

Reactions of SO₃ with the O/H Radical Pool under Combustion Conditions[†]

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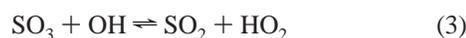
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Received: November 13, 2006; In Final Form: January 25, 2007

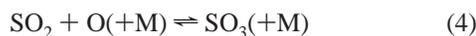
The reactions of SO₃ with H, O, and OH radicals have been investigated by ab initio calculations. For the SO₃ + H reaction (1), the lowest energy pathway involves initial formation of HSO₃ and rearrangement to HOSO₂, followed by dissociation to OH + SO₂. The reaction is fast, with $k_1 = 8.4 \times 10^9 T^{1.22} \exp(-13.9 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (700–2000 K). The SO₃ + O → SO₂ + O₂ reaction (2) may proceed on both the triplet and singlet surfaces, but due to a high barrier the reaction is predicted to be slow. The rate constant can be described as $k_2 = 2.8 \times 10^4 T^{2.57} \exp(-122.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $T > 1000 \text{ K}$. The SO₃ + OH reaction to form SO₂ + HO₂ (3) proceeds by direct abstraction but is comparatively slow, with $k_3 = 4.8 \times 10^4 T^{2.46} \exp(-114.1 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (800–2000 K). The revised rate constants and detailed reaction mechanism are consistent with experimental data from batch reactors, flow reactors, and laminar flames on oxidation of SO₂ to SO₃. The SO₃ + O reaction is found to be insignificant during most conditions of interest; even in lean flames, SO₃ + H is the major consumption reaction for SO₃.

Introduction

High-temperature sulfur reactions continue to be of both theoretical and practical interest.¹ The combustion of fuel-bound sulfur results in formation of oxides of sulfur, mainly SO₂ and SO₃. Sulfur trioxide in combustion systems causes formation of sulfuric acid, which will condense and corrode metal surfaces at temperatures below the dew point.^{2,3} In addition, it may contribute to aerosols and particulate emissions.^{4–6} A better understanding of the mechanisms for SO₃ formation and destruction is a necessary step in the effort to minimize these problems. A number of reactions may conceivably affect the SO₃ concentration. Reactions of particular interest are those of SO₃ with H, O, and OH,



Depending on the reaction conditions, these steps may serve to either consume SO₃ (forward direction) or form SO₃ (reverse direction). Another important reaction for the SO₃/SO₂ ratio is the pressure-dependent step,



Under the excess oxygen conditions typical of the post-flame region in a combustion system it is believed that the SO₃/SO₂ ratio is mainly controlled by the sequence (4), (2),^{2,7–10} whereas reactions 1 and 3 presumably are less important. Although the SO₃ formation step (4) is characterized over a wide temperature

and pressure range,^{11,12} there is a significant uncertainty in the rate constants for the consumption reactions (1)–(3). There are no reported measurements for the SO₃ + H reaction; kinetic models for sulfur chemistry rely on estimated values for k_1 ^{13–15} or adopt a QRRK estimate⁷ for the reverse reaction SO₂ + OH.^{10,16,17} The rate constant for the reaction between SO₃ and O (2) has not been measured directly and reported data vary by several orders of magnitude. Indirect determinations have been reported on the basis of results from laminar premixed flames^{18–22} and, for the reverse step, from reactor experiments.^{10,23} A recent re-interpretation of selected flame results,¹² based on a more accurate value of k_4 , indicates a fairly high rate constant for reaction SO₃ + O ⇌ SO₂ + O₂, in agreement with earlier evaluations,^{20–22} and a fast reaction is also supported by other experiments.^{18,19,23} In conflict with these results, Alzueta et al.¹⁰ recommend a very low rate constant, which indicates that the reaction is insignificant under most conditions of interest. In the absence of measurements, the SO₃ + OH reaction (3) has been omitted from most previous modeling studies of sulfur chemistry,^{7,10,14–16} but it is potentially an important step.

The objective of the present work is to use ab initio calculations to obtain reliable estimates for the reactions of SO₃ with H, O, and OH. A recent reaction mechanism for sulfur chemistry¹⁷ is updated with the new values for k_1 , k_2 , and k_3 , and predictions with the revised model are compared to a range of experimental results from literature on the oxidation of SO₂ to SO₃. Finally, the implications for modeling the SO₃/SO₂ ratio in practical combustion systems are outlined.

Ab Initio Calculations

Computational Methodology. The geometries of reactants, bound minima, products, and connecting transition states (TSs) were derived with the B3LYP level of density functional theory

[†] Part of the special issue "James A. Miller Festschrift".

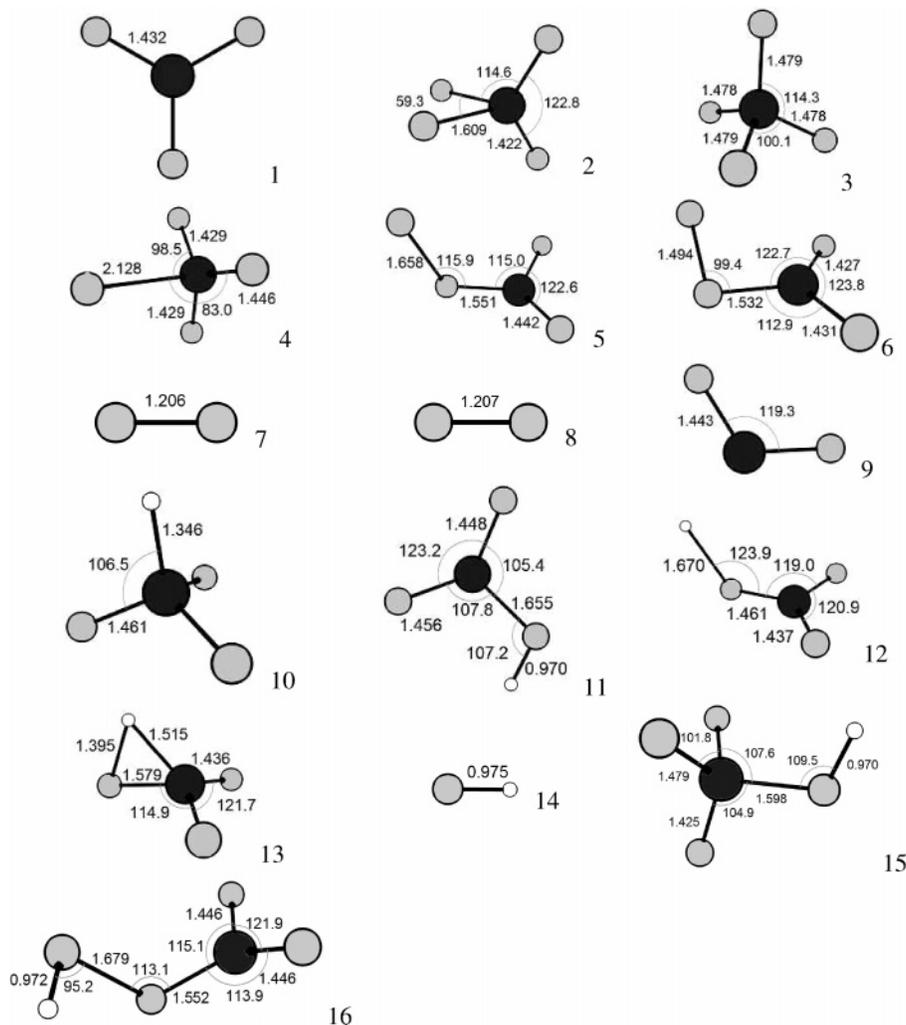


Figure 1. Computed B3LYP/6-311G(2d,d,p) geometries (distances in 10^{-10} m and angles in degrees): 1, D_{3h} SO₃ $^1A_1'$; 2, C_{2v} SO₄ $^1A_1'$; 3 C_{2v} SO₄ $^3A_2'$; 4, C_s TS1 $^3A''$; 5, C_{2v} TS2 $^3A''$; 6, C_1 TS3 1A ; 7, O₂ $^3\Sigma$; 8, 1O_2 ; 9, C_{2v} SO₂ $^1A_1'$; 10, C_{3v} HSO₃ $^2A_2'$; 11, C_1 HOSO₂ 2A ; 12, C_s TS4 $^2A'$; 13, C_s TS5 $^2A'$; 14, OH $^2\Pi$; 15, HOSO₃ $^2A''$; 16, C_1 TS6 2A .

TABLE 1: CBS-QB3 Energies (0 K, in au; 1 au = 2625.5 kJ mol⁻¹) and B3LYP/6-311G(2d,d,p) Vibrational Frequencies (cm⁻¹, Scaled by 0.99) Computed for the Reactants, Intermediates, Products, and Transition States in the H, O, and OH Reactions with SO₃ Shown in Figure 1

molecule	energy, au	frequencies, cm ⁻¹
O 3P	-74.98763	
SO ₃ $^1A_1'$	-623.15539	488, 508, 508, 1034, 1350, 1350
SO ₄ $^1A_1'$	-698.18631	299, 464, 465, 480, 635, 654, 895, 1224, 1403
SO ₄ $^3A_2'$	-698.17571	299, 350, 384, 384, 438, 779, 780, 941, 1159
TS1 $^3A''$	-698.14226	214i, 125, 130, 469, 494, 499, 1022, 1267, 1346
TS2 $^3A''$	-698.09006	897i, 96, 167, 436, 461, 511, 748, 1114, 1303
TS3 1A	-698.09604	530i, 142, 286, 412, 468, 654, 841, 1177, 1376
O ₂ $^3\Sigma$	-150.16462	1625
1O_2	-150.11901	1611
SO ₂ $^1A_1'$	-548.03762	508, 1141, 1335
HSO ₃ $^2A_2'$	-623.68528	178, 178, 567, 944, 944, 1039, 1104, 1104, 2580
HOSO ₂ 2A	-623.73026	262, 399, 405, 507, 679, 1059, 1105, 1265, 3715
TS4 $^2A'$	-623.63844	975i, 178, 297, 490, 498, 550, 977, 1255, 1334
TS5 $^2A'$	-623.64774	1486i, 406, 463, 525, 643, 775, 1139, 1334, 1887
OH $^2\Pi$	-75.64969	3668
H 2S	-0.49982	
HOSO ₃ $^2A''$	-698.85077	214, 266, 361, 408, 429, 522, 791, 840, 1022, 1150, 1240, 3724
TS6 2A	-698.75939	745i, 87, 175, 243, 444, 469, 515, 743, 1082, 1102, 1281, 3711

combined with the 6-311G(2d,d,p) basis set.²⁴ These results are shown in Figure 1. Vibrational frequencies at the same level of theory were scaled by a standard factor of 0.99²⁴ and are listed in Table 1. For thermochemistry calculations, all internal motions were treated as harmonic oscillators, with the usual

assumption of separability of rotations and vibrations. Improved single-point energies were obtained with the CBS-QB3 composite approach of Petersson and co-workers, which approximates CCSD(T) calculations extrapolated to the infinite basis set limit and has been shown to give atomization energies

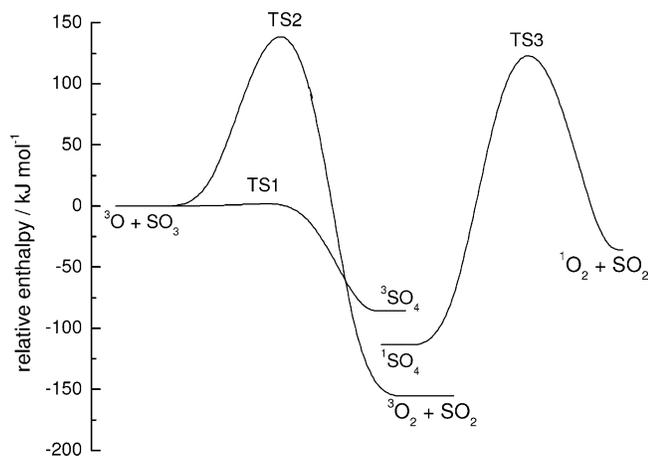


Figure 2. Potential energy diagram for O + SO₃ based on CBS-QB3 calculations, showing relative enthalpies at 0 K.

with mean absolute deviation of 2.4 kJ mol⁻¹.²⁴ Simple transition state theory (TST) was applied to obtain rate constants *k*, in the form

$$k = \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{reactants}}} \exp(-E_0/RT)$$

where the partition functions *Q* and the 0 K energy barriers *E*₀ were derived from the CBS-QB3 data.

SO₃ + O Reaction. The potential energy diagram is shown in Figure 2. Several states of SO₄ have been investigated in the past,^{25,26} which arise from symmetry breaking in tetrahedral SO₄. Here we focus on the lowest energy singlet and triplet states. Direct abstraction to form ³O₂ + SO₂ via TS2 is found to have a high barrier of 139 kJ mol⁻¹. The computed Δ_rH₀ is -155.5 kJ mol⁻¹, which compares well with the JANAF evaluation of -151.1 ± 0.7 kJ mol⁻¹.²⁷ TST yields a rate constant of 4.1 × 10⁷T^{1.71} exp(-138.1 kJ mol⁻¹/RT) cm³ mol⁻¹ s⁻¹ for T > 1000 K. In contrast, spin-allowed addition via TS1 to form triplet SO₄ is predicted to occur with a small barrier of only 2 kJ mol⁻¹. This low barrier may be consistent with the experiments over 300–500 K of Westenberg and de Haas,²⁸ who argued in favor of pressure-dependent adduct formation (they did not observe SO₄ by mass spectrometry. Possibly the adduct decomposed before or during ionization). The computed bond dissociation enthalpy at 0 K, D₀(O–SO₃) = 85.8 kJ mol⁻¹, implies Δ_rH₀(³SO₄) = -229.0 kJ mol⁻¹, with an uncertainty of around 5 kJ mol⁻¹. However, at combustion temperatures this triplet adduct will not be thermodynamically stable. We have not been able to find a reaction path for the spin-allowed dissociation of ³SO₄ to ³O₂ + SO₂, but intersystem crossing to the somewhat more stable singlet SO₄ (predicted Δ_rH₀(¹SO₄) = -256.8 kJ mol⁻¹) may be possible, especially if collisionally assisted. Spin-allowed dissociation of this singlet adduct to ¹O₂ + SO₂ via TS3 has a computed barrier of 123 kJ mol⁻¹. Treatment of this step as the bottleneck with the assumption that ¹SO₄ is in rapid equilibrium with the reactants via TST leads to a rate constant of 1.1 × 10⁷T^{1.55} exp(-120.5 kJ mol⁻¹/RT) cm³ mol⁻¹ s⁻¹ for T > 1000 K. The single-reference CBS-QB3 energy for ¹O₂ + SO₂ is poorly defined because singlet oxygen is a multireference species. The experimental 0 K enthalpies of SO₂ with O₂ in the a ¹Δ_g, b ¹Δ_g⁺, and c ¹Σ_u states, relative to the reactants, are -56.8, -5.8, and 239.6 kJ mol⁻¹.²⁷ As expected, these values bracket the computed Δ_rH₀ of -36 kJ mol⁻¹, which presumably corresponds to some combination of the singlet states of O₂. Multireference studies of this pathway may be needed.

TABLE 2: B3LYP/aug-cc-pV(T+d)Z Energies (Including Zero Point Energies) for Stationary Points on the O + SO₃ Potential Energy Surface and Enthalpies at 0 K Relative to Reactants

species	B3LYP energy (au)	B3LYP enthalpy (kJ/mol)	CBS-QB3 enthalpy (kJ/mol)
³ O	-75.09418	0	0
SO ₃	-623.93744		
O ₂	-150.38092	-180	-155, -151 ^a
SO ₂	-548.71939		
³ SO ₄	-699.07583	-116	-86
¹ SO ₄	-699.06654	-92	-114
TS1	-699.03623	-12	2
TS2	-698.99222	103	139
TS3	-698.98777	115	123
¹ O ₂	-150.34887 ^b	-87 ^c	-36, ^c -57 ^{a,c}

^a Experiment.²⁷ ^b Corrected spin-unrestricted result (see text). ^c Includes SO₂.

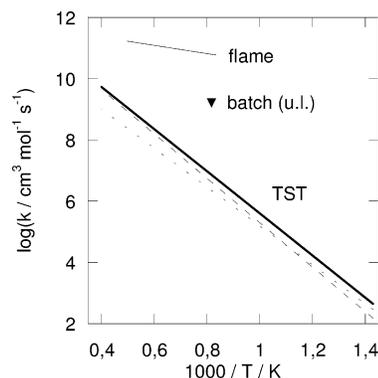


Figure 3. Arrhenius plot for the SO₃ + O reaction. Thin solid line: the rate constant derived by Yilmaz et al.¹² based on flame measurements.^{20,21,22} Solid triangle: upper limit (ref 10, present work) based on batch reactor data.³¹ Long-dashed line: TST for O + SO₃ triplet abstraction. Short-dashed line: TST for O + SO₃ singlet addition/elimination. Thick solid line: TST total rate constant.

An alternative approach is based on density functional theory (DFT). For comparison, we reoptimized the O + SO₃ stationary points at the B3LYP/aug-cc-pV(T+d)Z level of theory, where the basis set includes tight d functions on sulfur.²⁹ The energies, including unscaled zero point vibrational energies, are summarized in Table 2. For singlet oxygen, the spin-restricted wavefunction is unstable with respect to becoming spin-unrestricted, with an expectation value for the spin operator, ⟨S²⟩, equal to 1.005. An improved estimate of the ¹O₂ energy that corrects for spin contamination is obtained via the procedure of Yamaguchi et al.,³⁰ and the result is shown in Table 2. The derived ³Σ⁻¹Δ gap for O₂ is 84 kJ mol⁻¹, in good accord with the experimental value of 95 kJ mol⁻¹.²⁷ For the other singlet species, the spin-restricted DFT results were stable with respect to relaxation of spin constraints, although this does not rule out some multireference character in the wavefunctions. As may be seen from the relative enthalpies shown in Table 2, the DFT results underestimate ΔH₀ for O-atom abstraction from SO₃ by about 30 kJ mol⁻¹. DFT yields lowered reaction barriers, by 8–36 kJ mol⁻¹. DFT also reverses the order of singlet and triplet states for SO₄ by comparison with CBS-QB3 theory. A singlet ground state was obtained by McKee²⁵ and, until multireference calculations are available, we prefer CBS-QB3 data for the transition state theory analysis.

The singlet and triplet paths have similar rate constants above 1000 K, as may be seen in Figure 3. The current recommendation for *k*₂ is the sum of both channels, *k*₂ = 2.8 × 10⁴T^{2.57} exp(-122.3 kJ mol⁻¹/RT) cm³ mol⁻¹ s⁻¹. It is several

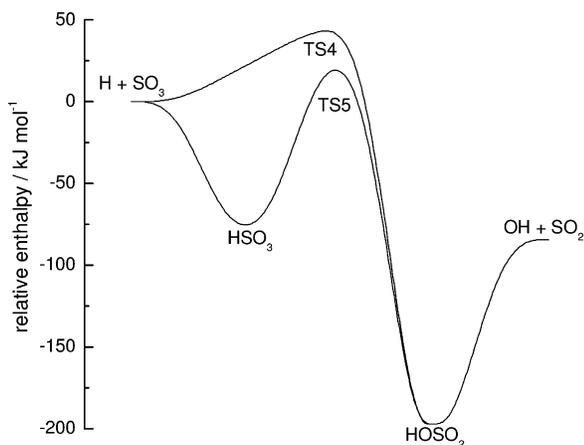


Figure 4. Potential energy diagram for H + SO₃ based on CBS-QB3 calculations, showing relative enthalpies at 0 K.

orders of magnitude lower than values derived from flames,^{12,20–22} but a low value is in agreement with the recommendation of Alzueta et al.¹⁰ based on batch reactor data.³¹ The flame and batch reactor results are discussed further below.

SO₃ + H Reaction. Two bound minima, corresponding to formation of an S–H or an O–H bond by H-atom addition, were characterized and are shown in Figure 4. TSs were found for both addition processes and, like in the analogous H + SO₂ system,³² formation of the less strongly bound HSO₃ species is more kinetically favorable than formation of the more thermodynamically stable HOSO₂ molecule. Isomerization between these addition products is also possible and is important because the lowest energy pathway on Figure 4 involves initial formation of HSO₃ followed by rearrangement to HOSO₂, followed by dissociation to OH + SO₂. As a check on the accuracy of the CBS-QB3 energies, we compute $\Delta_f H_0$ for the overall reaction to be $-84.5 \text{ kJ mol}^{-1}$, which compares well with the experimental value of $-83.2 \text{ kJ mol}^{-1}$, which is based on JANAF data²⁷ except for OH.³³

The predicted binding enthalpies of the adducts at 0 K are $D_0(\text{H}-\text{SO}_3) = 79.1 \text{ kJ mol}^{-1}$ and $D_0(\text{H}-\text{OSO}_2) = 197.2 \text{ kJ mol}^{-1}$, respectively. The corresponding $\Delta_f H_0$ are -253.1 and $-371.2 \text{ kJ mol}^{-1}$, respectively, and the computed $\Delta_f H_{298}(\text{HOSO}_2) = -379.2 \text{ kJ mol}^{-1}$ agrees with $-373 \pm 6 \text{ kJ mol}^{-1}$ measured by Pilling and co-workers based on the OH + SO₂ equilibrium.³⁴ At low temperatures HSO₃ could be a sink for H atoms, but this molecule is not stable at high temperatures. We found no barrier for the initial addition $\text{H} + \text{SO}_3 \rightarrow \text{HSO}_3$ and the bottleneck in the overall reaction will be at TS5. This controls isomerization to HOSO₂ which, being created with an internal energy well in excess of the threshold for OH + SO₂ production (see Figure 4), is expected to dissociate immediately. TS5 was analyzed via TST for the temperatures of interest, 700–2000 K, and the results may be summarized as $k = 8.4 \times 10^9 T^{1.22} \exp(-13.9 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Because the reaction is fast, $k \approx 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, tunneling contributions can be neglected. In Figure 5 the present value of k_1 is compared with the only other literature determination, the QRRK estimate for the reverse reaction by Bozzelli and co-workers.⁷ The two rate constants are seen to be in agreement within a factor of 2 in the investigated temperature range.

SO₃ + OH Reaction. Computational results for an adduct formed between OH and SO₃ were reported by Wang et al.²⁶ and Wang and Hou.³⁵ Our similar computed structure is shown in Figure 1. We derive a binding enthalpy $D_0(\text{HO}-\text{SO}_3) = 120.1 \text{ kJ mol}^{-1}$. This implies $\Delta_f H_0(\text{HO}-\text{SO}_3) = -473.0 \text{ kJ mol}^{-1}$. Under atmospheric conditions this addition path could be a loss

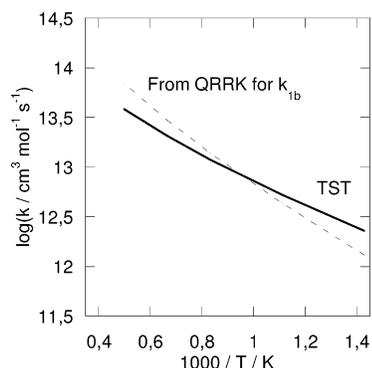


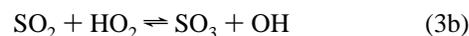
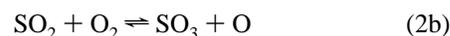
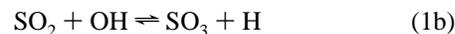
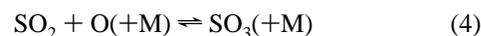
Figure 5. Arrhenius plot for the SO₃ + H reaction. Dashed line: the rate constant derived from the QRRK estimate for the reverse reaction by Glarborg et al.⁷ Solid line: TST rate constant from the present work.

process for SO₃. However, in flames the adduct is insufficiently stable to be a sink for SO₃. For example, at 800 K the calculated equilibrium constant for $\text{OH} + \text{SO}_3 \rightleftharpoons \text{HSO}_4$ is $K_c = 1.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$. With a conservative upper limit for [OH] of $10^{-8} \text{ mol cm}^{-3}$, then on the assumption that $[\text{SO}_3] < [\text{OH}]$, the equilibrium fraction of SO₃ bound as adduct is less than 2%. At higher temperatures and/or lower [OH], an even smaller fraction of the SO₃ will be bound at equilibrium.

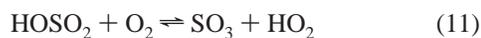
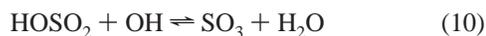
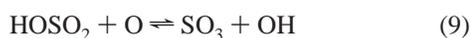
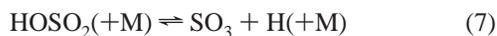
A small concentration of HOSO₃ could be significant if it rapidly reacts to new products before decomposing thermally back to OH + SO₃. In contrast to the analogous OH + SO₂ adduct, which reacts readily with O₂, the thermochemistry for $\text{O}_2 + \text{HOSO}_3 \rightarrow \text{HO}_2 + \text{SO}_4$ is unfavorable. The latest $\Delta_f H_0(\text{HO}_2) = 15.2 \pm 0.3 \text{ kJ mol}^{-1}$ ³⁶ implies $\Delta_r H_0 = 231 \text{ kJ mol}^{-1}$ for HO₂ formation. O atom elimination from HOSO₃ is predicted to be endothermic by 349 kJ mol^{-1} and can therefore be ignored. We have not found a reaction path for elimination of O₂. Wang and Hou³⁵ assigned a transition state for elimination of HO₂ from HOSO₃ but our own investigations, including following the intrinsic reaction coordinate, suggest instead this TS (labeled TS6 in Figure 1) corresponds to direct abstraction by OH from SO₃. TS6 for direct abstraction lies $120.0 \text{ kJ mol}^{-1}$ above OH + SO₃ and the corresponding rate constant for HO₂ + SO₂ formation is summarized over 800–2000 K as $4.8 \times 10^4 T^{2.46} \exp(-114.1 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Detailed Kinetic Model

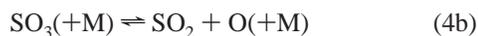
The revised rate constants for the SO₃ + H (1), SO₃ + O (2), and SO₃ + OH (3) reactions were implemented in a detailed chemical kinetic model for high-temperature sulfur chemistry, drawn largely from recent work by the authors.^{12,17} The reaction mechanism consists of a H₂/O₂ subset and a full description of the H/S/O reaction system. The mechanism contains the elementary steps that could conceivably influence the SO₂/SO₃ ratio at high temperatures. The sulfur oxides subset of the mechanism is listed in Table 3. The formation of SO₃ may proceed by a direct oxidation of SO₂,



or it may involve HOSO₂ as an intermediate,



The destruction of SO_3 may occur by



Most of the reactions and rate constants have been discussed in some detail in previous work.^{7,10–12,16,17} In addition to k_1 , k_2 , and k_3 , only one rate constant has been modified in the present work. For the $\text{SO}_2 + \text{SO}_2$ reaction (6), we use an estimate, based on batch reactor results on $\text{SO}_2 + \text{O}_2$,³¹ discussed below, and shock tube results on SO_2 decomposition.³⁷ Both studies indicate a reaction with a high activation energy, in the range 275–315 kJ/mol.

Modeling Results and Discussion

Predictions with the detailed chemical kinetic mechanism were compared with experimental results from the literature on oxidation of SO_2 to SO_3 . The purpose of the modeling part has been to evaluate whether the novel values of k_1 , k_2 , and k_3 are consistent with the available experimental results and to discuss the implications. Results from batch reactors and flow reactors (assuming plug flow) were modeled with SENKIN,³⁹ which is part of the CHEMKIN library.⁴⁰ SENKIN performs an integration in time. The results of the SENKIN calculations were compared to flow reactor data using the nominal residence time in the isothermal part of the reactor.

The experimental data on SO_3 formation from SO_2 include results from premixed flames,^{18–22} batch reactors,³¹ and flow reactors.^{7,23,43} The flame results have consistently been interpreted in terms of a fast rate constant for the $\text{SO}_3 + \text{O}$ reaction (2). On the basis of a more accurate value of k_4 , the authors¹² recently reanalyzed the results of Smith and co-workers^{21,22} and Merryman and Levy²⁰ to obtain a value of $k'_2 = 7.8 \times 10^{11} \exp(-3065/T) \text{ cm}^3/(\text{mol s})$, in support of the earlier estimates. The flame interpretations^{12,20–22} were all based on the assumption that the SO_3 level resulted from a balance between formation by $\text{SO}_2 + \text{O}(+\text{M})$ (4) and consumption by $\text{SO}_3 + \text{O}$ (2), i.e., that the $\text{SO}_3 + \text{H}$ and $\text{SO}_3 + \text{OH}$ reactions could be disregarded due to a high O/H ratio in these flames. The present work indicates that the $\text{SO}_3 + \text{O}$ reaction is too slow to be an important consumption step for SO_3 , even at the high temperatures in flames.

For the flames of Smith and co-workers,^{21,22} which contained only trace amounts of water vapor as a hydrogen source, as well as for the flame of Merryman and Levy,²⁰ we estimate

TABLE 3: Rate Coefficients for Key Reactions in the Reaction Mechanism (Units: cm, mol, s, K)

no.	reaction	A	n	E/R	ref
1	$\text{SO}_3 + \text{H} \rightleftharpoons \text{SO}_2 + \text{OH}$	8.4E09	1.22	1670	pw
2	$\text{SO}_3 + \text{O} \rightleftharpoons \text{SO}_2 + \text{O}_2$	2.8E04	2.57	14700	pw
3	$\text{SO}_3 + \text{OH} \rightleftharpoons \text{SO}_2 + \text{HO}_2$	4.8E04	2.46	13700	pw
4	$\text{SO}_2 + \text{O}(+\text{M}) \rightleftharpoons \text{SO}_3(+\text{M})^a$	3.7E11	0.00	850	11
	low-pressure limit	2.4E27	-3.60	2610	
	Troe parameters 0.442, 316, 7442				
	low-pressure limit (N_2)	2.9E27	-3.58	2620	12
	Troe parameters (N_2) 0.43, 371, 7442				
5	$\text{SO}_2 + \text{OH}(+\text{M}) \rightleftharpoons \text{HOSO}_2(+\text{M})^b$	5.7E12	-0.27	0	34
	low-pressure limit	1.7E27	-4.09	0	
	Troe parameters 0.10, 1E-30, 1E30				
6	$\text{SO}_2 + \text{SO}_2 \rightleftharpoons \text{SO}_3 + \text{SO}$	5.0E07	2.00	37750	37, est
7	$\text{HOSO}_2 \rightleftharpoons \text{SO}_3 + \text{H}$	1.4E18	-2.91	27630	7, 1 atm
8.	$\text{HOSO}_2 + \text{H} \rightleftharpoons \text{SO}_2 + \text{H}_2\text{O}$	1.0E12	0.00	0	7
9.	$\text{HOSO}_2 + \text{O} \rightleftharpoons \text{SO}_3 + \text{OH}$	5.0E12	0.00	0	7
10.	$\text{HOSO}_2 + \text{OH} \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$	1.0E12	0.00	0	7
11.	$\text{HOSO}_2 + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{SO}_3$	7.8E11	0.00	330	38

^a Enhanced third-body coefficients: $\text{N}_2 = 0$, $\text{SO}_2 = 10$, $\text{H}_2\text{O} = 10$.

^b Enhanced third-body coefficients: $\text{N}_2 = 1$, $\text{SO}_2 = 5$, $\text{H}_2\text{O} = 5$.

from kinetic modeling an O/H ratio ≈ 100 at the location where $d[\text{SO}_3]/dt = 0$ (at 1269 K^{12,21,22} and 1685 K,²⁰ respectively). According to the results of the present study $k_1/k_2 \approx 10^5$, indicating that the $\text{SO}_3 + \text{H}$ reaction (1), not $\text{SO}_3 + \text{O}$ (2), is the controlling SO_3 consumption reaction in these lean flames. This is supported by the fact that the ratio k_1/k'_2 is about the same order of magnitude, ≈ 100 , as the estimated O/H ratio in these flames. This means that there is no conflict between the present estimate for k_2 and the flame results, even though the flame data have been used to support a much higher value for k_2 previously.

Support for a high value of k_2 came recently from work by the authors on thermal dissociation of SO_3 in a quartz flow reactor.¹² In this work, a sink for atomic oxygen was required to explain the experimental results, and the loss of O was attributed partly to reaction with SO_3 (2). This interpretation is in conflict with the present value of k_2 . The most likely explanation is loss of O on the reactor surface, but more work is required to confirm this. Sulfur trioxide is known to absorb strongly on glass surfaces where it acts to promote recombination of atomic oxygen.^{2,41,42}

There are only few results reported in literature on the oxidation of SO_2 by O_2 in the absence of combustibles. Cullis et al.³¹ studied gaseous oxidation of SO_2 by O_2 in a silica batch reactor in the temperature range 1173–1323 K (the upper limit dictated by the position of equilibrium between SO_2 and SO_3). The conversion of reactants was detected by measuring the pressure change in the vessel. It was confirmed by changes in the surface to volume ratio that the reaction observed was essentially homogeneous. Cullis et al. did not use the data to derive rate coefficients, partly because of considerable scatter and partly because the mechanism of SO_3 formation was uncertain. Due to the fairly small conversion of SO_2 under the reaction conditions, rate measurements were difficult and not readily reproducible; however, the data obtained were average results of a large number of experiments.

Figures 6 and 7 compare the experimental results of Cullis et al.³¹ to modeling predictions with the detailed mechanism. The data indicate that the reaction increases roughly linearly with the concentration of sulfur dioxide, but only slightly with the concentration of oxygen (Figure 6), and that it has a high activation energy, about 315 kcal/mol (Figure 7). Assuming the presence of trace amounts of water vapor (50 ppm), calculations

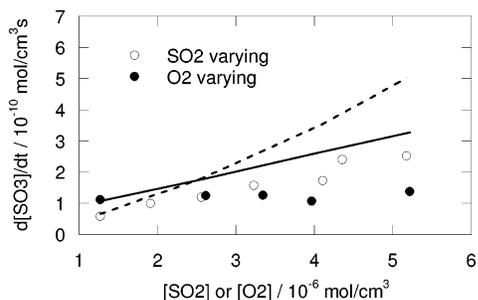


Figure 6. Comparison of experimental data³¹ and modeling predictions for the SO₃ formation rate in a quartz batch reactor at a temperature of 1223 K and varying concentrations of SO₂ and O₂. In the modeling, trace amounts of water vapor (50 ppm) have been assumed to be present. Experimental data are shown as symbols; modeling predictions, as solid (O₂ varying) or dashed (SO₂ varying) lines.

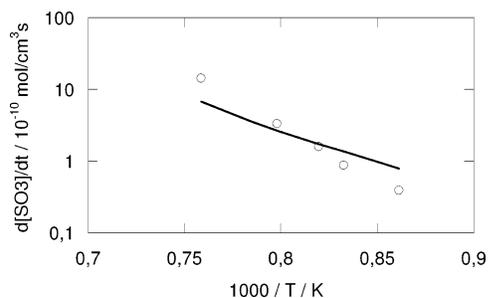
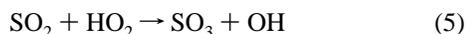
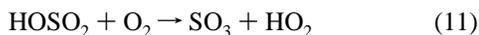


Figure 7. Comparison of experimental data³¹ and modeling predictions for the SO₃ formation rate in a quartz batch reactor for [SO₂] = [O₂] = 2.6 × 10⁻⁶ mol cm⁻³ and varying temperature. In the modeling, trace amounts of water vapor (50 ppm) have been assumed to be present. Experimental data are shown as symbols, modeling predictions as lines.

indicate that SO₃ is formed mainly by the sequence



As the temperature increases, the sequence SO₂ + SO₂ → SO₃ + SO (6), SO + O₂ → SO₂ + O, SO₂ + O + M → SO₃ + M (4) becomes more important. The modeling predictions are probably in agreement with the batch reactor results within the experimental uncertainty (Figures 6 and 7), but the mechanism of SO₃ formation under these conditions is still in question.

According to our modeling, the reaction sequence, SO₂ + O₂ → SO₃ + O (2b), SO₂ + O(+M) → SO₃(+M) (4), is not important for the SO₃ formation. However, the batch reactor data can be used to obtain an upper limit for *k*₂. Assuming that O is in steady state, we obtain d[SO₃]/dt = 2*k*_{2b}[SO₂][O₂]. From this equation, an upper limit of 14 cm³ mol⁻¹ s⁻¹ can be derived for *k*_{2b} at 1223 K, corresponding to *k*₂(1223 K) ≤ 1.6 × 10⁹ cm³/(mol s) (Figure 3).

Experiments on oxidation of SO₂ to SO₃ by O₂ under flow reactor conditions have been reported by Flint and Lindsay,⁴³ Burdett et al.,²³ and Jørgensen et al.⁴⁴ These studies were all conducted at atmospheric pressure in electrically heated laminar flow reactors made of quartz or silica. In the present work the data from Flint and Lindsay and from Jørgensen et al. are selected for model validation; the results from Burdett et al. suffer from uncertainty in the reactor temperature profile.

Figure 8 compares modeling predictions with the data of Flint and Lindsay.⁴³ Their experiments were conducted with 1400 ppm SO₂ and 8% H₂O in air at temperatures between 573 and

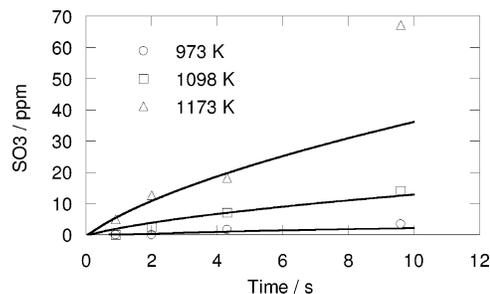


Figure 8. Comparison of experimental data⁴³ and modeling predictions for SO₃ formation in a quartz reactor at temperatures of 973–1173 K and atmospheric pressure. The quartz tube was 185 cm long and 1.6 cm internal diameter (*S/V* = 1.3 cm⁻¹). The inlet gases contained 0.14% SO₂, 8% H₂O, and air to balance. Symbols denote experimental results; solid lines denote modeling predictions.

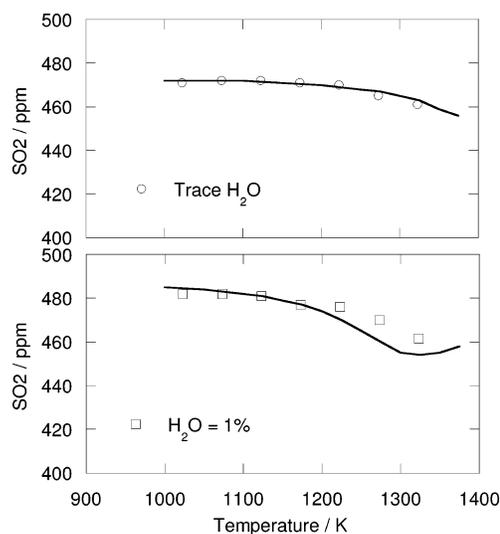


Figure 9. Comparison of experimental data⁴⁴ and modeling predictions for SO₂ oxidation in a quartz reactor at temperatures of 1023–1323 K and atmospheric pressure. The isothermal zone was 40 cm long and the reactor had a 3.15 cm internal diameter (*S/V* = 0.6 cm⁻¹). The inlet gas compositions were 472 ppm SO₂, 60% O₂, trace H₂O (assumed 200 ppm), and N₂ to balance (upper figure); 485 ppm SO₂, 60% O₂, 1% H₂O, and N₂ to balance (lower figure). The residence time as a function of temperature is 5380[K]/*T*. Symbols denote experimental results; solid lines denote modeling predictions.

1173 K. Formation of SO₃ was detected only at 973 K and above. Except for a single data point, the modeling predictions are in good agreement with the flow reactor data. Flint and Lindsay attributed the SO₃ formation to the influence of catalysis by silica, but the present work indicates that it is largely a homogeneous reaction.

Figure 9 compares modeling predictions with the data of Jørgensen et al.⁴⁴ These experiments were conducted with about 480 ppm SO₂, 60% O₂, water vapor (trace amounts or 1%) in N₂ at temperatures between 1023 and 1323 K. Again the modeling predictions are in good agreement with the experimental results, under both semidry and moist conditions. At the highest temperatures in the moist set, the SO₃ concentration becomes limited by thermal equilibrium and the predicted SO₂ level increases.

Rate of production and sensitivity analysis indicate that the key reactions in SO₃ formation are SO₂ + OH(+M) → HOSO₂(+M) (5), HOSO₂ + O₂ → HO₂ + SO₃ (11), and to a lesser extent SO₂ + HO₂ → SO₃ + OH (3b) and SO₂ + OH ⇌ SO₃ + H (1b). Modeling predictions with the high rate constant for the SO₃ + O reaction (2) derived from flames^{12,20–22} lead

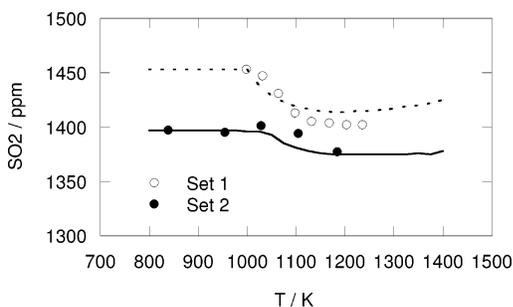
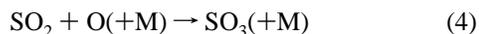


Figure 10. Comparison of experimental data⁷ and modeling predictions for conversion of SO₂ as function of temperature during moist CO oxidation in a quartz flow reactor. Experimental data are shown as symbols; modeling predictions, as lines. Data set 1: 448 ppm CO, 1453 ppm SO₂, 4.3% O₂, and 1% H₂O, residence time as a function of temperature 243[K]/T. Data set 2: 446 ppm CO, 1395 ppm SO₂, 4.1% O₂, and 8.7% H₂O, residence time as a function of temperature 244[K]/T.

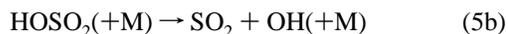
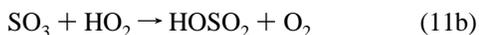
to a significant overprediction of the SO₃ formation rate through the inverse step, SO₂ + O₂ → SO₃ + O (2b), under the conditions of Figures 8 and 9. This is in support of the low value of *k*₂ estimated in the present work.

The experiments discussed above^{23,31,43,44} were all conducted in the absence of combustibles. Radical formation from combustion has been shown to enhance the SO₂ oxidation rate significantly.⁴⁵ Glarborg et al.⁷ studied SO₂ conversion during moist CO oxidation. The experiments were conducted using a quartz flow reactor, designed to approximate plug flow. It was placed in a three-zone electrically heated oven, allowing a uniform temperature profile with an uncertainty of ±10 K over the reactor length. The reactants CO, SO₂, O₂, and H₂O were heated separately and mixed in a crossflow at the reactor inlet. The product gas was quenched at the exit of the reactor with cooling air and dried prior to analysis.

The experimental data are compared with modeling predictions in Figure 10. The agreement is within the experimental uncertainty. Compared to conditions in the absence of combustibles, the enhanced radical levels open up new pathways to formation and consumption of SO₃. The dominating SO₃ formation reaction is now recombination of SO₂ with atomic O,



and SO₃ decomposition proceeds mainly by the reactions



It is noteworthy that although reactions 5 and 11 are important for SO₃ formation in moist SO₂/O₂ systems, they proceed in the reverse direction (11b, 5b) at higher radical levels and serve to consume SO₃.

Although the revised rate constant for the SO₃ + H reaction (1) has only a small impact compared to earlier modeling for the SO₂/SO₃ ratio in combustion, the updated value for the SO₃ + O reaction (2) has important implications. This reaction has been assumed to be an important consumption step for SO₃ in flames^{18–22} and in flow reactor experiments,^{7,10} whereas the reverse step between SO₂ and O₂ (2b) has been believed to contribute to SO₃ formation in SO₂/O₂ systems.^{6,23} The present analysis indicate that reaction 2 is too slow to be important in

any of these systems and that the observed SO₃ consumption must be attributed to other reactions, primarily SO₃ + H (1). Also the SO₃ + OH reaction (3) is generally too slow to be significant, but the reverse step between SO₂ and HO₂ (3b) may contribute to SO₃ formation under conditions with low radical levels.

Conclusions

In the present study, ab initio calculations were carried out to estimate rate constants for the reactions of SO₃ with H, O, and OH at high temperatures. The SO₃ + H → SO₂ + OH reaction (1) is fast, with $k_1 = 8.4 \times 10^9 T^{1.22} \exp(-13.9 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Contrary to reaction 1, the reactions of SO₃ with O (2) and OH (3) appear to be quite slow due to high barriers to reaction, $k_2 = 2.8 \times 10^4 T^{2.57} \exp(-122.3 \text{ kJ mol}^{-1}/RT)$ and $k_3 = 4.8 \times 10^4 T^{2.46} \exp(-114.1 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Modeling predictions with a revised reaction mechanism for SO₂/SO₃ chemistry are in good agreement with a range of experimental data from reactor experiments. The calculations indicate that oxidation of SO₂ to SO₃ with and without presence of combustibles involve primarily recombination of SO₂ with O and OH radicals. Reaction 1 may limit the SO₃ concentration, and reactions 2 and 3 are unimportant for the SO₂/SO₃ ratio under most conditions of interest.

Acknowledgment. We acknowledge support from the CHEC (Combustion and Harmful Emission Control) Research Program, PSO-Elkraft (Grant FU-2207), the Robert A. Welch Foundation (Grant B-1174) and the UNT Faculty Research Fund. A three month guest professorship for P.M. at DTU was funded by the Otto Mønsted Fund. Computer facilities were provided at the National Center for Supercomputing Applications (Grant CHE000015N), at the Research Cluster operated by UNT Academic Computing Services, and purchased with funding from the National Science Foundation (Grant CHE-0342824).

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