An ab Initio Study of Sulfinic Acid and Related Species

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Geometries and vibrational frequencies of five isomers of H_2SO_2 have been derived at the HF/3-21G(*) and MP2/3-21G(*) levels of theory, and energies were obtained using MP4/6-31G**//MP2/3-21G(*) theory. In order of decreasing stability the isomers are $\text{S}(\text{OH})_2$, HSO_2H (sulfinic acid, two conformers), sulfone, HSO_2OH , and H_2SOO . Pathways leading to HSO_2H formation were analyzed to determine why the more stable $\text{S}(\text{OH})_2$ was not seen in matrix-isolation experiments. The barrier to isomerization between the two isomers was estimated to be 190 kJ mol^{-1} relative to HSO_2H , and the stability of HSO_2H with respect to dissociation was also considered.

Introduction

Molecules with the stoichiometry H_2SO_2 have been proposed as intermediates in the oxidation of H_2S ,¹ but there is little experimental information available about these species despite their possible importance in the atmospheric chemistry of sulfur. Accordingly, we have extended an earlier theoretical study² of HSO_2 and HOSO to several H_2SO_2 isomers, in order to explore their relative and absolute energies and aspects of their kinetics and to predict their vibrational spectra to aid possible IR detection. An additional impetus for this work is a recent IR study of matrix-isolated sulfinic acid,³ HSO_2H , which provides an opportunity to compare theory with experiment. H_2SO_2 has also been proposed as an intermediate in the high-temperature reduction of SO_2 by H_2 ,⁴ and some implications for the combustion chemistry of sulfur are considered. One goal of the present work is to add to the relatively small data base of theoretical analyses of sulfur-containing molecules⁵ which are significant in flame and atmospheric chemistry.

Methodology

Standard ab initio molecular orbital theory, described elsewhere,⁶ was employed in this work. All results were obtained by use of the GAUSSIAN 90 program⁷ on a VAX 6310, a Solbourne 5E/902, and a Cray Y-MP/832 computer. Details of the calculations have been described previously² and are briefly summarized here. A full geometry optimization was carried out for each closed-shell species using the 3-21G(*) basis set at the spin-restricted HF level. Harmonic vibrational frequencies were calculated for each structure to verify it as a true minimum or a transition state. All frequencies at the HF level were scaled by a standard factor of 0.9 to take account of known inadequacies at this level. Equilibrium geometries were then reoptimized using Møller-Plesset second-order perturbation theory to take electron correlation into account. We denote these results as MP2/3-21G(*). Unscaled vibrational frequencies were also calculated at the MP2 level, and the stability of the HF wave function was verified for each structure. Finally, energies at these MP2/3-

21G(*) geometries were calculated using MP4 theory and the larger 6-31G* basis set and are denoted as MP4/6-31G**//MP2/3-21G(*).

Results and Discussion

The calculated geometries, vibrational frequencies, and energies are listed in Tables I and II. Figure 1 is an illustration of the equilibrium geometries.

Geometries. The HF/3-21G(*) geometries of sulfone and the A-isomer of sulfinic acid (HSO_2H) agree well with the results of Boyd et al.⁸ derived with the smaller STO-3G(*) basis set. Our geometries for HSO_2OH and $\text{S}(\text{OH})_2$ are similar to those of Plummer et al.¹ at the STO-3G(*) basis; however, our result for H_2SOO does not agree. Our S-O bond lengths at both levels of calculation differed markedly from Plummer's result of $2.07 \text{ \AA}$, while our S-O-O angles contrast Plummer's value of 114.0° (see Table I). Because our result was derived using a larger basis set, we believe that it is more reliable. Comparison of our geometries for the A-isomer of HSO_2H , $\text{S}(\text{OH})_2$, and sulfone with those calculated by Basch⁵ at the HF/6-31G* level yield negligible differences; we hence conclude that there is no significant dependence on basis set at the HF level. This is similar to the lack of dependence reported earlier for HSO_2 and HOSO .² The similarity of our HF structures to those derived here at the MP2 level further indicates that the inclusion of electron correlation has little effect on geometry for the closed-shell species analyzed here. Sulfinic acid has been observed experimentally by Fender et al. using IR spectroscopy.³ For their force-field analysis they assigned standard bond lengths of $1.43 \text{ \AA}$ (S=O), $1.35 \text{ \AA}$ (S-H), and $0.96 \text{ \AA}$ (O-H) which lie midway between our calculated HF/3-21G(*) and MP2/3-21G(*) distances, except that our calculations (Table I) suggest the presence of both S-O and S=O bonds.

Vibrational Frequencies. Basch has presented a limited set of harmonic frequencies of stretching modes for the HSO_2H A-isomer, sulfone, and $\text{S}(\text{OH})_2$ at the HF/6-31G* level.⁵ We find that our frequencies at both the HF and MP2 levels are in close agreement with those reported values. The vibrational spectra of isotopomers of sulfinic acid have been measured by Fender et al.,³ which provide the only available comparison with theory for the molecules studied here, and the data for HSO_2H is summarized in Table III. We find that our three highest calculated frequencies (see Table I; the O-H stretch at $\nu \approx 3500 \text{ cm}^{-1}$ could not be observed³ and is excluded from comparison) are in reasonable agreement with the three largest experimental values of 2591 , 1209 , and 1093 cm^{-1} ; the mean absolute error for these three frequencies is 7.4% at the MP2 level and 3.3% at the HF level. Agreement with the other measured frequencies is much poorer. All calculated ν are found to be too high. The two lowest calculated frequencies show a mean error of 37% (MP2) and

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TABLE I: Ab Initio Geometries and Frequencies

species	calculation	geometry ^a and frequencies ^b
HSO ₂ H A-conformer	HF/3-21G(*)	$r(\text{SO}_1) = 1.462$, $r(\text{SO}_2) = 1.616$, $r(\text{OH}) = 0.938$, $r(\text{SH}) = 1.346$, $\psi = 106.3$, $\vartheta = 109.2$, $\varphi = 115.0$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = 33.1$, $\delta(\text{H}_1\text{SO}_1\text{O}_2) = 101.4$ $\nu = 302, 458, 813, 1011, 1080, 1128, 1179, 2416, 3415$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.487$, $r(\text{SO}_2) = 1.668$, $r(\text{OH}) = 1.000$, $r(\text{SH}) = 1.380$, $\psi = 107.3$, $\vartheta = 112.0$, $\varphi = 112.3$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = 44.4$, $\delta(\text{H}_1\text{SO}_1\text{O}_2) = 101.2$ $\nu = 311, 467, 749, 1003, 1151, 1185, 1258, 2366, 3438$
HSO ₂ H B-conformer	HF/3-21G(*)	$r(\text{SO}_1) = 1.458$, $r(\text{SO}_2) = 1.628$, $r(\text{OH}) = 0.970$, $r(\text{SH}) = 1.333$, $\psi = 108.6$, $\vartheta = 111.3$, $\varphi = 114.0$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = -79.2$, $\delta(\text{H}_1\text{O}_2\text{SH}_2) = 171.3$ $\nu = 303, 427, 807, 986, 1114, 1163, 1201, 2515, 3465$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.488$, $r(\text{SO}_2) = 1.689$, $r(\text{OH}) = 0.997$, $r(\text{SH}) = 1.363$, $\psi = 109.7$, $\vartheta = 113.2$, $\varphi = 108.7$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = -81.9$, $\delta(\text{H}_1\text{O}_2\text{SH}_2) = 168.5$ $\nu = 367, 470, 738, 1025, 1168, 1243, 1276, 2512, 3477$
HOSO anion	HF/3-21G(*)	$r(\text{SO}_1) = 1.554$, $r(\text{SO}_2) = 1.732$, $r(\text{OH}) = 0.972$, $\vartheta = 108.7$, $\varphi = 108.3$, $\delta = 64.3$ $\nu = 238, 408, 659, 870, 1090, 3369$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.577$, $r(\text{SO}_2) = 1.826$, $r(\text{OH}) = 1.003$, $\vartheta = 112.0$, $\varphi = 103.4$, $\delta = 71.7$ $\nu = 282, 413, 550, 1007, 1077, 3325$
HSO ₂ anion	HF/3-21G(*)	$r(\text{SO}_1) = 1.493$, $r(\text{SO}_2) = 1.493$, $r(\text{SH}) = 1.396$, $\vartheta = 114.8$, $\psi_1 = 102.0$, $\psi_2 = 102.0$ $\nu = 468, 959, 1104, 1109, 1129, 1972$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.516$, $r(\text{SO}_2) = 1.516$, $r(\text{SH}) = 1.475$, $\vartheta = 115.6$, $\psi_1 = 102.2$, $\psi_2 = 102.2$ $\nu = 480, 1013, 1074, 1125, 1216, 1596$
S(OH) ₂	HF/3-21G(*)	$r(\text{SO}) = 1.634$, $r(\text{OH}) = 0.970$, $\varphi_1 = 113.0$, $\varphi_2 = 113.0$, $\vartheta = 102.9$, $\delta(\text{H}_1\text{O}_1\text{SO}_2) = 80.9$, $\delta(\text{H}_2\text{O}_2\text{SO}_1) = 80.9$ $\nu = 328, 482, 516, 809, 818, 1177, 1177, 3432, 3434$
	MP2/3-21G(*)	$r(\text{SO}) = 1.672$, $r(\text{OH}) = 0.998$, $\varphi_1 = 109.4$, $\varphi_2 = 109.4$, $\vartheta = 105.2$, $\delta(\text{H}_1\text{O}_1\text{SO}_2) = 82.4$, $\delta(\text{H}_2\text{O}_2\text{SO}_1) = 82.4$ $\nu = 332, 566, 566, 788, 801, 1254, 1259, 3440, 3441$
HSOOH	HF/3-21G(*)	$r(\text{SH}) = 1.328$, $r(\text{SO}) = 1.654$, $r(\text{OO}) = 1.480$, $r(\text{OH}) = 0.974$, $\psi = 98.4$, $\eta = 108.6$, $\gamma = 99.0$, $\delta(\text{H}_2\text{O}_2\text{O}_1\text{S}) = 165.2$, $\delta(\text{H}_1\text{SO}_1\text{O}_2) = 82.4$ $\nu = 103, 304, 370, 741, 1003, 1035, 1322, 2592, 3411$
	MP2/3-21G(*)	$r(\text{SH}) = 1.344$, $r(\text{SO}) = 1.681$, $r(\text{OO}) = 1.571$, $r(\text{OH}) = 1.005$, $\psi = 99.8$, $\eta = 105.6$, $\gamma = 105.6$, $\delta(\text{H}_2\text{O}_2\text{O}_1\text{S}) = 170.9$, $\delta(\text{H}_1\text{SO}_1\text{O}_2) = 83.8$ $\nu = 95, 348, 395, 718, 865, 1033, 1279, 2722, 3388$
H ₂ SOO	HF/3-21G(*)	$r(\text{OO}) = 1.618$, $r(\text{SO}) = 1.554$, $r(\text{SH}_1) = 1.327$, $r(\text{SH}_2) = 1.338$, $\eta = 89.9$, $\psi_1 = 105.4$, $\psi_2 = 103.2$, $\delta(\text{H}_1\text{SO}_2\text{O}_1) = 68.3$, $\delta(\text{H}_2\text{SO}_2\text{O}_1) = -195.1$ $\nu = 244, 323, 659, 828, 997, 1059, 1265, 2517, 2598$
	MP2/3-21G(*)	$r(\text{OO}) = 1.641$, $r(\text{SO}) = 1.750$, $r(\text{SH}_1) = 1.367$, $r(\text{SH}_2) = 1.367$, $\eta = 62.0$, $\psi_1 = 132.0$, $\psi_2 = 91.3$, $\delta(\text{H}_1\text{SO}_2\text{O}_1) = 55.1$, $\delta(\text{H}_2\text{SO}_2\text{O}_1) = -217.6$ $\nu = 273, 653, 737, 1000, 1077, 1207, 1498, 2477, 2527$
sulfone	HF/3-21G(*)	$r(\text{SO}_1) = 1.429$, $r(\text{SO}_2) = 1.429$, $r(\text{SH}_1) = 1.327$, $r(\text{SH}_2) = 1.327$, $\psi_1 = 108.4$, $\psi_2 = 108.4$, $\vartheta = 122.4$, $\delta(\text{H}_1\text{SH}_2\text{O}_1) = 127.3$, $\delta(\text{H}_2\text{SH}_1\text{O}_2) = -127.4$ $\nu = 503, 905, 1046, 1107, 1271, 1351, 1403, 2568, 2594$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.456$, $r(\text{SO}_2) = 1.456$, $r(\text{SH}_1) = 1.357$, $r(\text{SH}_2) = 1.357$, $\psi_1 = 108.4$, $\psi_2 = 108.4$, $\vartheta = 123.4$, $\delta(\text{H}_1\text{SH}_2\text{O}_1) = 128.2$, $\delta(\text{H}_2\text{SH}_1\text{O}_2) = -128.2$ $\nu = 511, 918, 1059, 1162, 1299, 1410, 1505, 2569, 2602$
HSO ₂ H to S(OH) ₂ TS	HF/3-21G(*)	$r(\text{SO}_1) = 1.656$, $r(\text{SO}_2) = 1.632$, $r(\text{OH}) = 0.971$, $r(\text{SH}) = 1.375$, $\psi = 99.9$, $\vartheta = 108.7$, $\varphi = 113.5$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = -79.3$, $\delta(\text{H}_1\text{O}_2\text{SH}_2) = -135.3$ $\nu = 2192i, 265, 398, 667, 833, 905, 1250, 2641, 3814$
	MP2/3-21G(*)	$r(\text{SO}_1) = 1.633$, $r(\text{SO}_2) = 1.692$, $r(\text{OH}) = 0.988$, $r(\text{SH}) = 1.373$, $\psi = 96.7$, $\vartheta = 113.9$, $\varphi = 108.8$, $\delta(\text{H}_1\text{O}_2\text{SO}_1) = -94.0$, $\delta(\text{H}_1\text{O}_2\text{SH}_2) = -152.3$ $\nu = 1896i, 335, 442, 712, 739, 1012, 1175, 2623, 3453$

^a Angles are in degrees and distances are in angstroms. See Figure 1 for definitions of coordinates. ^b Frequencies are given in cm⁻¹. HF results are scaled by a factor of 0.9, while MP2 results are unscaled.

18.9% (HF) with respect to the experimental values of 340 and 270 cm⁻¹. The middle-range calculated frequencies corresponding to the experimental values of 762, 476, and 450 cm⁻¹ show even greater deviations from the experimental results. The mean error for these calculations is 77.4% (MP2) and 77.5% (HF). Presumably these large differences between the observed frequencies and the calculated harmonic frequencies indicate that coupling between normal modes and especially anharmonicity may be important in sulfinic acid. Clearly, the predicted frequencies for the other molecules studied here, other than for the high-frequency stretching modes, must be considered with caution.

Thermochemistry. The order of decreasing stability of the six H₂SO₂ isomers with respect to their MP4 energies (including zero-point energies) is S(OH)₂ > HSO₂H B-conformer ≥ HSO₂H A-conformer > sulfone > HSOOH > H₂SOO. The least stable isomer, H₂SOO, is unlikely to be observed because it is unstable with respect to dissociation to H₂S + O₂, with an estimated ΔH_0° of -227 kJ mol⁻¹. The errors in the calculated frequencies of HSO₂H lead to an error in the zero-point vibrational energy (ZPE) of about 10 kJ mol⁻¹; this must be considered when comparing isomers with energies that lie close together. To test our data,

we compared our calculated enthalpies at 0 K with literature values⁹ for two reactions. The experimental ΔH_0° of

are -277 ± 1 and -216 ± 2 kJ mol⁻¹, respectively.⁹ The calculated values are -274 and -207 kJ mol⁻¹, which correspond to errors of only +3 and -9 kJ mol⁻¹, respectively. On the basis of these differences plus possible errors in ZPE, we suggest error limits of ±20 kJ mol⁻¹ for the energies summarized in Table II.

We also considered the reactions

The heats of formation of HSO and HOS have not been measured, but Benson¹⁰ has estimated ΔH_f° (HSO) = -21 ± 17 kJ mol⁻¹,

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TABLE II: Ab Initio Energies

species	calculation	energy, au	ΔH_0^a , kJ mol ⁻¹
HSO ₂ H A-conformer	HF/3-21G(*)	-545.6396	1
	MP2/3-21G(*)	-546.0230	
	MP4/6-31G*//MP2/3-21G(*)	-548.8065	
HSO ₂ H B-conformer	HF/3-21G(*)	-545.6375	1
	MP2/3-21G(*)	-546.0244	
	MP4/6-31G*//MP2/3-21G(*)	-548.8070	
HOSO anion	HF/3-21G(*)	-545.0566	1467
	MP2/3-21G(*)	-545.4329	
	MP4/6-31G*//MP2/3-21G(*)	-548.2483	
HSO ₂ anion	HF/3-21G(*)	-545.0588	1440
	MP2/3-21G(*)	-545.4397	
	MP4/6-31G*//MP2/3-21G(*)	-548.2568	
S(OH) ₂	HF/3-21G(*)	-545.6757	-56
	MP2/3-21G(*)	-546.0484	
	MP4/6-31G*//MP2/3-21G(*)	-548.8238	
HSOOH	HF/3-21G(*)	-545.5944	161
	MP2/3-21G(*)	-545.9784	
	MP4/6-31G*//MP2/3-21G(*)	-548.7456	
H ₂ SOO	HF/3-21G(*)	-545.4951	400
	MP2/3-21G(*)	-545.8889	
	MP4/6-31G*//MP2/3-21G(*)	-548.6546	
sulfone	HF/3-21G(*)	-545.6107	78
	MP2/3-21G(*)	-546.0052	
	MP4/6-31G*//MP2/3-21G(*)	-548.7771	
H ₂	HF/3-21G(*)	-1.1230	
	MP2/3-21G(*)	-1.1403	
	MP4/6-31G*//MP2/3-21G(*)	-1.1406	
O ₂	HF/3-21G(*)	-148.7691	
	MP2/3-21G(*)	-149.0344	
	MP4/6-31G*//MP2/3-21G(*)	-149.9449	
H ₂ O	HF/3-21G(*)	-75.5850	
	MP2/3-21G(*)	-75.7096	
	MP4/6-31G*//MP2/3-21G(*)	-76.1863	
H ₂ S	HF/3-21G(*)	-396.8196	
	MP2/3-21G(*)	-396.9563	
	MP4/6-31G*//MP2/3-21G(*)	-398.7962	
HOS	HF/3-21G(*)	-470.6473	
	MP2/3-21G(*)	-470.8838	
	MP4/6-31G*//MP2/3-21G(*)	-473.1991	
HSO	HF/3-21G(*)	-470.6430	
	MP2/3-21G(*)	-470.8725	
	MP4/6-31G*//MP2/3-21G(*)	-473.2015	
HSO ₂ H to S(OH) ₂ TS	HF/3-21G(*)	-545.5356	190
	MP2/3-21G(*)	-545.9396	
	MP4/6-31G*//MP2/3-21G(*)	-548.7587	
HSO ₂ H conformer-A to -B TS	HF/3-21G(*)	-545.6253	27
	MP2/3-21G(*)	-546.0094	
	MP4/6-31G*//MP2/3-21G(*)	-548.7968	

^a Enthalpy at 0 K relative to HSO₂H, B-conformer using MP4/6-31G* energies combined with zero-point energies calculated at the MP2/3-21G(*) level.

TABLE III: IR Spectrum of Sulfinic Acid Measured by Fender et al.³

freq, cm ⁻¹	assignt	freq, cm ⁻¹	assignt
2591	H-S stretch	476	H-S-OH bend
1209	S-O stretch	450	O-S-OH bend
1093	S-O-H bend	340	S-O wag
762	S-OH stretch	270	torsion

and $\Delta H_f^\circ(298)(\text{HOS}) = 21 \pm 17$ kJ mol⁻¹. We have estimated ΔH_f° for HSO and HOS from ΔH_0° of reactions 3 and 4 combined with the experimental ΔH_f° of SO₂ and OH: our results are $\Delta H_f^\circ(\text{HSO}) = -21$ kJ mol⁻¹ and $\Delta H_f^\circ(\text{HOS}) = -1$ kJ mol⁻¹.

We have investigated the gas-phase acidity of sulfinic acid and our results are in qualitative accord with an earlier study by Boyd et al.⁸ Our estimated enthalpies at the MP4 level, including ZPE, for the reactions

Figure 1. Sketch of molecular structures showing definitions of bond angles: (A, B) two conformers of sulfinic acid, HSO₂H; (C) HSOOH; (D) sulfone; (E) HSO₂⁻ anion; (F) HOSO⁻ anion; (G) H₂SOO; (H) S(OH)₂.

are 1444 and 1467 kJ mol⁻¹, respectively. The slightly greater stability of the dissociation product in (5) is consistent with the charge distribution of HSO₂H calculated at the HF level: H₁ (see Figure 1) has a net atomic charge of +0.472, while H₂ has a much smaller positive charge of +0.047.

A transition state for internal rotation of the A-conformer around the S-O₂ bond to form the B-conformer has been characterized: there is a rotational barrier of 27 kJ mol⁻¹. At high temperatures, the small height of this barrier should allow the molecule to exist as a free rotor.

Chemistry in Solid Ar Matrices. It is interesting to note that although S(OH)₂ is 56 kJ mol⁻¹ more stable than HSO₂H, only HSO₂H has been observed experimentally.³ To explain this, the thermodynamics of successive addition of H atoms to SO₂ was investigated (see Figure 2). The initial H atom addition may follow path A or B to form one of the products HOSO or HSO₂.

Figure 2. Possible products arising from the sequential addition of H atoms to SO_2 .

TABLE IV: Possible Dissociation Products of HSO_2H

products	$\Delta H^\circ_0,^a$ kJ mol $^{-1}$	products	$\Delta H^\circ_0,^a$ kJ mol $^{-1}$
$\text{SO}_2 + \text{H}_2$	-101	$\text{H}_2\text{S} + \text{O}_2$	173
$\text{H}_2\text{O} + \text{SO}$	-34	$\text{HSO}_2 + \text{H}$	247
$\text{HOSO} + \text{H}$	125		

^a Enthalpies at 0 K, relative to HSO_2H , using MP4/6-31G* energies combined with zero-point energies calculated at the MP2/3-21G(*) level.

These reactions were investigated in an earlier study,² and the formation of the HOSO radical (path A) was found to be more exothermic than addition to form HSO_2 (path B). However, it was also indicated in that work that although HOSO is more stable, there is a lower activation barrier to formation of HSO_2 , so that path B is favored kinetically. Addition of a second H atom may follow paths C or D to HSO_2H . Path C is the thermodynamically controlled route, because HSO_2H is 78 kJ mol $^{-1}$ more stable than sulfone. Thus, we suggest that HSO_2H is formed via steps B and C. We verified the absence of any significant barrier to step C at the HF/3-21G(*) and MP2/3-21G(*) levels of calculation. Similarly, steps E and F also have no significant kinetic barriers, but the initial step A to formation of HOSO is kinetically unfavorable as noted above.

We also considered formation of S(OH)_2 by isomerization of the less stable HSO_2H (path G). We have characterized a transition state for path G, with a barrier of approximately 190 kJ mol $^{-1}$ (see Tables I and II). Transition-state theory was applied to investigate the kinetics of the isomerization of sulfinic acid. First-order rate constants k for the high-pressure limit were calculated for the temperature range 298–2000 K, and the fit to the Arrhenius plot yields $k \approx 3.0 \times 10^{13} \exp(-2.3 \times 10^4 \text{ K}/T) \text{ s}^{-1}$. Thus, equilibration of HSO_2H and S(OH)_2 at low temperatures is negligible.

High-Temperature Chemistry. Possible decomposition products of sulfinic acid, together with the predicted ΔH°_0 for each channel,

are summarized in Table IV. HSO_2H is seen to be thermodynamically unstable with respect to both $\text{SO}_2 + \text{H}_2$ and $\text{H}_2\text{O} + \text{SO}$, although there may be kinetic barriers to these decompositions. Arutyunov et al.⁴ suggested a species of stoichiometry H_2SO_2 might be formed by the process

at 1000–1200 K, but combination of the H_2 bond energy⁹ of 432 kJ mol $^{-1}$ with the data of Table IV shows ΔH°_0 to be about +185 kJ mol $^{-1}$. The analogous reaction of the more stable HOSO has $\Delta H^\circ_0 \approx +307$ kJ mol $^{-1}$, so reaction 7 is probably insignificant. An alternative formation pathway for HSO_2H in flames is by H atom addition to HOSO, as analyzed in the previous section, which is exothermic (Table IV) and appears to have no energy barrier. This would provide a reaction that competes with the second step of the cycle

which has been invoked to explain the SO_2 -catalyzed recombination of H atoms in flames.¹¹ The subsequent high-temperature chemistry of sulfinic acid, whether through reactions with other flame species or dissociation e.g. to $\text{H}_2 + \text{SO}_2$, remains to be investigated.

Conclusions

On the basis of ab initio calculations, we have compared the stability of sulfinic acid with several of its isomers. The calculated vibrational frequencies may aid in the identification of these species by IR spectroscopy. The S(OH)_2 molecule is the most stable isomer, followed by sulfinic acid, which may exist in two possible conformations that differ by only 1 kJ mol $^{-1}$. We have located a small barrier to internal rotation of 27 kJ mol $^{-1}$, and we have also characterized a transition state from sulfinic acid, which has been observed, to the more stable S(OH)_2 , which has not been experimentally detected. The barrier to isomerization of approximately 190 kJ mol $^{-1}$ prevents formation of the thermodynamic product at low temperatures.

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