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Theoretical Study of OH and H_2O Addition to SO_2

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The G2 computational method is applied to the study of the hydroxyl radical oxidation of SO_2 to SO_3 as well as the hydrolysis of SO_2 to H_2SO_3. A key intermediate in the oxidation process is the $HOSO_2$ radical, which is predicted to have a S−OH bond enthalpy (ΔH_{298}) of 26.2 kcal/mol, 4.3 kcal/mol lower than the currently accepted value of 30.5 kcal/mol. The radical is characterized by a 2c-2e S−OH bond with an unpaired electron delocalized into the π^* orbital of the SO_2 moiety. The hydrolysis of SO_2 to H_2SO_3 was computed with and without a catalytic water. The $SO_2{\cdot}H_2O$ and $SO_2{\cdot}2H_2O$ complexes and transition states are very similar to those computed for SO_3 plus water. The uncatalyzed reaction has an activation barrier of 33.9 kcal/mol, which is reduced to 20.0 kcal/mol with one catalytic water. Since the reaction of SO_2 with two waters is nearly thermoneutral (4.5 kcal/mol endothermic), the reaction may be more amenable to thermodynamic study compared to the $SO_3 + 2H_2O$ reaction, which is much more exothermic.

Introduction

The global anthropogenic emission of sulfur into the atmosphere, mainly in the form of SO_2, is about 10^{14} g/yr.[2] It is believed[3−5] that SO_2 is converted into H_2SO_4 by the series of steps given below (eqs 1−3).

$$SO_2 + OH + M \rightarrow HOSO_2 + M \qquad (1)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + O_2H \qquad (2)$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \qquad (3)$$

The first reaction has been been studied by a variety of techniques.[6−10] The optimized geometry and vibrational frequencies of $HOSO_2$ have also been reported at the HF/3-21G* level.[11] Experimentally, the existence of the $HOSO_2$ radical is on firm ground. It has been formed by neutralization/reionization mass spectrometry,[12] and vibrational frequencies have been measured in a low-temperature matrix.[13] No theoretical calculations on the transition state of eq 1 have been reported.

An early estimate by Benson[14] put the HO−SO_2 bond energy at 37 ± 2 kcal/mol. On the basis of more recent experiments, Gleason and Howard determined the upper limit of the bond enthalpy to be 33 kcal/mol.[15] The most recent compilation of themochemical data gives a value of 30.5 kcal/mol.[16]

The formation of SO_3 from $HOSO_2$ (eq 2) has been studied in a low-pressure discharge flow reactor by directly measuring the loss of $HOSO_2$ using chemical ionization mass spectrometry.[17] At the MP4/6-31G**//HF/3-21G* level plus thermal corrections, eq 2 is calculated to be endothermic by 12.3 kcal/mol.[11] Since the reaction is known to proceed readily,[17] this result is inconsistent with experiment.

The third reaction (eq 3) has received the most attention, both experimentally[18−24] and theoretically.[25−27] It was assumed that the gas-phase reaction involved the initial formation of a SO_3-water complex, which then formed H_2SO_4. In an early study of the reaction by theoretical methods, Chen and Plummer[25] calculated the binding energy of the $SO_3{\cdot}H_2O$ complex to be 21.4 kcal/mol. More recently, Hofmann and Schleyer[26] have carried out a careful study of the reaction with much larger basis sets and high levels of electron correlation. They found the $SO_3{\cdot}H_2O$ complex to be bound by 7.9 kcal/mol with a 27.4 kcal/mol barrier for conversion to H_2SO_4 (enthalpies at 298K with MP4/6-311+G(2df,p)//MP2/6-31+G(d) energies).

Back-to-back publications by Kolb et al.[24] and Morokuma and Muguruma[27] gave experimental and theoretical support to the conversion of SO_3 to H_2SO_4 with the catalytic effect of an additional water (eqs 4−7).

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4{\cdot}H_2O \qquad (4)$$

$$SO_3 + (H_2O)_2 \rightarrow SO_3{\cdot}H_2O + H_2O \qquad (5)$$

$$SO_3{\cdot}H_2O + H_2O \rightarrow H_2SO_4{\cdot}H_2O \qquad (6)$$

$$SO_3{\cdot}2H_2O \rightarrow H_2SO_4{\cdot}H_2O \qquad (7)$$

The uncatalyzed reaction (eqs 8, 9) had a much higher activation

$$SO_3 + H_2O + M \rightarrow SO_3{\cdot}H_2O \qquad (8)$$

$$SO_3{\cdot}H_2O \rightarrow H_2SO_4 \qquad (9)$$

barrier (32.2 kcal/mol) relative to eq 4 (0.7 kcal/mol), eq 6 (5.3 kcal/mol), or eq 7 (13 kcal/mol).

Kolb et al.,[24] using an atmospheric pressure turbulent flow reactor to measure first-order decays with chemical ionization mass spectrometry, determined the reaction rate to be second order in water vapor. They could not determine the relative contribution of eq 4 or eq 6. The activation barrier of eq 7 was considered to be too high for that reaction to participate in the mechanism.

Hofmann-Sievert and Castleman[28] and, more recently, Akhmatskaya et al.[29] have looked at water clusters ($(H_2O)_n$, $n = 2−10$ and $n = 200$) reacting with SO_3 to form H_2SO_4. Their results show that SO_3 is readily converted to sulfuric acid by the water cluster. In addition, Akhmatskaya et al.[29] have carried out Monte Carlo simulations on $[SO_3(H_2O)_2](H_2O)_n$ with $n = 10$ and found that the 10 “extra” waters reduced the activation barrier for formation of H_2SO_4 by 10.0 kcal/mol.

The $SO_3{\cdot}H_2O$ complex has been identified by IR in an argon matrix[30] and, more recently, by microwave spectra of five isotopically substituted derivatives, which has allowed structural

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TABLE 1: Energies, Enthalpies (298 K), and Free Energies (298 K) in hartrees at the G2 Level

	point group	state	E_0	H(298 K)	G(298 K)
H	K	^2S	−0.500 00	−0.497 64	−0.510 65
OH	$C_{\infty v}$	$^2\Sigma$	−75.643 91	−75.640 61	−75.660 81
H_2O	C_{2v}	$^1A_1$	−76.332 06	−76.328 28	−76.349 66
$(H_2O)_2$	C_s	$^1A'$	−152.669 10	−152.662 03	−152.695 50
O_2	$D_{\infty h}$	$^3\Sigma_g^-$	−150.148 22	−150.144 91	−150.168 12
HO_2	C_s	$^2A'$	−150.727 92	−150.724 11	−150.750 03
SO_2	C_{2v}	$^1A_1$	−548.015 74	−548.011 73	−548.039 78
SO_2	C_{2v}	$^3B_1$	−547.898 56	−547.894 35	−547.923 94
SO_3	D_{3h}	$^1A_1'$	−623.125 32	−623.120 86	−623.149 75
$HOSO_2$	C_1	^2A	−623.699 28	−623.694 12	−623.726 49
$HOSO_2$ (cis)	C_s	$^2A'$	−623.693 86	−623.693 69	−623.725 42
$HOSO_2$ (trans)	C_s	$^2A'$	−623.689 15	−623.688 95	−623.720 72
$HOSO_2$ (cis)	C_s	$^2A''$	−623.661 45	−623.656 28	−623.688 68
$HOSO_2$ (trans)	C_s	$^2A''$	−623.656 84	−623.651 33	−623.684 54
HSO_3	C_{3v}	$^2A_2$	−623.644 84	−623.640 30	−623.670 69
HOOSO	C_1	^2A	−623.618 88	−623.612 95	−623.647 20
TS($HOSO_2 \rightarrow HSO_3$)	C_s	$^2A'$	−623.617 66	−623.612 89	−623.644 65
TS(OH + SO_2)	C_1	^2A	−623.662 79	−623.657 16	−623.690 85
$SO_2 \cdot H_2O$	C_s	$^1A'$	−624.353 32	−624.345 60	−624.383 67
H_2SO_3	C_s	$^1A'$	−624.338 55	−624.332 82	−624.366 25
$SO_2 \cdot 2H_2O$	C_1	^1A	−700.695 83	−700.685 44	−700.729 48
$H_2SO_3 \cdot H_2O$	C_s	^1A	−700.685 22	−700.678 18	−700.716 56
TS−1H_2O	C_1	^1A	−624.296 68	−624.291 50	−624.323 35
TS−2H_2O	C_1	^1A	−700.660 42	−700.653 39	−700.689 57

parameters to be determined.[31] The S−O interaction is 2.432 Å, and the H−O−H plane makes a 103° angle with the S−O axis. While the orientation of the water with respect to SO_3 could not be determined by experiment, high-level theory[26] suggests an eclipsed geometry which would allow each hydrogen to interact with a different oxygen of SO_3.

Our goals in this study are 2-fold: to investigate the nature of the SO_2−OH complex and to consider the reaction of SO_2 with one and two water molecules to form sulfurous acid (eqs 10−15). While the hydrolysis reactions are not usually considered in atmospheric cycles, they may have relevance when the water vapor concentration is high and OH radical concentration low. Also, since the SO_2/H_2O reaction is less exothermic than the SO_3/H_2O reaction, the former reaction may be more amenable to study by equilibrium techniques.

$$SO_2 + H_2O + M \rightarrow SO_2 \cdot H_2O + M \tag{10}$$

$$SO_2 \cdot H_2O \rightarrow H_2SO_3 \tag{11}$$

$$SO_2 + (H_2O)_2 \rightarrow H_2SO_3 \cdot H_2O \tag{12}$$

$$SO_2 + (H_2O)_2 \rightarrow SO_2 \cdot H_2O + H_2O \tag{13}$$

$$SO_2 \cdot H_2O + H_2O \rightarrow H_2SO_3 \cdot H_2O \tag{14}$$

$$SO_2 \cdot 2H_2O \rightarrow H_2SO_3 \cdot H_2O \tag{15}$$

TABLE 2: Relative Energies, Enthalpies, and Free Energies (kcal/mol) at the G2 Level on the $HOSO_2$ Potential Energy Surface

	ΔE	ΔH (298 K)	ΔG (298 K)
SO_2 + OH	0.0	0.0	0.0
SO_3 + H	21.5	21.2	25.2
$HOSO_2$	−24.9	−26.2	−16.2
$HOSO_2$ ($^2A'$ cis)	−21.5	−25.9	−15.6
$HOSO_2$ ($^2A'$ trans)	−18.5	−23.0	−12.6
$HOSO_2$ ($^2A''$ cis)	−1.1	−2.5	7.5
$HOSO_2$ ($^2A''$ trans)	1.8	0.6	10.1
HSO_3	9.3	7.6	18.8
HOOSO	25.6	24.7	33.5
TS($HOSO_2 \rightarrow HSO_3$)	26.3	24.8	35.1
TS(OH + SO_2)	−2.0	−3.0	6.1
$HOSO_2$ + O_2 ($^3\Sigma_g^-$)	0.0	0.0	0.0
SO_3 + O_2H	−3.6	−3.7	−3.2

TABLE 3: Relative Energies, Enthalpies, and Free Energies (kcal/mol) at the G2 Level for the Reactions $SO_2 + n(H_2O)$, $n = 1, 2$

	ΔE	ΔH (298 K)	ΔG (298 K)
$SO_2 + H_2O$	0.0	0.0	0.0
$SO_2 \cdot H_2O$	−3.5	−3.5	3.6
TS−1H_2O	32.1	30.4	41.5
H_2SO_3	5.8	4.5	14.6
$SO_2 + 2H_2O$	0.0	0.0	0.0
$SO_2 + (H_2O)_2$	−3.1	−3.4	2.4
$SO_2 \cdot H_2O + H_2O$	−3.5	−3.5	3.6
$SO_2 \cdot 2H_2O$	−10.0	−10.7	6.0
TS−1H_2O + H_2O	32.1	30.4	41.5
TS−2H_2O	12.2	9.3	31.1
$H_2SO_3 \cdot H_2O$	−3.4	−6.2	14.1
$H_2SO_3 + H_2O$	5.8	4.5	14.6

Computational Method

All calculations were carried out with the Gaussian94 program package.[32] G2 energies were computed in the standard way,[33] while enthalpy corrections and free energies at 1 atm and 298K were computed using HF/6-31G(d) frequencies in the harmonic approximation without scaling. Energies, enthalpies, and free energies at the G2 level are given in Table 1, while relative energies (kcal/mol) on the HSO_3 potential energy surface are presented in Table 2 and on the $SO_2 \cdot H_2O$ and $SO_2 \cdot 2H_2O$ surfaces in Table 3. Figures of molecular structures on the HSO_3 potential energy surface at the MP2(FULL)/6-31G(d) level are given in Figure 1 and on the $SO_2 \cdot H_2O$ and $SO_2 \cdot 2H_2O$ potential energy surfaces in Figure 2.

Results and Discussion

$HOSO_2$. The nature of the interaction between a radical and a neutral species containing a lone pair is influenced by the energy for rehybridization and the strength of the 2c-2e (two-center two-electron) bond between the radical and neutral species.[34] When the rehybridization energy is high (i.e. no low-lying empty orbitals), a 2c-3e bond may be formed. This is

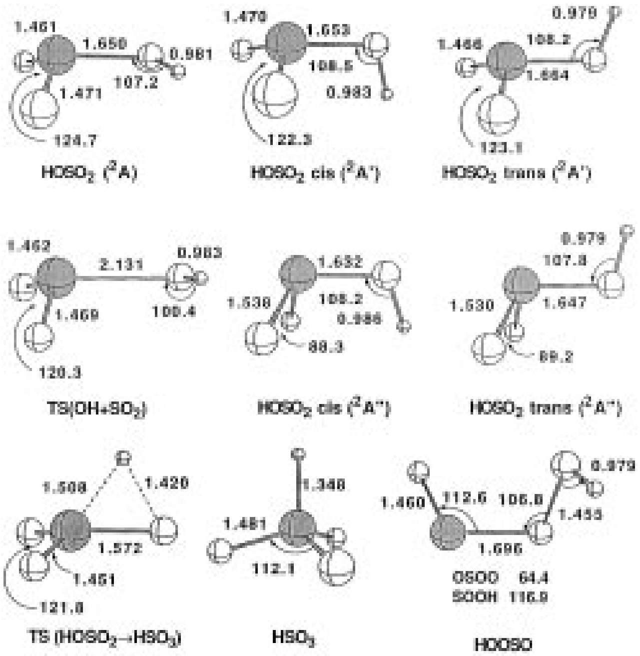

Figure 1. Molecular plots of species relevant to the addition of OH to SO_2. Selected geometric parameters are at the MP2(FULL)/6-31G-(d) level.

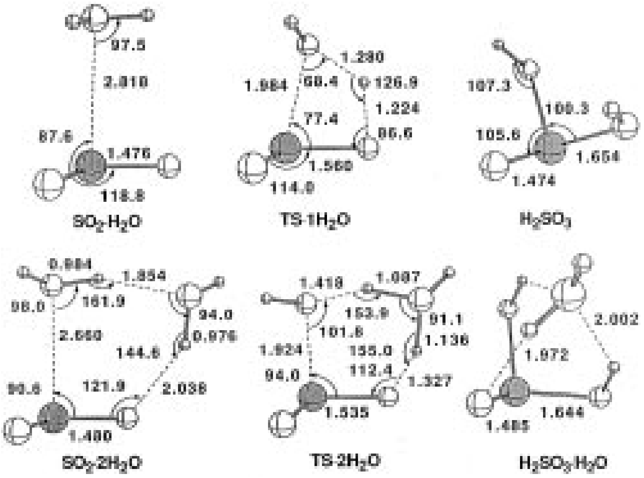

Figure 2. Molecular plots of species relevant to the addition of one (top row) and two waters (bottom row) to SO_2. Selected geometric parameters are at the MP2(FULL)/6-31G(d) level.

the case for $HOS(CH_3)_2$[35] and $HOS(H)CH_3$,[36] where the O−S distance is 1.9−2.0 Å and the unpaired spin density is evenly shared between sulfur and oxygen. In SO_2, the presence of an empty π^* orbital allows the facile rehybridization around the sulfur resulting in a $^2A'$ state with a 2c-2e S−O bond and unpaired spin density delocalized in the π^* orbital. In the lowest-energy gauche conformation, the OH radical is bound by 26.2 kcal/mol. There are small rotation activation barriers of 0.3 and 3.2 kcal/mol for rotating over the cis and trans transition states, respectively. The 26.2 kcal/mol bond enthalpy is somewhat smaller than the latest experimental estimate[16] of 30.5 kcal/mol.

Alternatively, an electron from the sulfur lone pair can be promoted into a σ^* orbital, which would lead to the formation of a $^2A''$ state for $HOSO_2$. As expected (since the σ^* orbitals is higher in energy than the π^* orbital), the $^2A''$ state is higher than the $^2A'$ state; by 23.4 kcal/mol in the cis orientation and 23.6 kcal/mol in the trans orientation (Table 2).

TABLE 4: Estimated and Calculated $X-SO_2$, X = H, F, Cl, OH, Bond Enthalpies (kcal/mol)

$X-SO_2$	singlet−triplet splitting[a]	standard 2c−2e bond enthalpy (BE)[b]	predicted $X-SO_2$ BE[d]	calculated $X-SO_2$ BE
H	73.5	81−87	10.5	15.0[e]
F	73.5	68−118, 90.8[c]	17.3	28.7[f]
Cl	73.5	60−61	−13.0	−7.7[f]
OH	73.5			26.2[g]

[a] Singlet−triplet splitting in SO_2 calculated from enthalpy differences in Table 1. [b] Standard bond enthalpies (kcal/mol) from: Shriver, D.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 69; Huheey, J. E. *Inorganic Chemistry*; 3rd ed.; Harper & Row: Cambridge, 1983; p A-32. [c] Standard 2c-2e S−F bond enthalpy taken from $SF_2 \rightarrow SF + F$. See ref 38. [d] The difference between the singlet−triplet splitting in SO_2 and the standard 2c-2e bond enthalpy is the estimate of the $X-SO_2$ bond enthalpy (kcal/mol). [e] G2 bond enthalpy (ΔH_{298}) taken from: Laakso, D.; Smith, C. E.; Goumri, A.; Rocha, J.−D. R.; Marshall, P. *Chem. Phys. Lett.* **1994**, *227*, 377. [f] Bond energy at QCISD/6-31G(d)+ZPC taken from: Li, Z. *Chem. Phys. Lett.* **1997**, *269*, 128. [g] This work.

An estimate of the $X-SO_2$ bond enthalpy can be made by subtracting the singlet−triplet splitting in SO_2 ($^1A_1-{}^3B_1$, 73.5 kcal/mol), which is an estimate of the required promotion energy, from the standard 2c-2e S−X bond enthalpy.[34] Estimated and calculated bond enthalpies for $X-SO_2$, X = H, F, Cl are presented in Table 4. The standard 2c-2e bond enthalpy of S−H (81−87 kcal/mol) and S−Cl (60−61 kcal/mol) do not vary significantly between different sources. In contrast, the standard 2c-2e S−F bond enthalpy varies from 68 to 118 kcal/mol.[37] In a recent study of the thermochemistry of SF_n, $n = 1-6$, Cheung et al.[38] reported experimental bond energies from 43.4 kcal/mol (SF_4-F) to 101.0 kcal/mol (SF_5-F). We choose the reaction enthalpy of $SF_2 \rightarrow SF + F$ as our standard 2c-2e S−F bond (90.8 kcal/mol) in Table 4.

The results in Table 4 indicate that the positive bond enthalpy of $X-SO_2$, X = H and F, and the negative bond enthalpy of X = Cl are a consequence of the intrinsic 2c-2e S−X bond enthalpies. Thus, the smaller 2c-2e S−Cl bond enthalpy does not compensate for the energy required to rehybridize around sulfur resulting in an unstable complex. Using the results of Table 4, an estimate of about 95 kcal/mol can be made for the standard 2c-2e S−O bond (73.5 + 26.2 − 5).

Since electronic reorganization is required prior to bond formation, an activation barrier is expected in the addition of OH to SO_2. The transition state is characterized by a long S−OH distance of 2.131 Å (Figure 1). The O−S−O angle in the transition state has opened up 0.5°, and the S−O average bond length has decreased 0.01 Å compared to free SO_2. While the energy of the transition state is 5.6 kcal/mol *above* reactants at the MP2(FULL)/6-21G(d) level, at the G2 level, the enthalpy of the transition state (ΔH_{298}) is 3.0 kcal/mol *below* reactants (Table 2). Thus, it appears that the maximum along the reaction path must occur at a different location on the G2 surface. We are currently exploring the possiblity that formation of a 2c-3e bonded complex precedes the formation of the $HOSO_2$ radical. In that event, the 2c-3e complex may form without activation (no electronic reorganization required) followed by an activation barrier to $HOSO_2$.

We also investigated the rearrangement of $HOSO_2$ to HSO_3. Several reports have appeared on the relative stability of the bisulfite ion ($HOSO_2^-$) and sulfonate ion (HSO_3^-) in the gas phase[39,40] as well as in the aqueous phase.[40] The preferred gas-phase structure is highly dependent on the level of theory with the sulfonate ion predicted to be 3.2 kcal/mol more stable at the G2 level and the bisulfite ion 3.7 kcal/mol more stable at

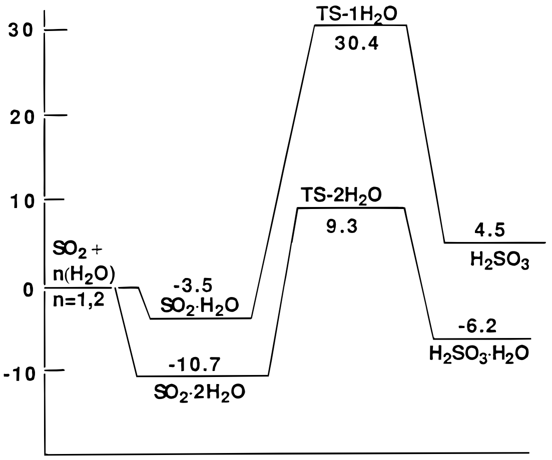

Figure 3. Enthalpy (298 K) profile for the reaction of one and two waters with SO_2. Scale on the left is in units of kcal/mol.

the BD(T)/6-31G(d,p)//MP2/6-31G(d,p) level.[40] The present G2 results predict the HSO_3 radical to be 33.8 kcal/mol less stable than $HOSO_2$ but bound by 13.6 kcal/mol relative to H + SO_3. The HSO_3 radical should have kinetic stability since rearrangement to the more stable $HOSO_2$ has a barrier of 17.2 kcal/mol (Table 2).

HOOSO. The formation of a O−O 2c-2e bond between OH and SO_2 is predicted to be much less favorable. In fact, the HOOSO radical is predicted to be 24.7 kcal/mol higher in energy than OH plus SO_2 (Table 2). Presumably, the electronic promotion energy necessary to reach the appropriate biradical configuration of SO_2 is not compensated for by the formation of a 2c-2e O−O bond with the hydroxyl radical.

$HOSO_2 + O_2 \rightarrow SO_3 + O_2H$. Using an early estimate for the heat of formation of $HOSO_2$ by Benson[14] (−98 ± 2 kcal/mol), eq 2 is predicted to be endothermic by 6 kcal/mol. Since the reaction is known[15] to have a small activation barrier (0.7 kcal/mol), the estimated heat of formation of $HOSO_2$ is clearly too low. The latest compilation[16] gives −92.0 kcal/mol, which reduces the endothermicity of the reaction to 0.9 kcal/mol. In comparison, the enthalpy of reaction at the G2 level is −3.7 kcal/mol (Table 2), which implies a heat of formation for $HOSO_2$ of −87.4 kcal/mol.

$SO_2 + n(H_2O)$, $n = 1$. The initial complex between SO_2 and H_2O (Figure 2) is much looser and weaker than the $SO_3{\cdot}H_2O$ complex[30,31] which can be attributed to the fact that SO_2 is a poorer Lewis acid compared to SO_3.[41] The S−O distance in $SO_2{\cdot}H_2O$ is 2.818 Å (MP2/6-31G(d)) compared to 2.453 in $SO_3{\cdot}H_2O$ (MP2/6-31+G(d)),[26] and the binding energy is 3.5 kcal/mol in $SO_2{\cdot}H_2O$ (ΔH_{298} G2) compared to 7.9 in $SO_3{\cdot}H_2O$ (ΔH_{298} MP4/6-311+G(2df,p)//MP2/6-31+G(d)).[26] However, the interaction in $SO_2{\cdot}H_2O$ is not dominated by hydrogen bonding as evidenced by the sandwich orientation of the SO_2 and H_2O molecular planes (Figure 2). In addition, the two OH bonds of H_2O are eclipsing the S−O bonds of SO_2 to maximize dipole interactions as well as intracomplex H-bonding.

The transition state for addition of H_2O to SO_2 to form H_2SO_3 is very similar to the analogous reaction, $SO_3 + H_2O \rightarrow H_2SO_4$.[26,27] The most significant difference is in the length of the forming S−OH bond (Figure 2) which is about 0.1 Å longer in the transition state to form H_2SO_3 (1.984 versus 1.896 Å[26]). The activation barrier for formation of H_2SO_3 (Figure 3, ΔH_{298} G2, 33.9 kcal/mol) is 8.1 kcal/mol higher than the activation barrier for formation of H_2SO_4 (ΔH_{298} 25.8 kcal/mol; MP4/6-311+G(2df,p)//MP2/6-31+G(d)).[26]

$SO_2 + n(H_2O)$, $n = 2$. The second water molecule has a larger binding enthalpy to SO_2 than the first (Figure 3, 3.5 versus 7.2 kcal/mol) because the second water can simultaneously form two hydrogen bonds (Figure 2). The activation barrier for eq 14 is 12.8 kcal/mol (ΔH_{298} G2), which is 1.3 kcal/mol higher than for eq 6 (11.5 kcal/mol; ΔH_0 MP4/6-311G(2df,p)//MP2/6-31+G(d) + ZPC)).[27] In the SO_2 plus water reaction (Figure 3), one catalytic water reduces the activation barrier by 21.1 kcal/mol (33.9 − 12.8; eq 11−eq 14), while in the SO_3 plus water reaction, one catalytic water reduces the activation barrier by 26.9 kcal/mol (32.2 − 5.3; eq 9−eq 6).[27] Thus, while the second water is catalytic for formation of both H_2SO_3 and H_2SO_4, it appears that the effect in the latter reaction is more pronounced.

At 298K, SO_2 plus two water molecules has the lowest calculated free energies (Table 3). Relative to $SO_2 + 2H_2O$, the free energy of activation to form H_2SO_3 is 41.5 kcal/mol with one water and 31.1 kcal/mol with two waters. Despite an unfavorable entropy contribution of the second water molecule, the free energy of activation is reduced 10.4 kcal/mol. For comparison, Hofmann and Schleyer[26] have reported the free energy of activation to form H_2SO_4 with one water is 28.6 kcal/mol.

Conclusions

The addition of a OH radical to SO_2 takes place with little or no activation barrier to form the $HOSO_2$ radical. The electronic activation in the transition state is associated with the promotion of an electron from the lone pair on sulfur to the empty π^* orbital (n → p*), which occurs concurrently with formation of a 2c-2e bond to the hydroxyl radical. The HO−SO_2 bond enthalpy is calculated to be 26.2 kcal/mol, about 4 kcal/mol lower than the currently accepted value of 30.5 kcal/mol,[16] and the reaction $HOSO_2 + O_2 \rightarrow SO_3 + O_2H$ is predicted to be 3.7 kcal/mol exothermic.

In the hydrolysis reaction of SO_2 with one and two waters, the first water molecule binds to SO_2 with a binding enthalpy of 3.5 kcal/mol, while the second water has a much stronger binding enthalpy (7.3 kcal/mol) due to its ability to form two hydrogen bonds. The activation barrier for formation of $H_2SO_3{\cdot}H_2O$ from $SO_2{\cdot}H_2O + H_2O$ (eq 14) is predicted to be reduced by 21.1 kcal/mol compared to the formation of H_2SO_3 from $SO_2{\cdot}H_2O$ (eq 11). In general, the SO_2/water complexes and transition states are very analogous to the corresponding structures on the SO_3/water potential energy surface.

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