are only indicative of condensed phase behavior.

Conclusions

The direct formation of sulfuric acid from water and sulfur trioxide via a bimolecular complex has been investigated by means of modern *ab initio* molecular orbital theory. At RMP4SDQ/6-311+G(2df,p)//RMP2(fu)/6-31+G*+ZPE, the stabilization of the H₂O·SO₃ complex is -7.9 kcal/mol and a barrier for its isomerization to H₂SO₄ is +27.0 kcal/mol. These values are considerably lower and considerably higher, respectively, than previous results.^{5,6} For room temperature the free energy change for the complexation reaction of H₂O and SO₃, ΔG_{298}° , is 0.0 kcal/mol, and the reaction barrier $\Delta G_{298}^{\ddagger}$ is +28.6 kcal/mol. Thus the formation of sulfuric acid via a direct reaction of one H₂O with one SO₃ seems unlikely. A crucial medium effect on the intermolecular distance in the intermediate complex was shown by SCRF computations. The formation of H₂SO₄ could occur more easily in a cluster with two or more water molecules. This is under investigation. Heterogeneous catalysis might also lead to rapid isomerization of the complex.

For the SO₃·H₂O complex a new energy decomposition procedure based on a simple NBO/point charge model indicates that electrostatic and charge transfer interactions between the two molecules are of comparable importance for the stabilization. Without the latter the intermolecular distance would be substantially larger. Polarization has a less energetic effect, although it is the main contribution to the reorganization of the electron distribution.

The deviation of the reported vibrational frequencies for H₂O·SO₃ from the free molecules is in reasonable agreement with the experimental observations. Calculated heat capacities and entropies for H₂O, SO₃, and H₂SO₄ are in perfect agreement with experimental data even with modest theoretical treatments, while the estimation for the heat of reaction for the formation of sulfuric acid (-20.5 kcal/mol) only agrees with the 22.1 ± 2.3 kcal/mol derived from the JANAF data¹⁷ when a large basis set is used.