Determination of the Rate Coefficients of the \( \text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M} \) Reaction

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ABSTRACT: Rate coefficients of the title reaction \( R_{31} \) (\( \text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M} \)) and \( R_{56} \) (\( \text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH} \)), important in the conversion of \( \text{S(IV)} \) to \( \text{S(VI)} \), were obtained at \( T = 970–1150 \) \( \text{K} \) and \( \rho_{\text{ave}} = 16.2 \, \mu\text{mol cm}^{-3} \) behind reflected shock waves by a perturbation method. Shock-heated \( \text{H}_2/\text{O}_2/\text{Ar} \) mixtures were perturbed by adding small amounts of \( \text{SO}_2 \) (1%, 2%, and 3%) and the \( \text{OH} \) temporal profiles were then measured using laser absorption spectroscopy. Reaction rate coefficients were elucidated by matching the characteristic reaction times acquired from the individual experimental absorption profiles via simultaneous optimization of \( k_{31} \) and \( k_{56} \) values in the reaction modeling (for satisfactory matches to the observed characteristic times, it was necessary to take into account \( R_{56} \)). In the experimental conditions of this study, \( R_{31} \) is in the low-pressure limit. The rate coefficient expressions fitted using the combined data of this study and the previous experimental results are:

\[
 k_{31} = 6.1 \times 10^{24} \, T^{-3.0} \exp(-1980 \, \text{K}/T) \, \text{cm}^6 \, \text{mol}^{-2} \, \text{s}^{-1} \, \text{at} \, T = 300–2500 \, \text{K};
\]

\[
 k_{56} = 3.9 \times 10^{11} \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1} \, \text{at} \, T = 970–1150 \, \text{K}.
\]

Computer simulations of typical aircraft engine environments, using the reaction mechanism with the above \( k_{31,0} \) and \( k_{56} \) expressions, gave the maximum \( \text{S(IV)} \) to \( \text{S(VI)} \) conversion yield of ca. 3.5% and 2.5% for the constant density and constant pressure flow condition, respectively. Moreover, maximum conversions occur at

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INTRODUCTION

Contrails and contrail-induced cirrus clouds may affect the global climate via radiative forcing and the alteration of atmospheric chemistry [1–3]. The critical chemical species in contrails, in addition to soot, ions, and water vapor, are sulfates and sulfuric acid formed by oxidation of fuel sulfur, i.e., low oxidation state fuel bound S(II), mostly thiols and sulfides, are rapidly and nearly quantitatively converted to S(IV), i.e., SO2, in the high-temperature oxidative environment of the combustor, and then on to S(VI), mostly SO3 and small amounts of sulfates, formed in the cooler, but still harsh environment of the turbine and exhaust nozzle [4–6]. Sulfates and sulfuric acid, formed in the aircraft exhaust plume, enhance the formation of contrails and cirrus clouds through homogeneous binary nucleation of H2SO4/H2O and heterogeneous condensation of H2SO4/H2O on soot particles or ions [4–9].

Owing to the significant role of S(VI) (SO3 and H2SO4) in the formation of contrail and cirrus cloud, the conversion fraction of S(IV) to S(VI) has been measured or calculated by various authors: The measured fractions were about 0.34%–4.5% [10,11] or 3.3% ± 1.8% [12], while calculations from measured particulate volume, presuming only H2SO4 and H2O are in the particles, span a wide range from 0.4% to 80% [10,11,13–15].

The route to sulfuric acid formation in the homogeneous gas phase has been considered as R0 (fuel-bound S =→ SO2), R31 (SO2 + O + M =→ SO3 + M), R32 (SO2 + OH (+M) =→ HOSO2 (+M)), R52 (HOSO2 + O2 =→ SO3 + HO2), and R57 (SO3 + H2O =→ H2SO4). It is believed that R0 occurs inside the combustor, R31, R32, and R52 in the turbine and engine exit nozzle, and R57 in the exhaust plume. R31 is considered as the principal reaction pathway for the conversion of sulfur from the S(IV) to the S(VI) oxidation state. As seen in Fig. 6, the experimentally measured rate coefficients of the spin-forbidden R31 (SO2(X1A1) + O(3P) + M =→ SO3(1A′) + M) exhibit an unusual behavior—an increase with temperature (T <∼450 K) [16,17] followed by a sharp decrease with further increase of temperature (T >∼1400 K) [18–20]. This unusual behavior of rate coefficients with respect to temperature was first rationalized by Astholz et al. [19] in terms of potential energy barrier arising from the triplet–singlet intersystem crossing and diminishing collision efficiency with temperature in the stabilization of the collision complex formed (see the section Discussion for details).

Despite its important role in contrail formation, the rates of this reaction have never been measured at temperatures typical of aircraft operation (900–1200 K). Moreover, there are large discrepancies among the extrapolated values from the existing rate coefficient expressions to this temperature region. For example, at T = 1000 K the calculated or extrapolated values from the early studies are (in cm6 mol−2 s−1) 2.8 × 1015 [21], 4.1 × 1015 [17], 9.6 × 1015 [16], 1.0 × 1016 [20], and 3.2 × 1016 [19]. An order of magnitude discrepancy is easily recognized. Recently, Naidoo et al. [22] measured the rate coefficients of R31 in the temperature range of 290–840 K and reported the Rice–Ramsperger–Kassel–Marcus (RRKM) fitted parameters for k31,[0/Ar], k31,∞ and broadening factor fκ for T = 220–2500 K. The k31,[0/Ar] value of Naidoo et al. at T = 1000 K gives 2.8 × 1015 cm6 mol−2 s−1. We have previously reported results for this reaction over a more limited temperature range [23]. In the present work, we extended our previous efforts and completed the measurement of the rate coefficients of R31 at T = 970–1150 K using a shock tube and OH laser absorption technique.

SELECTION OF EXPERIMENTAL CONDITIONS AND COMPUTER SIMULATION

Determination of the rate coefficients of R31 was performed via a perturbation method utilizing the abundant and well-characterized O-atoms provided by the shock-induced ignition of H2/O2/Ar mixtures. This permitted the use of experimentally convenient mixture dilutions and reaction time scales as well as sensitive OH absorption diagnostics in the easily accessible near ultraviolet wavelength regime. We perturbed the H2/O2/Ar reaction system with small amounts of SO2 and recorded the differences in temporal behavior of the OH absorption. In this regard, construction of a robust reaction mechanism of the SO2/H2O/Ar system is essential. Our reaction mechanism is given in Table 2 in the Supporting Information.

For the temperature and pressure range relevant to S(IV) to S(VI) conversion, the major O-atom production reaction is R1 (H + O2 =→ OH + O) and the
main O-atom consumption reaction is R2 (O + H2 → OH + H). O-atom production rates are further modified by R0 (H + O2 + M → HO2 + M) through the channeling of some H-atoms away from chain branching. In the SO2/H2/O2/Ar system, R31 (SO2 + O + M → SO3 + M) and R2 compete for O-atoms. In rich H2/O2/Ar mixtures, this competition would be dominated by R2 and thus the addition of SO2 would barely affect the course of reaction. Therefore, we restrict our consideration to lean H2/O2/Ar mixtures only. On the basis of our previous study [24], we selected H2/O2/Ar = 0.5/10.0/89.5 (θ = 0.025) as the baseline mixture. Using this mixture, we performed a series of sensitivity analyses to determine both the optimum levels of SO2 addition and the best set of reaction characteristics to use. We determined that matching the characteristic times (τmax, τ75, τ50, and τ25 defined in the Results section) and employing three mixtures containing 1.0%, 2.0%, and 3.0% SO2 would give the best balance of overall reaction sensitivity and experimental convenience. Figure 1 shows sensitivity spectra obtained using the Table 2 reaction mechanism at a typical experimental condition. The sensitivity of R31 was found to be increased with both decreasing T and increasing SO2/H2 ratio in the mixture. Although excellent R31 sensitivities were computed at low temperatures, the characteristic times became prohibitively long.

The Table 2 mechanism was composed of 57 elementary reactions in 18 chemical species. For H2/O2 reactions, we used our reaction mechanism of 20 elementary reactions [24] with a change in k14 (HO2 + OH → H2O + O2) from 2.0 × 1013 to 3.0 × 1013 cm3 mol−1 s−1 following the recommendation of Srinivasan et al. [25]. The H2/O2 reactions were combined with additional 35 reactions that are related to SO2 oxidation by H2S, O2 species from Rasmussen et al. [26]. Then we consider the oxidation of SO2 by HO2 radical, important in our experimental conditions, through the reaction R36 (SO2 + HO2 → SO3 + OH) of which rate coefficients are obtained as part of the simultaneous optimization with R31 (see below). Also, we added R57 (SO3 + H2O → H2SO4) [27] for final product formation for completeness. However, the contribution of this reaction to the reaction progress is negligible.

All simulations were performed using our custom code that has advantageous built-in features for optimization. This code has been thoroughly tested against existing kinetic codes [28]. Recently updated values for the thermodynamic data [29,30] have been used for all species except for HOSO, HSO2, and HOSO2. The thermodynamic properties of these species were estimated using the available experimental data and theoretical calculations. The NASA polynomial coefficients of these species are given in Table 1 in the Supporting Information.

**EXPERIMENTAL**

The shock tube-laser absorption technique employed in this study is described in detail elsewhere [31]. Briefly, a rolled square stainless steel shock tube, 63.5 mm in cross section, was used for experiments. The test section was routinely pumped below 3 μTorr by a Varian V60 Turbopump. A combined leak and outgassing rate of the test section was 5 μTorr min−1. To minimize problems due to wall loss of SO2, all fills were done in a two-step process. First, the shock tube was filled with mixture to the desired starting pressure and the room temperature absorption of SO2 was measured. The tube was then evacuated and refilled to the same pressure with fresh test gas. All shocks were then initiated within 1 min of admitting the test gas mixture.

Shock speeds were measured using four flush-mounted 113A21 PCB Piezotronics pressure transducers coupled to Phillips PM6666 programmable countertimers. The last pressure transducer was axially coincident with the center of the observation windows, 12.7 mm distant from the end wall. Measured shock speeds were fitted to a second-order polynomial in distance. The extrapolated speed to the end wall was used together with NASA thermodynamic data [29] in solving the relationships for the reflected shock properties [32], assuming full vibrational relaxation and no chemical reaction at the shock front. The postreflected shock...
properties were corrected for boundary layer/ reflected shock interaction effects using the methodology described by Hwang et al. [28].

The combined OH and SO2 absorption profiles were measured at 310.032 nm (in air), corresponding to the P1(5) line of the (0,0) band of the OH AΣ^+ ← XΣ^+ transition. UV light was produced by a CW argon ion laser (Coherent Innova 200) pumped ring-dye laser (Coherent 899-21) running Kiton Red 620 dye. Intra-cavity frequency doubling was achieved with an angle tuned LiIO3 crystal. For absorption measurements, a triple beam scheme was employed: a probe beam passed through the center of two 25.4-mm-diameter S1-UVA quartz windows (12.7 mm distant from the shock tube end wall), an intensity reference beam, and a wavelength reference beam. Passage through an unconstrained burner-stabilized methane/air flame was used to provide the wavelength reference, i.e., the center absorption of the OH P1(5) line. Each detector was a combination of interference filter (λ_0 = 310 ± 10 nm fwhm), a PMT (Thorn EMI9924QB), and a high-speed buffer/amplifier. A custom dynode chain was used for these experiments to assure the linearity of the absorption signal. The probe, reference, difference (probe dc–reference ac), and the last pressure transducer signals were recorded on a four-channel Nicolet 4094C digital oscilloscope equipped with Nicolet 4570 plug-in units. Reaction progress was followed using the difference signal. The S/N of the difference signal was usually better than 60. The overall electronic time constant determined for the entire PMT-buffer–cable system was less than 0.5 μs.

SO2/H2/O2/Ar test gas mixtures were prepared manometrically and allowed to stand for at least 48 h before use. A pump-fill-pump-fill cycle was used for the SO2 addition to minimize the effect of wall loss. The maximum uncertainty in mixture composition was less than 0.5% of the nominal mole fraction for each component. The stated purities of the gases were H2, 99.9995% (MG Industries, Malvern, PA; scientific grade); O2, 99.998% (MG Industries; scientific grade); SO2 (anhydrous), 99.98 wt% (MG Industries; scientific grade); Ar, 99.9999% (MG Industries; sputtering grade). All gases were used without further purification.

**RESULTS**

A typical absorption profile is shown in Fig. 2. The reflected shock passage at time zero is shown in the form of a schlieren peak at the extreme left-hand edge of the experimental trace. The initial absorption is entirely due to SO2.

Because both SO2 and OH absorb 310-nm UV light, the absorption coefficients of SO2 were measured and used in the simulation of experimental reaction progress. OH absorption coefficients were calculated using our recent values of the spectral line broadening parameters and other molecular properties [33]. The mean room temperature base e absorption coefficient of SO2 measured by pump-fill-pump-fill method was ε_e(SO2) = (7.0 ± 0.4) × 10^4 cm^2 mol^-1, which is about 30% smaller than the spectroscopic measurement of Vandeale et al. [34].

Figure 3 shows the SO2 absorption coefficients measured at room temperature and at temperatures behind incident and reflected shock waves. A temperature-dependent fitting gives

ε_e(SO2) = 1.3 × 10^5 exp(−180 K/T) cm^2 mol^-1.

For reaction progress and sensitivity analyses, the following set of observables was obtained from an experimental absorption profile: an initial SO2 absorption after reflected shock passage, A_{SO2,0} = 1 - I_{SO2,0}/I_0; a maximum absorption, A_{max} = (1 - I/I_0)_{max}; and four characteristic times (τ_{max}, τ_{25}, τ_{50}, and τ_{75}). Evaluation of τ_{max}, time to reach A_{max}, is straightforward. For τ_{25}, however, it was necessary to use a subtracted absorption signal (A'_{max} = A_{max} - A_{SO2,0}) for the experiments that resulted in large A_{SO2,0} and small A_{max}. Thus τ_{25}, τ_{50}, and τ_{75} were defined as the time to reach 25%, 50%, and 75% of A'_{max}, respectively. Figure 4 shows τ_{50} values measured in 1.0%, 2.0%, and
The least-squares fit is $\varepsilon_{e}(\text{SO}_2) = 1.3 \times 10^5 \exp(-180 \text{K}/T) \text{cm}^2 \text{mol}^{-1}$ The vertical error bars represent error limits at the 95% confidence level.

Figure 3 Base $e$ absorption coefficients of SO$_2$ at 310 nm. 172

Figure 4 Measured $\tau_{50}$ values of the baseline and SO$_2$-perturbed mixtures. Symbols are as follows: filled square, SO$_2$/H$_2$/O$_2$/Ar = 0.0/0.5/10/89.5 (base line mixture); star, SO$_2$/H$_2$/O$_2$/Ar = 1.0/0.5/10/88.5; open circle, SO$_2$/H$_2$/O$_2$/Ar = 2.0/0.5/10.0/87.5; open diamond, SO$_2$/H$_2$/O$_2$/Ar = 3.0/0.5/10.0/86.5.

DISCUSSION

No measurements had been made for the reactions between SO$_2$ and HO$_2$ at combustion temperatures. Three room temperature measurements have been performed to simultaneously determine the rate coefficients of R$_{47}$ (HOSO + O$_2$ $\rightarrow$ SO$_3$ + HO$_2$), R$_{50}$ (HSO$_2$ + O$_2$ $\rightarrow$ SO$_2$ + HO$_2$), and R$_{56}$ (SO$_2$ + HO$_2$ $\rightarrow$ SO$_3$ + OH). The first two reactions (R$_{47}$ and R$_{50}$) have already included in the reaction mechanism of Rasmussen et al. [26] that was adopted in this work without any modification. R$_{56}$ has been studied experimentally at low temperatures ($T < 300$ K) for atmospheric applications [35–38] and theoretically at high temperatures for combustion applications [39,40] (see the section Discussion). The inclusion of the reaction R$_{56}$, which has some sensitivity on the characteristic times (Fig. 1), is necessary to unravel the contributions by R$_{31}$ and R$_{56}$ to the disproportionate enhancement of the characteristic times with [SO$_2$]$_0$.

Using the Table 2 mechanism, computer simulations for experimental observables have been performed to simultaneously determine the rate coefficients of R$_{31}$ (SO$_2$ + O + M $\rightarrow$ SO$_3$ + M) and R$_{56}$ (SO$_2$ + HO$_2$ $\rightarrow$ SO$_3$ + OH). Determination of the rate coefficients was accomplished using a method similar to the solution mapping [41,42], i.e., for each experiment, only the $k_{31}$ and $k_{56}$ were systematically varied and the corresponding values of the function, $\Gamma(x) = \sum_i \left( \frac{\tau_{i,\text{calculated}}(x) - \tau_{i,\text{experimental}}}{\tau_{i,\text{experimental}}} \right)^2$, where $i = \{\tau_{25}, \tau_{50}, \tau_{75}, \tau_{\text{max}}\}$ and $x = \{k_{31}, k_{56}\}$, were calculated. Then an exhaustive search was made for the minimum value of $\Gamma(x)$ to find the optimized values of $x = \{k_{31}, k_{56}\}$. A simulated absorption profile is shown in Fig. 2. The resulting rate coefficients of R$_{56}$ and R$_{31}$ are plotted in Figs. 5 and 6, respectively. Experimental conditions, measured observables, and the rate coefficients determined for individual experiments are given in Table 3 in the Supporting Information.

No measurements had been made for the reactions between SO$_2$ and HO$_2$ at combustion temperatures. Three room temperature measurements have been made and calculations have been performed for combustion temperatures. Three product channels have been considered: R$_{47}$ (HOSO + O$_2$ $\rightarrow$ SO$_3$ + HO$_2$), R$_{50}$ (HSO$_2$ + O$_2$ $\rightarrow$ SO$_2$ + HO$_2$), and R$_{56}$ (SO$_2$ + HO$_2$ $\rightarrow$ SO$_3$ + OH). As for the first two reactions, included in the reaction mechanism of Rasmussen et al. [26] and also used
in this study, there have been no experimental studies. For the third reaction channel, only the room temperature rate coefficients are available [35–38], which vary from \(k_{56} \leq 6.0 \times 10^5\) to \(k_{56} = 5.2 \times 10^9\) cm\(^3\) mol\(^{-1}\) s\(^{-1}\). Of these, the two studies (Graham et al. [37] and Burrows et al. [38]) using direct in situ spectroscopic measurements of the reactants observed no measurable reaction with \(\text{SO}_2\) and thus returned only upper limit values. The lower of these, Graham et al. [37], perforce obviates the other. Reaction with \(\text{SO}_2\) was observed using the somewhat indirect photochemical \(^{18}\text{O}_2\) competitive isotope-labeling technique method of Payne et al. [36]; however, on the basis of a steady-state analysis of their kinetic scheme, they argue that the rate of \(R_{56}\) directly depends upon the ratio of isotopically labeled \(\text{CO}_2\) produced in their reactor. The large discrepancy between these studies has not been thoroughly explored and remains a bit of a mystery. Indeed, all three room temperature determinations may have been affected by unforeseen problems with handling the reactants or by unforeseen subtleties and complications in the overall reaction systems used. A glimmer of this is perhaps the negative reaction rate observed by Graham et al. at their higher \(\text{SO}_2\) concentration. To date, the generally accepted community value for \(k_{56}\) is that of Graham et al. recommended by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry [35].

Recently, there have been two theoretical investigations of \(R_{56}\) going to products relevant to combustion conditions. Hindiyarti et al. [39] performed ab initio energy and structure calculations coupled to transition state theory (TST) to obtain a rate coefficient expression for \(k_{56}\) (\(\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}\)) given as

\[
4.8 \times 10^4 \times 10^{24} \exp(-13720 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

in the temperature range of 800–2000 K. Wang and Hou [40] investigated the complicated reaction pathways leading from \(\text{SO}_2 + \text{HO}_2\) to the various products and posited that the effectively barrier-free \(\text{HOSO} + \text{O}_2\) (\(R_{-57}\)) channel is the dominant reaction at “normal” temperature. Their argument can be presented in a simple form as the competitive play between reaction dynamics and reaction energetics: \(R_{-50}\) (\(\text{HSO}_2 + \text{O}_2 \rightarrow\)

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**Figure 5** Rate coefficients of \(R_{56}\) (\(\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}\)). Symbols are as follows: circle, our data; diamond, Payne et al. [36]; square, Graham et al. [37]; triangle, Burrows et al. [38]. Lines are solid, a least-squares fit to our data, \(k_{56} = 1.36 \times 10^{11} \exp(-3420 K/T)\) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) at \(T = 970–1150\) K with estimated error of \(\pm 30\%\); dashed, extrapolation of our expression to room temperature; light solid, a three-parameter fit of our data with the lower limit value of the room temperature data of Payne et al., \(k_{56} = 1.5 \times 10^{-3} T^6 \exp(100 K/T)\) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) at \(T = 300–2000\) K; dot–dashed, calculated from \(k_{56} = 4.8 \times 10^4 T^{2.46} \exp(-13720 K/T)\) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) of Hindiyarti et al. [39] with \(K_{c,56}\). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**Figure 6** Low-pressure limits rate coefficient data of \(R_{31}\). Symbols are as follows: plus, Nettleton and Stirling [45]; open square, Westenberg and deHaas [16]; open triangle up, Astholz et al. [18,19]; open triangle right, Atkinson and Pitts [17]; filled triangle left, Merryman and Levy [44]; open diamond, values from the rate coefficient expression of Smith et al. [20]; star, Naidoo et al. [22]; open circle, this study. Lines are (in cm\(^6\) mol\(^{-2}\) s\(^{-1}\)) long dashed, Troe [21], \(k_{31,0}[\text{Ar}] = 4.0 \times 10^{28} T^{-4.0} \exp(-2650 K/T)\), \(T = 300–2500\) K; dot–dashed, Naidoo et al. [22], \(k_{31,0}[\text{Ar}] = 2.4 \times 10^{37} T^{-3.0} \exp(-2610 K/T), T = 220–2500\) K; solid, this study, \(k_{31,0}[\text{Ar}] = 2.9 \times 10^{35} T^{-6.0} \exp(-4780 K/T) + 6.1 \times 10^{24} T^{-3.0} \exp(-1980 K/T), T = 300–2500\) K. The average deviation of the high temperature experimental data of Astholz et al. (\(T > 1700\) K) [18,19] from our fit is ca. \(\pm 30\%\).
SO₂ + HO₂ is both kinetically and thermochemically disfavored (high barrier height and high endothermicity), R₅₆ is kinetically disfavored but thermochemically favored (a moderate barrier but strong exothermicity), and R₄₋₇ is kinetically favored but thermochemically disfavored (no effective barrier but moderate endothermicity). Based upon this argument, only the rate coefficients for R₄₋₇ (and stabilization of the intermediate complex, important near room temperature) were calculated using TST and a master equation analysis. The results pass through the middle of the room temperature experimental data and are claimed to support the IUPAC evaluation. It should be noted that the difference between the calculated endothermicity of R₄₋₇ and the calculated barrier height for R₅₆ is only 35 kJ mol⁻¹ for their RCCSD(T)-cf calculation. Furthermore, while they do a good job of calculating the endothermicity of R₅₀ and R₅₆, they may be low for R₄₋₇ (see their Table 1). As both R₄₋₇ and R₅₆ are competitive channels that pass through the same intermediate complex, increasing the endothermicity of R₄₋₇ increases the relative flux through the R₅₆ channel making it a significant reaction pathway. Even so, accepting Wang and Hou’s basic argument we would still expect no net flux, and thus no significant effect upon the course of reaction, for the R₄₋₇ channel given the excess O₂ in our system and the barrier-free reverse reaction back to reactants for that channel. This was borne out in our simulations where we found that contribution to SO₂ oxidation by either R₄₋₇ (R₄₋₇) or R₅₀ (R₅₀) is insignificant under our experimental conditions (T = 970–1150 K). Rather, R₅₆ plays an increasingly important role as the temperature is lowered and the SO₂ concentration is raised. For instance, using our highest SO₂ mixture, SO₂/H₂/O₂/Ar = 3.0/0.5/10.0/86.5, at T = 1033 K and P = 1.45 atm, ca. 32% of SO₃ was formed by R₅₆, whereas ca. 66% of SO₃ was formed by R₃₁ at times between 0.5 and 2.0 ms; while for our lowest SO₂ mixture SO₂/H₂/O₂/Ar = 1.0/0.5/10.0/88.5 at T = 996 K and P = 1.31 atm, ca. 16% of SO₃ was formed by R₅₆, whereas ca. 82% of SO₃ was formed by R₃₁ at the same time interval. The optimized k₅₆ values are plotted in Fig. 5 together with those of Hindiyarti et al. calculated from Kₑ₅₆, and the various room temperature measurements. Our data are well fitted as

\[
k₅₆ = 1.36 \times 10^{11} \exp(-3420 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

at T = 970–1150 K with estimated error limits of ±30% and is shown as the dark solid line, which is extrapolated to room temperature (dashed line). It is interesting to note that the room temperature value of our expression is not far above the upper limit value of Graham et al. [37], the value recommended by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry [35]. As an enlightening exercise, we can find an equally good fit to our data by employing a gentle upwardly curving expression (of the basic form predicted by Wang and Hou [40]) that passes through the data of Payne et al [36]. This is shown as the light solid line in Fig. 5. Indeed, due to experimental scatter and the relatively narrow temperature range our data appear as essentially a single point on a graph like Fig. 5. Thus we can always find a good curve fit that passes through both our data and nearly any given room temperature value. Our data cannot help elucidate the rate of this reaction at lower temperatures. As we have noted earlier, this channel becomes more important with decreasing temperature and so can play an important role in combustion exhaust.

Our k₃₁ₑff values show, first, a very slight negative temperature dependence at T = 970–1150 K and \(\rho_{av} = 16.2 \umol \text{ cm}^{-3}\) and second, about 15–30% higher than those from k₃₁₀ expression of Naidoo et al. [22] at the same conditions. This is the indirect indication that we obtained the low-pressure limit rate coefficients (k₃₁₀). Thus, at each experimental condition, k₃₁₀/[M] was obtained by scaling k₃₁₀ with the corresponding collision-efficiency-corrected density, \([M] = \rho \times [1 + x_O_2(\varepsilon_{O_2} - 1) + x_{SO_2}(\varepsilon_{SO_2} - 1)].\) Here the collision efficiencies are \(\varepsilon_{O_2} = 1.3, \varepsilon_{SO_2} = 9.0\) and \(\varepsilon_{other \ species} = 1.0\), including \(\varepsilon_{Ar}\). The k₃₁₀/[Ar] values obtained in this manner are listed in Table 3 in the Supporting Information and plotted in Fig. 6.

All possible uncertainties in our k₃₁₀/[Ar] values are estimated as follows: The presence of H atoms from sources other than the initiation reaction, R₋₁₁ (HO₂ + H ← H₂ + O₂), and the uncertainty in [SO₂]₀ are considered first. The effect of H-atom impurity was explored by injecting \([H]₀ = 0.1 \ppb\) into the system—this [H]₀ is about five times larger than the kinetically produced [H]₀ in our experimental conditions. The k₃₁₀,₀ values were increased by less than 20% and 3% with 1.0% SO₂/H₂/O₂/Ar mixture and 3.0% SO₂/H₂/O₂/Ar mixture, respectively. The effect of the 0.5% uncertainty in the nominal [SO₂]₀ mole fractions was negligible. Here we placed a factor of 1.2 uncertainties in k₃₁₀ owing to the possible presence of impurity as H atoms.

The influence of the uncertainties from other reaction rate coefficients on the determination of k₃₁₀/[Ar] is examined next. As seen in the sensitivity figure, R₀ (H + O₂ + M → HO₂ + M) exhibits the largest sensitivity. For the rate coefficients of R₀ we used k₉₀/[Ar] = \(5.55 \times 10^{18} \text{ T}^{-1.15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}\) of Hwang et al. [24] with uncertainty limits of 30%. The uncertainties in k₃₁₀/[Ar] due to the coupling between R₃₁ and R₀ were estimated by varying the rate coefficients of R₀ of
Hwang et al. by the given uncertainty limits and then observing the propagated effects on \( k_{31,0}/[\text{Ar}] \). With 30% reduction of \( k_{9,0}/[\text{Ar}] \), the resulting changes in \( k_{31,0}/[\text{Ar}] \) are 90%, 50%, and 40% for 1.0%, 2.0%, and 3.0% \( \text{SO}_2/\text{H}_2/\text{O}_2/\text{Ar} \) mixtures, respectively. But, for 1.0% \( \text{SO}_2 \) mixtures, the changes in reaction profiles were so great that reasonable matches to the characteristic times, particularly at both low \( [\text{SO}_2]_0 \) and low-temperature conditions. The reverse argument is also true, and there is a range of \( k_{14} \) values to choose among (see below). Using the lowest reported \( k_{14} \) expression, Kappel et al. [46], instead of Srinivasan et al. [25] used in this study, only increases the \( k_{31,0}/[\text{Ar}] \) values by 6% at our most sensitive conditions.

The situation for \( R_{14} \) is certainly confusing at this time as can be seen in the rather busy nature of Fig. 7. The reaction has been studied quite extensively, both directly and indirectly, both experimentally and computationally, by numerous techniques covering the temperature range relevant from atmospheric chemistry to flames. There is general agreement that the rate coefficient values of Keyser [47] at low temperatures and Goodings and Hayhurst [48] at high temperatures are firmly rooted; for the midtemperature range of 1050 K, the rate coefficient expression shown above represents all the data within 26% error limits. Although we were unable to perform this study using \( \text{N}_2 \) as a collider gas, those modeling this reaction in Air might want to use the commonly referenced collider efficiency ratio of 0.77 (\( \text{Ar}/\text{N}_2 \)) recommended by Atkinson et al. [35].

The rate coefficients from our expression are compared with those of previous studies. At \( T = 1050 \) K, the rate coefficient (in unit of \( \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)) from the above equation \( (3.1 \times 10^{15}) \) is about a factor of 7 and 3 smaller than the extrapolated value of Astholz et al. \( (2.2 \times 10^{16}) \) [18,19] and Smith et al. \( (9.0 \times 10^{15}) \) [20], respectively. But it is about 15% larger than the fit of Troe \( (2.7 \times 10^{15}) \) [21] and RRKM fit of Naidoo et al. \( (2.7 \times 10^{15}) \) [22]. There is a competition for \( \text{SO}_2 \) between \( \text{O} \) and \( \text{HO}_2 \). If \( \text{HO}_2 \) loss due to \( R_{14} \) \( (\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2) \) were increased, then there would be more \( \text{SO}_2 \) available and the overall reaction would be delayed even more. This would then require a decrease in \( k_{31,0}/[\text{Ar}] \) to account for the observed characteristic times, particularly at both low \( [\text{SO}_2]_0 \) and low-temperature conditions.

The differences between the experimental and computed characteristic times for individual runs are on average less than 2% for \( \tau_{50} \) and \( \tau_{75} \) and 4% for \( \tau_{25} \) and \( \tau_{\text{max}} \). Taking into account all of the uncertainties discussed above plus additional uncertainties for \( P_0 \), shock speed, signal-to-noise ratio, etc., we estimated maximum uncertainty limits, \( U = \sqrt{\Sigma U_i^2} \approx 3.0 \) for individual runs.

A good fit to the data of this study and the previous experiments [16–19,22,44,45] is found using a combination of two non-Arrhenius-type expressions given as

\[
k_{31,0}/[\text{Ar}] = 2.9 \times 10^{15} \tau^{-6.0} \exp(-4780 \text{ K}/T) + 6.1 \times 10^{-24} T^{-3.0} \exp(-1980 \text{ K}/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}
\]

at \( T = 300–2500 \) K. As seen in Fig. 6, our data show the largest scatter. The rate coefficient expression shown above represents all the data within 26% error limits. Although we were unable to perform this study using \( \text{N}_2 \) as a collider gas, those modeling this reaction in Air might want to use the commonly referenced collider efficiency ratio of 0.77 (\( \text{Ar}/\text{N}_2 \)) recommended by Atkinson et al. [35].

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The situation for \( R_{14} \) is certainly confusing at this time as can be seen in the rather busy nature of Fig. 7. The reaction has been studied quite extensively, both directly and indirectly, both experimentally and computationally, by numerous techniques covering the temperature range relevant from atmospheric chemistry to flames. There is general agreement that the rate coefficient values of Keyser [47] at low temperatures and Goodings and Hayhurst [48] at high temperatures are firmly rooted; for the midtemperature range

![Figure 7 Rate coefficients of \( R_{14} (\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2) \). Symbols are as follows: plus, Cox et al. [56]; open triangle down, Sridharan et al. [57]; star, Goodings and Hayhurst [48]; open diamond, Keyser [47]; open square, Hippler et al. [50]; filled circle, Kappel et al. at \( P = 4 \) bar [46]; filled triangle up, Srinivasan et al. [25]. Lines are (in cm\(^3\) mol\(^{-1}\) s\(^{-1}\)): solid connecting two open diamonds, Hippler and Troe [49]; dashed, Gonzalez et al. [54]; solid, Kappel et al. [46]; solid connecting two open triangles up, Srinivasan et al. [25]; dot–dashed, Sivaramakrishnan et al. [52]; light solid, Rasmussen et al. [51].]
of interest in this study, the values are still in flux. Troe and coworkers [46,49,50] have published a series of increasingly refined shock tube measurements of R14 using various optical diagnostics to measure OH, HO2, and H2O2 temporal profiles. As can be seen in Fig. 7, their earlier data (930–1680 K) [50] had a deep and narrow “V” temperature dependence centered around 1250 K (open square). Their later data [46] had a similar but less pronounced feature centered around 1000 K (filled circle). Nevertheless, they reported rate coefficient expressions that were either a straight line, $k_{14} = (2 \pm 1) \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at $T = 1000–1250$ K [49] (solid line connecting two open diamonds), or an imperceptibly curved line, $k_{14} = 1.0 \times 10^{13} + 5.8 \times 10^{13} \exp(-2000 K/T)$ cm$^3$ mol$^{-1}$ s$^{-1}$ at $T = 950–1250$ K [46] (dark solid line). More recently, Srinivasan et al. [25] performed a direct determination of $k_{14}$ values via a joint optimization of the reactions OH + NO2 → HO2 + NO and HO2 + OH → H2O + O2 (R14) reactions behind reflected shocks using an OH diagnostic. Their recommended rate coefficient expression is $k_{14} = (3.0 \pm 1.8) \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at $T = 1200–1700$ K (solid line connecting two open triangles up)— this $k_{14}$ expression was used throughout this study. This expression is 25% lower than the best fit to their data, but they concluded that it is the best available experimental value for combustion-modeling applications based upon their consideration of other high-temperature data. Rasmussen et al. [51] performed a critical review of all the available data for this reaction as part of the analysis of their high-pressure laminar flow measurements of the CO/H2/O2/NO reaction system. In their temperature range, 600–900 K, there are no experimental measurements of R14. They proposed an expression that is the sum of three three-parameter rate coefficient expressions that does an excellent job of fitting the high-temperature data of Goodings and Hayhurst and Kappel et al., including the sharp dip, as well as the low-temperature data of Keyser. It also passes through the data of Srinivasan et al. (filled triangle up). Their expression is a factor of 3 lower than ours on average in the range of mutual overlap. Sivaramakrishnan et al. [52] derived an expression for $k_{14}$ indirectly as a result of their high pressure single pulse shock tube study of the oxidation of diluted CO mixtures doped with small quantities of H2. Their expression is given as the sum of five three-parameter rate coefficient expressions over the temperature range 298–1600 K that produces a narrow dip at $T = 1400$ K (dot–dashed line). They argue that this expression is needed to match the CO and CO2 concentration data at their highest temperatures, 1400–1500 K, and their highest pressures, 256 and 450 atm. The dip in their expression at 1400 K is shifted upward in temperature with respect to Hippler et al. (1250 K) and Kappel et al. (1000 K); it is also neither as deep nor as sharp. The Sivaramakrishnan et al. and our $k_{14}$ expressions agree within 10% over the temperature range of mutual overlap. Their expression decreases with temperature in this range, and they are mostly above us with the expressions crossing ca. 1075 K (the upper third of our temperature range). The most recent theoretical study of R14 has been performed by Gonzalez et al. [53,54] (see references therein for a thorough review of previous theoretical work), where they determined ab initio geometries at the HF and MP2 levels and energies at the MP4 level. They are careful to detail the problems with calculating the surfaces at this level of theory. For the singlet reaction surface, they determined that this pathway would be unimportant near room temperature, their area of focus, due to the 63.6 K mol$^{-1}$ barrier heights. For the triplet reaction surface, they do predict that reaction can occur at room temperature. However, they cautioned that their calculations were not sufficiently adequate to quantitatively determine the coupling between the nonplanar surfaces at the MP2 level. Given that caveat, they moved forward to predict a rate coefficient expression using vibrational/rotational adiabatic theory. Their calculated temperature dependence of $k_{14}$ values was then combined with the room temperature experimental data to produce the best estimate of the $k_{14}$ expression given as $k_{14} = 4.3 \times 10^{13} (T/300)^{-0.21} \exp(57 K/T)$ cm$^3$ mol$^{-1}$ s$^{-1}$ at $T = 298–1100$ K (dashed line).

The direct experimental evidence has produced three effectively straight line rate coefficient expressions, each within the error bars of the others, all lying within the range $(2–3) \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ and overlapping around 1250 K. It cannot be overemphasized that none of them shows any evidence of the narrow “V” behavior. The indirect experimental evidence has produced a very complex expression but one that is within 10% of the Srinivasan et al. expression used in this study around 1000 K and well within the error bars of all three direct studies. The available theoretical evidence, while carefully qualified by its authors, gives a very mildly curved rate coefficient expression that passes through the error bars of the direct experiments. Combining the published data given in the three studies with the low-temperature data of Keyser and the high-temperature data of Goodings and Hayhurst would strongly suggest the same sort of broad and shallow bowl-shaped appearance that is the signature of the HO2 self-reaction. Clearly, the advances made by the theoretical community during the intervening decades since the most recent computational study would help to elucidate the nature of this important reaction and guide future experiments.
DETERMINATION OF THE RATE COEFFICIENTS OF THE $\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$ REACTION

Figure 8 (a) Conversion yield of S(IV) to S(VI), calculated at a constant density condition ($\rho = 16.0$ μmol cm$^{-3}$) using the Table 2 mechanism as functions of temperature and reaction (residence) time. Symbols are for reaction time: triangle, 1 ms; square, 2 ms; circle, 5 ms. (b) Conversion yield calculated at a constant pressure condition ($P = 1$ atm). Symbols are as in panel a.

Among our mixtures, 1.0% SO$_2$ gave the highest conversion yield of S(IV) to S(VI), i.e., SO$_2$ to SO$_3$ (the contribution to S(VI) from HOSO$_2$ and H$_2$SO$_4$ being negligible at our experimental conditions). Thus we computed the maximum conversion, $[\text{SO}_3]_{\text{max}}/[\text{SO}_2]_0$, in the SO$_2$/H$_2$/O$_2$/Ar = 1.0/0.5/10.0/88.5 mixture using the Table 2 mechanism as functions of temperature and reaction time (residence time) at a constant density ($\rho = 16.0$ μmol cm$^{-3}$) and a constant pressure ($P = 1$ atm) flow conditions. As seen in Figs. 8a and 8b, for either flow condition, maximum conversion occurs at temperatures around 1200 K and slightly increases with reaction time. The maximum conversion yield is ca. 3.5% and 2.5% for the constant density and constant pressure flow condition, respectively. Flux analyses show that SO$_3$ is mainly produced by R$_{31}$ ($\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$). At low temperatures, there is some contribution from R$_{56}$ ($\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}$). The major consumption channels are R$_{34}$ (SO$_3$ + H $\rightarrow$ SO$_2$ + OH), R$_{35}$ (SO$_3$ + O $\rightarrow$ SO$_2$ + O$_2$) and R$_{-52}$ (HOSO$_2$ + O$_2$ $\leftrightarrow$ SO$_3$ + HO$_2$). It is noteworthy that the maximum conversion occurs at temperatures above that of the maximum $k_{31,0}$ values. Undoubtedly, this is because that the conversion yield is dependent upon not only the rate coefficient values of $k_{31,0}$ and $k_{56}$ but also the availability (concentrations) of H, O, and HO$_2$ in the system.

The unusual behavior in the rate coefficients of the spin-forbidden title reaction, R$_{31}$ ($\text{SO}_2(X^1A_1') + \text{O}(^3\text{P}) + \text{M} \rightarrow \text{SO}_3(X^1A_1') + \text{M}$) has been rationalized by Astholz et al. [19] in terms of the potential barrier arising from triplet–singlet crossing of the SO$_3$ complex formed ($\text{SO}_3(3A^+_1) \rightarrow \text{SO}_3(1A^+_1)$) and decrease of the collision efficiency ($\beta_c$) with temperature in stabilizing the collision complex, i.e., the rate coefficients are controlled by the competition between the barrier crossing and the stabilization of the complex. Astholz et al. used $V_0 = 13.8 \pm 4$ kJ mol$^{-1}$ and a factor of 4 decrease of $\beta_c$ from 300 K ($\beta_c = 0.4$) to 2000 K ($\beta_c = 0.1$), whereas Naidoo et al. [22] used 15.9 kJ mol$^{-1}$ in their calculations. However, for understanding of this reaction in more detail, high-level quantum calculations are beneficial to elucidate the nature of the triplet SO$_3$ potential curve—it may be repulsive around the crossing—and the coupling between triplet–singlet states. Recognizing the triplet–singlet crossing actually occurs along the seam at the lowest crossing point, it is highly desirable to calculate the potential energy surface (PES) around the crossing point. If the seam crossing probability is energy dependent, a new temperature effect could be introduced.

We now consider the possibility of SO$_3$ formation by a molecular reaction channel involving the relatively abundant amounts of SO$_2$ and O$_2$ available in the hot oxidizing environment of the high-pressure section of an aircraft engine. The most efficient version of the reaction would be the direct oxidation of SO$_2$ to SO$_3$ in the form of R$_{58}$ ($\text{SO}_2 + \text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{SO}_3$).
Such a reaction may be viewed as proceeding, similar to \( \text{S}_2\text{O}_6 \) reactions [55], via \( \text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_4 + \text{SO}_2 \rightarrow \text{O}_2 \text{S}_\text{OSO}_2 \rightarrow \text{SO}_3 + \text{SO}_3 \) or \( \text{SO}_2 + \text{SO}_2 + \text{O}_2 \rightarrow \text{O}_2 \text{S}_\text{OSO}_2 \rightarrow \text{SO}_3 + \text{SO}_3 \). Compared to \( \text{S}_2\text{O}_6 \) fragmentation reactions, either reaction shown above does not have an available donor electron for easy fragmentation to \( \text{SO}_3 \). Also a large number of rearrangements for intermediate formation would be required, so that high reaction rate coefficient values are not expected. Nevertheless, we can assign a maximum value to the rate coefficient of \( \text{R}_{58} \) at our test conditions based upon the observed flatness of the absorption profile preceding the exponential rise due to chain reaction. The proposed molecular reaction would start at time zero and be evidenced by a steady decrease in the initial absorption, entirely due to \( \text{SO}_2 \), as expected for a zero and be evidenced by a steady decrease in the initial absorption, entirely due to \( \text{SO}_2 \), as expected for a zero.

It is apparent that \( \text{R}_{58} \) affects the characteristic times and conversion yields for high [\( \text{SO}_2 \)]_0-containing mixtures. The extent of the effect is not large: As shown above, agreement in the characteristic times with and without \( \text{R}_{58} \) could be achieved by increasing \( k_{31,0} \) value within its error limit. And the absolute values of the conversion yield with \( \text{R}_{58} \) are still small. Lack of experimental or theoretical evidence for \( \text{R}_{58} \) and the reasons given above permitted us to exclude \( \text{R}_{58} \) in the Table 2 mechanism.

**CONCLUSIONS**

Thermochemical and structural data for HOSO, HSO_2, and HOSO_2 were critically reviewed, and the thermodynamic data for these species were estimated and NASA-type polynomial coefficients were established (Table 1 in the Supporting Information).

The title reaction was studied in the perturbed systems where the well-studied \( \text{H}_2\text{O}_2/\text{Ar} \) system was perturbed with small amounts of \( \text{SO}_2 \). A comprehensive reaction mechanism for \( \text{SO}_2/\text{H}_2\text{O}_2/\text{Ar} \) system was assembled (Table 2 in the Supporting Information). Optimum \( \text{SO}_2/\text{H}_2\text{O}_2/\text{Ar} \) mixture compositions and experimental conditions were obtained via a series of sensitivity analyses. Shock tube experiments were performed using an OH laser absorption spectroscopic technique. The measured absorption coefficients of...
SO$_2$ at $\lambda_0 = 310.032$ nm (air) and $T = 300$–1150 K are

$$\varepsilon_\lambda(\text{SO}_2) = 1.3 \times 10^5 \exp(-180 K / T) \text{ cm}^2 \text{ mol}^{-1}$$

The experimental results were analyzed via computer simulations, in that the rate coefficients of $R_{31}$ (SO$_2$ + O + M $\rightarrow$ SO$_3$ + M) and $R_{36}$ (SO$_2$ + HO$_2$ $\rightarrow$ SO$_3$ + OH) were simultaneously optimized against the experimental reaction characteristics (characteristic times). The rate coefficient expressions are

$$k_{31} = 1.36 \times 10^{11} \exp(-3420 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at $T = 970$–1150 K with estimated error limits of $\pm$ 30%, and

$$k_{31,0} / [\text{Ar}] = 2.9 \times 10^{15} T^{-6.0} \exp(-4780 K/T)$$

$$+ 6.1 \times 10^{24} T^{-3.0} \exp(-1980 K/T)$$

$\times \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

at $T = 300$–2500 K and $\rho_{\text{ave}} = 16.2 \mu\text{mol cm}^{-3}$ with error limits of 26%.

The calculated maximum S(IV) to S(VI) conversion yield, ca. 3.5% and 2.5% for the constant density and constant pressure flow condition, respectively, occurred at rather higher temperatures ($\sim 1200$ K) than lower where the maximum $k_{31,0}$ value is located ($\sim 800$ K). We found that the conversion yield is controlled by SO$_3$ production flux mainly through $R_{31}$ (SO$_2$ + O + M $\rightarrow$ SO$_3$ + M) and, to the lesser extent, through $R_{36}$ (SO$_2$ + HO$_2$ $\rightarrow$ SO$_3$ + OH) and consumption flux through the reactions with H (R$_{34}$, SO$_3$ + H $\rightarrow$ SO$_2$ + OH), O (R$_{53}$, SO$_3$ + O $\rightarrow$ SO$_2$ + O$_2$) and HO$_2$ (R$_{52}$, HOSO$_2$ + O$_2$ $\rightarrow$ SO$_3$ + HO$_2$) as well.

All experiments and computations in this study were performed at the NASA Glenn Research Center in Brook Park, Ohio.

**BIBLIOGRAPHY**