Sulfur Oxidation and Contrail Precursor Chemistry

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Abstract

Sulfuric acid (H_2SO_4), formed in commercial aircraft operations via fuel-S \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4, plays an important role in the formation of contrails. It is believed that the first step occurs inside the combustor, the second step in the engine exit nozzle, and the third step in the exhaust plume. Thus, measurements of the sulfur oxidation rates are critical to the understanding of contrail formation. Field measurements of contrails formed behind commercial aircraft indicate that significantly greater conversion of fuel-bound sulfur to sulfate aerosol occurs than can be explained by our current knowledge of contrail physics and chemistry. The conversion of sulfur from S(IV) to S(VI) oxidation state, required for sulfate aerosol formation, is thermodynamically favored for the conditions that exist within jet engines but is kinetically disfavored. The principal reaction pathway is O+SO_2+M \rightarrow SO_3+M. The rates of this reaction have never been measured in the temperature and pressure regimes available to aircraft operation.

In the first year (FY02) of this project, we performed a series of experiments to elucidate the rate information for the O+SO_2+M \rightarrow SO_3+M reaction. The work performed is described below, following the proposed work plan. Because we used the H_2/O_2 system for an O-atom source and rate coefficients were obtained via computer simulation, construction of a reaction mechanism and either recalculation or estimation of thermodynamic properties of H_2SO_4 species are described first.

Reaction Mechanism of the SO_2/H_2/O_2 System

For the H_2/O_2 system, we adopted a reaction mechanism of 20 elementary reactions that has been tested extensively at various conditions. Then, additional reactions for SO_2 oxidation by H_3O_y species in the SO_2/H_2/O_2 system and their rate coefficients were critically reviewed and a reaction mechanism of 19 reactions for this system was composed. A comprehensive but truncated reaction mechanism for the SO_2/H_2/O_2 system is given in Table I of Appendix A. A brief review of important rate coefficients is given in the Discussion section.

Thermodynamic data of relevant species of H_2/O_2/SO_2 System

In computer modeling using a reaction mechanism for practical combustion systems or for extracting rate coefficient information, reliable thermodynamic properties (\Delta H (298.15 K), H(T), S(T), G(T), C_p(T)) of the reacting species are necessary. Recently the value of D^{0}_{298.15}(H-OH)=118.81 \pm 0.07 \text{ kcal mol}^{-1} was measured by Ruscic et al. From this new bond dissociation
enthalpy of H$_2$O, $\Delta_{f}H^\circ(298.15 \text{ K})$ of OH=8.91 ± 0.07 kcal mol$^{-1}$ has been reestablished and the differences from the widely used value of Gurvich et al.$^5$ or JANAF$^6$ have been discussed in great detail.$^4$ Previously we had used 9.41 ± 0.05 kcal mol$^{-1}$ for $\Delta_{f}H^\circ(298.15 \text{ K})$ of OH, based upon the recommendation of Gurvich et al. The difference of 0.49 kcal mol$^{-1}$ from the new value of Ruscic et al. is quite large. Considering the uncertainty in obtaining $D^0(\text{O-H})$ by Gurvich et al. from spectroscopic measurements and an unambiguous direct measurement of $D^0(\text{H-OH})$ by a photoionization experiment by Ruscic et al., we adopted the new $\Delta_{f}H^\circ(298.15 \text{ K})$ of OH=8.91 ± 0.07 kcal mol$^{-1}$ of Ruscic et al. and readjusted all thermodynamic properties of OH accordingly. The thermodynamic properties of other species in the H$_2$/O$_2$ system are unchanged.

While thermodynamic properties of species in the H$_2$/O$_2$ system are more or less well established, those of H$_2$SO$_2$ species (HS, HSO, HOSO, HSO$_2$, and HOSO$_2$) are virtually unknown. Using available experimental data and theoretical calculations, thermodynamic data of these species are estimated. Details are described in Appendix B.

**Selection of Experimental Conditions via Sensitivity Analysis**

In determining rate coefficients of the reaction

$$O + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M} \quad (R21)$$

an O-atom source must be found. In this work O-atoms were produced from H$_2$/O$_2$ reactions. I.e., the H$_2$/O$_2$ reaction system was perturbed with a small amount of SO$_2$. The major reactions that consume and produce O-atoms in the H$_2$/O$_2$ system are, respectively

$$O + \text{H}_2 \rightarrow \text{OH} + \text{H} \quad (R2)$$

and

$$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad (R1)$$

Hence, in the SO$_2$/H$_2$/O$_2$ system, R21 would compete with R2. If we use rich H$_2$/O$_2$ mixtures, O-atoms would be consumed mainly by R2. This restricts us to consider lean H$_2$/O$_2$ mixtures only. Figure 1 shows $R=|\log([i]_p/[i]_0)|$ as a function of equivalence ratio $\phi$ of H$_2$/O$_2$ mixtures, where $i$=O, OH, and H. Small R values indicate production of a large amount of species $i$. Obviously, lean mixtures are more suitable than rich mixtures in this regard. However, at given jet engine exhaust nozzle temperatures (900 to 1200 K), the following reaction will compete with R1 for H-atoms

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (R9)$$

Thus, it is also desirable to select reaction mixtures that produce a less amount of H-atoms.

Sensitivity analyses for an elapsed time to reach half of the absorption maximum ($\tau_{50}$) were performed using the following baseline H$_2$/O$_2$ mixture (without SO$_2$) with various levels of sensitization by SO$_2$ at T=1000 K, $p = 15.0$ μmol cm$^{-3}$; 0.5% H$_2$/10.0% O$_2$ ($\phi = 0.025$), 0.15%–3.0% SO$_2$/0.5% H$_2$/10.0% O$_2$ ($\phi = 0.025$)/Ar. In the baseline mixture, R9, R1, R2, and R3 show sensitivities for $\tau_{50}$ in that order. Figure 2(a) shows a sensitivity spectra for 0.5% H$_2$/10.0%
Adding 0.15%, 0.25%, and 0.5% SO$_2$ to a 0.5% H$_2$/10.0% O$_2$/Ar mixture produced only a trace level of sensitivity for R21. The sensitivity of R21 was found to be dependent upon the SO$_2$/H$_2$ ratio in the mixture. Furthermore, as the SO$_2$/H$_2$ ratio is increased, the sensitivity of R21 and R9 is notably increased together with the relative importance of R21 over R9. Figure 2(b) shows a sensitivity spectra for the 2.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/88.5% Ar mixture. Based upon this sensitivity analyses we selected the following three mixtures: for the baseline experiments, 0.5% H$_2$/10.0% O$_2$/89.5% Ar; for sensitization experiments, 2.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/87.5% Ar and 3.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/86.5% Ar.

Experimental

The shock tube-laser absorption technique is described in detail elsewhere. Briefly, the test section of the shock tube was routinely pumped below 3 $\mu$Torr by a Varian V60 Turbopump. The combined leak and out-gassing rate of the test section was 5 $\mu$Torr min$^{-1}$. All shocks were initiated within 1 minute of admitting the test gas mixture. Shock velocities were measured using 4 flush-mounted 113A21 PCB Piezotronics pressure transducers coupled to Phillips PM6666 programmable counter-timers. The last pressure transducer was axially coincident with the center of the observation windows, 12.7 mm distant from the end wall. 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 in solving the standard relationships for the reflected shock properties, assuming full vibrational relaxation and no chemical reaction at the shock front. The computed reflected shock properties were corrected for boundary layer interaction effects using the similar method of Michael and Sutherland.

The combined OH and SO$_2$ absorption profiles were measured at 310.032 nm (in air), corresponding to the P1(5) line of the (0,0) band of the OH A$^2\Sigma^+ \leftarrow \chi^2\Pi$ transition—at this wavelength, SO$_2$ also shows some absorption. The 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. Intracavity frequency doubling was achieved with an angle tuned LiIO$_3$ crystal. For the detection of OH radicals and SO$_2$ molecules, a triple beam scheme was employed; probe beam, intensity reference beam and a wavelength reference beam (through a burner-stabilized methane/air flame). The detector was a combination of interference filter (310 nm with 10 nm fwhm)—PMT(Thorn EMI9924QB)—high speed buffer/amplifier. The S/N of the "probe beam-intensity reference beam" was usually better than 100. The overall electronic time constant determined for the entire PMT-buffer-cable system was less than 0.5 $\mu$s.

H$_2$/O$_2$/Ar and SO$_2$/H$_2$/O$_2$/Ar test gas mixtures were prepared manometrically and allowed to stand for 48 hr before use. Gases were used without further purification. The stated purities were: H$_2$, 99.9995% (MG Industries, Scientific Grade); O$_2$, 99.998% (MG Industries, Scientific Grade); SO$_2$ (anhydrous), 99.98 wt.% (MG Industries, Scientific Grade); Ar, 99.9999% (MG Industries, Sputtering Grade).
Results

Because 310 nm UV light is also absorbed by SO$_2$ molecules, it is necessary to determine absorption coefficients of SO$_2$ ($\varepsilon_{\text{e}}$(SO$_2$)). The values of $\varepsilon_{\text{e}}$(SO$_2$) determined are shown in Figure 3. A least squares fit to the data gives an expression

$$\varepsilon_{\text{e}}$(SO$_2$) = 2.16 \times 10^5 \exp(-765.0 \text{ K}/T) \text{ cm}^2 \text{ mol}^{-1}$

Evaluation of a characteristic time ($\tau_{50}$) in the baseline experiments was done in the usual way. However, in the sensitization experiments, because there have always been long delays for sensible absorption signal rise (OH production), initial absorption by SO$_2$ immediately after the reflected shock was subtracted from the total absorption signal and $\tau_{50}$ values were evaluated as in the baseline experiments. Figure 4 shows $\tau_{50}$ values measured for the baseline mixture, 0.5% H$_2$/10.0% O$_2$/89.5% Ar, and for the sensitization mixtures, 2.0, 3.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/86.5, 87.5% Ar. Throughout all of the experiments, densities were kept nearly the same between the baseline and sensitization experiments.

As seen in the figure, the $\tau_{50}$ values of sensitization mixtures are longer at low temperatures and increase with SO$_2$/H$_2$ ratio. At temperatures above 1200 K, the differences disappear between the two levels of sensitization.

Discussion

H$_2$/O$_2$ System

Because we generated O-atoms from the H$_2$/O$_2$ reaction system, a complete understanding of the H$_2$/O$_2$ reaction chemistry is a prerequisite for rate coefficient determination of the O+SO$_2$+M $\rightarrow$ SO$_3$+M reaction (R21). There are three key reactions in H$_2$/O$_2$ chemistry: chain branching H+O$_2$ $\rightarrow$ OH+O (R1), chain propagating O+H$_2$ $\rightarrow$ OH+H (R2) and chain terminating H+O$_2$+M $\rightarrow$ HO$_2$+M (R9). A comprehensive review of these three reactions is given here.

(a) Chain Branching H+O$_2$ $\rightarrow$ OH+O  \hspace{1cm} (R1)

Figure A(1) in Appendix A shows the rate coefficient expressions reported recently. The current widely used rate coefficient expressions are those of Du and Hessler, Baulch et al. and GRI. Du and Hessler obtained their $k_1$ expression, $k_1=9.76 \times 10^{13} \exp(-7474 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (960 to 5300 K) by combining their rate coefficient measurements at very high temperatures (3450 to 5300 K) with the results of Masten et al. (1450 to 3370 K), Shin and Michael (1103 to 2055 K) and Pirraglia et al. (962 to 1705 K). The compilation by Baulch et al. gives an expression identical to that of Du and Hessler. Pirraglia et al. combined their relatively low temperature results with the high temperature data of Frank and Just (1693 to 2577 K) and reported $k_1=1.9 \times 10^{14} \exp(-8272 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (962 to 2577 K). The GRI expression, $k_1=2.65 \times 10^{16} T^{-0.6707} \exp(-8575 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (300 to 3000 K) is a fit to the combined high temperature results of Yu et al. (which, in turn, the results of Yuan et al. and of Masten et al.) and the somewhat low rate coefficients of Pirraglia et al. (especially low temperature data) with the room temperature data compiled by Demore et al. Previously, we (GRC) reported $k_1=7.13 \times 10^{13}$
exp\((-6957 \text{ K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}\) (1050 to 2500 K) based upon OH radical growth rate that eliminates any H-atom producing contaminant effect.

Since the $\Delta_fH^0(298.15 \text{ K})$ value of OH has been remeasured (see above), virtually all $k_1$ values must be reexamined. Hence, with the new thermodata of OH we reevaluated our existing data. The rederived expression is $k_1=3.74 \times 10^{15} T^{-0.467} \exp(-7758 K/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Extrapolation of this expression to room temperature gives about a factor of 2.5 higher than the value recommended by Demore et al. As seen, this expression has a negative temperature dependence of the A-factor. The temperature dependence of the A-factor has been given by several authors: -0.907 by Schott,$^{20}$ -0.927 by Yuan et al.$^{18}$ -0.7 by Masten et al.$^{13}$ and -0.816 and +0.500 by theoretical calculations of Miller$^{21}$ and Miller and Garrett$^{22}$ respectively.

Due to the difficulty in performing experiments at relatively low temperatures, no group has extended their temperature range wide enough to obtain a consistent set of experimental data. Instead, the results of Pirraglia et al. (960 to 1200 K) have been extensively used for the fit of the $k_1$ expression by various authors. Recently we measured OH absorption profiles in various H$_2$/O$_2$ systems at temperatures down to 950 K and up to 3500 K. We are currently analyzing these results. A combination of these new results with the previous ones reported in this laboratory$^1$ will form a consistent set of data over the widest temperature range (950 to 3500 K) ever employed by a single laboratory. Based upon this data set, a new rate coefficient expression will be produced and the validity of its temperature dependence of the A-factor and the extrapolated value to room temperature will be tested.

(b) Chain Propagating $\text{O+H}_2 \rightarrow \text{OH+H}$ (R2)

SO$_2$ molecules in the SO$_2$/H$_2$/O$_2$ system are consumed mainly by $\text{O+SO}_2+M \rightarrow \text{SO}_3+M$ (R21). The chain propagating reaction R2 inherently competes with R21 for O-atoms. Figure A(2) in Appendix A shows representative $k_2$ expressions published. Previously we presented $k_2=1.87 \times 10^{14} \exp(-6854 K/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ (1420 to 2430 K). Reevaluation of OH absorption data obtained for $k_2$ evaluation with the new OH thermodata yielded $k_2=2.04 \times 10^{14} \exp(-6972 K/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. The differences between the old and new expressions are less than 3.5% in the given temperature range, the new expression being higher with temperature. One notable expression for $k_2$ is that of Sutherland et al.$^{23}$ Sutherland et al. reported a non-Arrhenius type rate coefficient expression, $k_2=5.06 \times 10^4 T^{-2.67} \exp(-3480 K/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ by combining their results of flash photolysis-shock tube work (880 to 2495 K) and the flash photolysis-resonance fluorescence technique (504 to 923 K) with the low temperature data of Presser and Gordon (297 to 471 K).$^{24}$ Our $k_2$ expression represents the high temperature data (880 to 2495 K) of Sutherland et al. quite well. However, due to the nature of a non-Arrhenius type curve fit, the extended temperature fit of Sutherland et al. over-predicts their results at temperatures around 950 K and above 2500 K. Therefore, in our temperature range (950 to 1100 K), extrapolation of our expression should be more appropriate.

(c) Chain Terminating $\text{H+O}_2+M \rightarrow \text{HO}_2+M$ (R9)

The chain terminating R9 reaction plays a governing role for ignition and flame characteristics at high pressure and especially at low temperature conditions (see sensitivity spectra in Figure 2).
For this reason, many authors\textsuperscript{1,25-42} investigated this reaction to determine rate coefficients. Experimental data and $k_9$ expressions are plotted in Figure A(3). At room temperature a consensus value has been established.\textsuperscript{33} However, in the temperature range of combustion ($T>750$ K), the scatter of rate coefficient data is very large. For example, at $T=\sim1000$ K, there is a factor of 3 scatter in the $k_9$ values. We performed a series of experiments to determine the $k_9$ values in the temperature range of 950 to 1150 K using a shock tube—laser OH absorption spectroscopy technique in H\textsubscript{2}/O\textsubscript{2} system. Experimental data were fit to $k_9=3.75\times10^{17} T^{-0.7}$ cm\textsuperscript{6} mol\textsuperscript{-2} s\textsuperscript{-1}. Our values positioned somewhat in the middle of the data scatter at $T=\sim1000$ K. Extrapolation of our $k_9$ expression also well represents the data of Hsu et al.\textsuperscript{32} at temperatures between 296 K and 640 K and the room temperature result of Carleton et al.\textsuperscript{33}

SO\textsubscript{2}/H\textsubscript{2}/O\textsubscript{2} System

As mentioned before, sensitization was used with 2\% and 3\% SO\textsubscript{2}. Sensitization resulted in a remarkable increase of $\tau_{50}$ (see Figure 4). The effect of sensitization level on $\tau_{50}$ becomes more noticeable as temperature decreases, but it diminishes as temperature increases. Nevertheless, this increase of $\tau_{50}$ is due to depletion of O-atoms by R21, so the H-atom production rate by R2 is reduced. This, in turn, reduces the branching rate of R1.

The rate coefficients of R21 are derived by computer simulation using the Table I mechanism in Appendix A. In computer simulation, at each experimental condition, only the starting $k_{21}$ value was varied so as to minimize the difference between the computed and experimental $\tau_{50}$. Figure 5 shows the provisional $k_{21}$ values obtained in this work. R21 is a pressure (density) dependent reaction. For this type of reaction, it is usual to use two rate coefficient expressions at the extreme conditions, a low pressure limit $k_{21,0}$ and a high pressure limit $k_{21,\infty}$. The rate coefficients in the fall-off region are then obtained by interpolation using these two extreme rate coefficients. Obviously R21 is in the fall-off region in our experimental conditions. Therefore we computed the starting $k_{21}$ value using the $k_{21,0}$, $k_{21,\infty}$, and a simple Lindemann-Hinshelwood interpolation formula

$$k_{21}/k_{21,\infty}=(k_{21,0}/k_{21,\infty})(1+k_{21,0}/k_{21,\infty})=x/(1+x)$$

where $x=k_{21,0}/k_{21,\infty}$.

For $k_{21,\infty}$ and $k_{21,0}$, we used the expressions given by Mueller et al.,\textsuperscript{43} $k_{21,\infty}=9.2\times10^{10} \exp(-1200 K/T)$ cm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} and by Troe,\textsuperscript{44} $k_{21,0}=4.0\times10^{28} T^{-4.0} \exp(-2650 K/T)$ cm\textsuperscript{6} mol\textsuperscript{-2} s\textsuperscript{-1}, respectively. The $k_{21,\infty}$ of Mueller et al. is the only high pressure limit expression ever reported. Several measurements of $k_{21,0}$ have been reported either at high temperatures (1435 to 2500 K) or at low temperatures (<430 K).\textsuperscript{19,47-50} In the temperature range of our interest (900 to 1100 K), no experimental measurements are available. The $k_{21,0}$ expression shown above was made by Troe by fitting the low and high temperature data. Note that at $T<500$ K, the rate coefficient value increases with temperature (positive activation energy), while at $T>500$ K, it decreases with temperature (negative activation energy). Our provisional $k_{21}$ values obtained in the fall-off region are about a factor of 2 to 3 higher than the theoretical calculations using the equation shown above.
Conclusions

Existing data for H$_2$/O$_2$ and SO$_2$/H$_2$/O$_2$ chemistry were critically reviewed and a reaction mechanism was assembled (Table I in Appendix A). Optimum H$_2$/O$_2$/Ar and SO$_2$/H$_2$/O$_2$/Ar mixture compositions and experimental conditions were established via a series of sensitivity analyses. Shock tube experiments were performed using OH laser absorption spectroscopy for the H$_2$/O$_2$/Ar mixtures to examine baseline behavior and for the SO$_2$/H$_2$/O$_2$/Ar mixtures to determine $k_{21}$ values for the conditions selected. The experimental results were analyzed via computer simulations and the provisional rate coefficients of R21 were obtained. The provisional rate coefficients of R21 ($k_{21}$ values) obtained in our experimental conditions are about a factor of 2 to 3 higher than the theoretical calculations using the expressions of $k_{21,0}$, $k_{21,\infty}$, and the parameters of the interpolation formula in Table I of Appendix A. Additionally, temperature dependent absorption coefficients of SO$_2$ at OH absorption wavelength were measured.

Measured or calculated thermochemical and structural data for HS, HSO, HOSO, HSO$_2$, and HOSO$_2$ species were critically reviewed and thermodynamic data for these species were obtained (Appendix B).

Future Work

In the second year of this project, besides what is contained in the project plan, the collision efficiency effect of SO$_2$ the on pressure dependent reactions, R9 and R21, and the interpolation formula used in determination of $k_{21}$ will be examined further. In pressure dependent reactions, reaction rates increase with pressure. The increase of collision efficiencies of collision partners is equivalent to an increase of density (pressure). If one assigns a high collision efficiency of SO$_2$ to R9 and R21, their reaction rates and $\tau_{50}$ values will increase and result in a lowering of $k_{21}$ values. (Currently we used a collision efficiency of 1 for SO$_2$ for R9 and R21.) Experiments at various densities will also be performed to optimize the falloff parameters. Data analysis will be completed for the experiments performed to determine the rate coefficients of the chain branching reaction R1.

References

Figure 1.—Absolute ratios of the peak concentrations of O- and H-atoms and OH radicals to the initial concentration of \( \text{H}_2 \) in the \( \text{H}_2/\text{O}_2/\text{Ar} \) mixtures as a function of the mixture equivalence ratio, \( \phi \), evaluated at \( T=1000 \text{ K} \) and \( \rho=15.0 \mu \text{mol cm}^{-3} \). Large values indicate the suppression of peak concentrations.

Figure 2(a).—Sensitivity spectra for \( \tau_{50} \) of the baseline mixture, 0.5\% \( \text{H}_2 \)/10.0\% \( \text{O}_2 \)/89.5\% \( \text{Ar} \). \( T=1000 \text{ K} \) and \( \rho=15.0 \mu \text{mol cm}^{-3} \).
2.0% SO₂, 0.5% H₂, 10.0% O₂, 87.5% Ar
T=1000 K, \( p = 15.0 \ \mu \text{mol cm}^{-3} \)

![Chemical Reactions Diagram]

**Figure 2(b).**—Sensitivity spectra for \( \tau_{59} \) of the 2.0% SO₂/0.5% H₂/10.0% O₂/87.5% Ar. T=1000 K and \( p = 15.0 \ \mu \text{mol cm}^{-3} \).

Absorption Coefficients of SO₂ at 310 nm
\[
\varepsilon_{4}(\text{SO}_2) = 2.16 \times 10^5 \exp(-765.0 \ K/T) \ \text{cm}^2 \ \text{mol}^{-1}
\]

![Absorption Coefficients Graph]

**Figure 3.**—Base ‘e’ absorption coefficients of SO₂ at 310 nm. The least squares fit expression is \( \varepsilon_{4}(\text{SO}_2) = 2.16 \times 10^5 \exp(-765.0/T) \) cm² mol⁻¹.
Figure 4.—Measured $\tau_{50}$ values of the baseline mixture, 0.5% H$_2$/10.0% O$_2$/89.5% Ar and two sensitization mixtures, 2.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/87.5% Ar and 3.0% SO$_2$/0.5% H$_2$/10.0% O$_2$/86.5% Ar.

\[ \text{O} + \text{SO}_2 (+M) = \text{SO}_3 (+M) \]

Figure 5.—The falloff $k_{21}$ values of the reaction R21, O+SO$_2$(+M) $\rightarrow$ SO$_3$(+M).
## Appendix A

### Table I.—Reaction Mechanism

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<td>0</td>
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<td>22</td>
<td>SO₂+OH+M=HOSO₂+M</td>
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<tr>
<td>23</td>
<td>HOSO+M=SO₂+H+M</td>
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<td>∞</td>
<td>∞</td>
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<tr>
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<td></td>
<td>e</td>
</tr>
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<td>SO₂+OH=SO₃+H</td>
<td>4.9E+02</td>
<td>2.69</td>
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Table I.—Reaction Mechanism\(^a\) (continued)

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<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>Θ</th>
<th>Note</th>
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<td>25 (\text{SO}+\text{O}+\text{M}=\text{SO}_2+\text{M})</td>
<td>(3.2\times10^{13})</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
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<td>(2.9\times10^{24})</td>
<td>-2.9</td>
<td>0.0</td>
<td>c</td>
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<tr>
<td></td>
<td>0.550</td>
<td>0.0</td>
<td>(\infty)</td>
<td>d</td>
</tr>
<tr>
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<td>Ar,1.00/ O(_2),1.33/ H(_2)O,10.0/</td>
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<td></td>
<td>e</td>
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<tr>
<td>26 (\text{SO}_3+\text{O}=\text{SO}_2+\text{O}_2)</td>
<td>(4.1\times10^{11})</td>
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<tr>
<td>27 (\text{SO}_3+\text{SO}=\text{SO}_2+\text{SO}_2)</td>
<td>(1.0\times10^{12})</td>
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<td>2013</td>
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<tr>
<td>28 (\text{SO}_3+\text{H}_2\text{O}=\text{H}_2\text{SO}_4)</td>
<td>(7.23\times10^{08})</td>
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<td></td>
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<td>29 (\text{SO}+\text{OH}+\text{M}=\text{HOSO}+\text{M})</td>
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<td></td>
<td>e</td>
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<tr>
<td>30 (\text{SO}+\text{OH}=\text{SO}_2+\text{H})</td>
<td>(5.2\times10^{13})</td>
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<td>31 (\text{SO}+\text{O}_2=\text{SO}_2+\text{O})</td>
<td>(6.2\times10^{03})</td>
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<td>32 (\text{HOSO}+\text{H}=\text{SO}+\text{H}_2\text{O})</td>
<td>(6.3\times10^{-10})</td>
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<tr>
<td>33 (\text{HOSO}+\text{OH}=\text{SO}_2+\text{H}_2\text{O})</td>
<td>(1.0\times10^{12})</td>
<td>0.0</td>
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<tr>
<td>34 (\text{HOSO}+\text{O}_2=\text{SO}_2+\text{HO}_2)</td>
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<td>35 (\text{HOSO}_2+\text{M}=\text{SO}_3+\text{H}+\text{M})</td>
<td>(3.2\times10^{16})</td>
<td>-0.81</td>
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<td>e</td>
</tr>
<tr>
<td>36 (\text{HOSO}_2+\text{H}=\text{SO}_2+\text{H}_2\text{O})</td>
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<tr>
<td>37 (\text{HOSO}_2+\text{O}=\text{SO}_3+\text{OH})</td>
<td>(5.0\times10^{12})</td>
<td>0.0</td>
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<td></td>
</tr>
<tr>
<td>38 (\text{HOSO}_2+\text{OH}=\text{SO}_3+\text{H}_2\text{O})</td>
<td>(1.0\times10^{12})</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39 (\text{HOSO}_2+\text{O}_2=\text{SO}_3+\text{HO}_2)</td>
<td>(7.8\times10^{11})</td>
<td>0.0</td>
<td>330</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Rate coefficients are in the form, \(k = AT^n \exp(-\Theta/T)\). Units are K, cm, mol, and s.

\(^b\) \(k_\infty\)

\(^c\) \(k_0\)

\(^d\) Falloff correction parameters.

\(^e\) Collision efficiencies.

\(^f\) Duplicated reaction.
Figure A1(a).—Rate coefficients of R1, H+O₂ → OH+O.

Figure A1(b).—Exploded plot of the Figure A1(a) for the temperature range of 950 to 1250 K.
Figure A2(a).—Rate coefficients of R2, O+H₂ → OH+H.

Figure A2(b).—Exploded plot of the Figure A2(a) for the temperature range of 830 to 1250 K.
H + O₂ + M = HO₂ + M

![Figure A3](image1)

Figure A3.—Rate coefficients of R9, H+O₂+M → HO₂+M.

O + SO₂ + M = SO₃ + M

![Figure A4(a)](image2)

Figure A4(a).—Low pressure limit rate coefficients ($k_{21,0}$) of R21, O+SO₂+M → SO₃+M.
Figure A4(b).—High pressure limit rate coefficients $(k_{21,\infty})$ of R21, $O + SO_2 \rightarrow SO_3$.

References

1. Hwang, S. M.; De Witt, K. J.; Rabinowitz, M. J.; This work 2002


Appendix B

Hydroxsulfonyl (HOSO₂)

Δᵣᴴ₀(298.15 K) = -391.2 kJ mol⁻¹

Vibrational Frequencies (cm⁻¹) and Degeneracies:

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Degeneracy</th>
</tr>
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<tbody>
<tr>
<td>3539.8</td>
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</tr>
<tr>
<td>1309.2</td>
<td>1</td>
</tr>
<tr>
<td>1296.2</td>
<td>1</td>
</tr>
<tr>
<td>1097.2</td>
<td>1</td>
</tr>
<tr>
<td>759.3</td>
<td>1</td>
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<tr>
<td>544</td>
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<tr>
<td>491</td>
<td>1</td>
</tr>
<tr>
<td>437</td>
<td>1</td>
</tr>
<tr>
<td>252</td>
<td>1</td>
</tr>
</tbody>
</table>

- torsion

Ground State Quantum Weight: 2 (²A')

Point Group: C₁

External Rotational Symmetry Number: σ = 1

Bond Length (angstrom):

r(S–O₁) = 1.612
r(S–O₂) = 1.444
r(S–O₃) = 1.436
r(O₁–H) = 0.967

Bond Angle (degree):

θ(S–O₁–H) = 107.2
θ(O₁–S–O₂) = 108.4
θ(O₁–S–O₃) = 106.0
τ(O₂–S–O₁–H) = 26.1
τ(O₃–S–O₁–H) = 161.1

Product of the Moment of Inertia: Iₓ, Iᵧ, Iz = 1.473 x 10⁻¹¹⁴ g cm³

Reduced Moment of Inertia: Iᵣ = 1.405 x 10⁻⁴⁰ g cm²

Internal Rotational Symmetry Number: n = 2

Barrier to Internal Rotation: V₀ = 9.5 kJ mol⁻¹

Enthalpy of Formation

From Benson's estimate for D₀²₉₈.₁₅(HO–SO₂) = 36 ± 3 kcal mol⁻¹, 1 Δᵣᴴ₀(298.15 K) = -409 kJ mol⁻¹ (-98 kcal mol⁻¹) was derived. This value of Δᵣᴴ₀(298.15 K) gives Δᵣᴴ₀(298.15 K) = 6 kcal mol⁻¹ for the reaction, HOSO₂ + O₂ → HO₂ + SO₃.

Margitan's rate coefficients measurement for the above reaction put an upper limit for the reaction endothermicity, Δᵣᴴ₀(298.15 K) ≤ 2 kcal mol⁻¹ (D₀²₉₈.₁₅(HO–SO₂) ≤ 32 kcal mol⁻¹).²

Gleason and Howard set a limit on the endothermicity of the reaction (1), Δᵣᴴ₀(298.15 K) ≤ 3
kcal mol$^{-1}$,\(^3\) which places a lower limit of $\Delta_fH^0(298.15\,\text{K}) \geq -395.4\,\text{kJ mol}^{-1}$ ($\geq -94.5\,\text{kcal mol}^{-1}$). Here we adopted Margitan's value of $\Delta_fH^0(298.15\,\text{K}) = 2\,\text{kcal mol}^{-1}$, which gives $\Delta_fH^0(298.15\,\text{K}) = -391.2\,\text{kJ mol}^{-1}$ ($-93.5\,\text{kcal mol}^{-1}$).

Heat Capacity and Entropy

The molecular structure of HOSO$_2$ was taken from the results of MP2 level calculation with cc-pVQZ basis set by Majumdar et al.\(^4\) The reduced moment of inertia, $I_r$, for the hindered internal rotation was calculated by assuming HOSO$_2$ is essentially a cis form.\(^4\) This assumption sets the internal rotational symmetry number, $n=2$. The rotational barrier was calculated using the equation, \(2\pi c \omega / n = (V_D / 2I_r)^{1/2}\), where $c$ is the speed of light and $\omega$ is the torsional frequency, 252 cm$^{-1}$.

Hashimoto et al. measured four vibrational frequencies of HOSO$_2$ in an argon matrix at 11 K.\(^5\) Nagase et al. confirmed the four vibrational frequencies using the same method of Hashimoto et al. and also calculated the geometry and vibrational frequencies at the unrestricted HF level with the 3–21G(*) basis set.\(^6\) Later, Kuo et al. measured vibrational frequencies of HOSO$_2$ in the argon matrix at 12 K.\(^7\) The four frequencies reported by Hashimoto et al. and Nagase et al. were again confirmed. An additional frequency corresponding to HOS bend at 1296.2 cm$^{-1}$ was measured.\(^7\) Here, we took five experimental frequencies (3539.8, 1309.2, 1296.2, 1097.2, 759.3) of Hashimoto et al., Nagase et al. and Kuo et al. and four computed frequencies (544, 491, 437, 252) of Nagase et al. for the derivation of heat capacity and entropy.

References

Hydroxysulfinyl (HOSO)

\[ \Delta_f H^0(0 \text{ K}) = -237.4 \pm 10 \text{ kJ mol}^{-1} \]

Vibrational Frequencies (cm\(^{-1}\)) and Degeneracies:

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Degeneracy</th>
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<td>1</td>
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<td>1073</td>
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<td>764</td>
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</tr>
<tr>
<td>343</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>1 – torsion</td>
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</table>

Ground State Quantum Weight: 2 (\(^2A^\)\)
Point Group: C\(_s\)
External Rotational Symmetry Number: \(\sigma = 1\)
Bond Length (angstrom):
- \(r(\text{S-O1}) = 1.661\)
- \(r(\text{S-O2}) = 1.482\)
- \(r(\text{O1-H}) = 0.983\)
Bond Angle (degree):
- \(\theta (\text{S-O1-H}) = 106.9\)
- \(\theta (\text{O1-S-O2}) = 109.8\)
Product of the Moment of Inertia: \(I_x I_y I_z = 2.539 \times 10^{-115} \text{ g cm}^6\)
Reduced Moment of Inertia: \(I_r = 1.585 \times 10^{-40} \text{ g cm}^2\)
Internal Rotational Symmetry Number: \(n = 2\)
Barrier to Internal Rotation: \(V_0 = 7.9 \text{ kJ mol}^{-1}\)

Enthalpy of Formation, Heat Capacity and Entropy

The enthalpy of formation of HOSO and its geometry and vibrational frequencies have not been measured experimentally. The most reliable information is from theoretical calculations of Laakso et al.\(^1\) Laakso et al. optimized geometry and vibrational frequencies at the MP2=FULL/6–31G* level. Energies were obtained with G2 theory. For the enthalpy of formation, the changes in G2 energy for the reaction, HOSO → OH+SO (\(\Delta_f H^0(0 \text{ K}) = 280.8 \text{ kJ mol}^{-1}\)) was obtained and then \(\Delta_f H^0(0 \text{ K})\) of HOSO was derived using the measured \(\Delta_f H^0(0 \text{ K})\) values of OH and SO in the JANAF tables.\(^2\) Laakso et al. proved the reliability of their calculation by comparing their G2 level \(\Delta_f H^0(0 \text{ K})\) for the reaction, HS+O\(_2\) → OH+SO with that of the experimental value from the JANAF tables. Only a small difference in the reaction enthalpy, \(\Delta_f H^0(0 \text{ K}) = 0.3 \text{ kJ mol}^{-1}\) resulted. However, a recent measurement and quantum calculation of \(D^0(\text{OH, 0 K})\)\(^3\) gave \(\Delta_f H^0(\text{OH, 0 K}) = 8.85 \pm 0.07 \text{ kcal mol}^{-1}\) \((37.03 \pm 0.29 \text{ kJ mol}^{-1})\). Thus the calculated \(\Delta_f H^0(0 \text{ K})\) value for HS+O\(_2\) → OH+SO reaction by Laakso et al. would be different from 0.3 \text{ kJ mol}^{-1}. Since \(D^0(0 \text{ K})\) for HOSO dissociation from Laakso et al. is the only available value, we adopted this value and calculated the enthalpy of formation of HOSO using the newly measured \(\Delta_f H^0\) of OH and NASA value of SO at 0 K. The recommended enthalpy of formation of HOSO is \(\Delta_f H^0(\text{HOSO, 0 K}) = \Delta_f H^0(\text{OH, 0 K}) + \Delta_f H^0(\text{SO, 0 K})\)
279.2 = 37.03 + 4.7143 - 279.2 kJ mol$^{-1}$ = $-237.4 \pm 10 \text{ kJ mol}^{-1} (-56.7 \pm 2.4 \text{ kcal mol}^{-1})$ with an error bound given by Laakso et al.

For the derivation of heat capacity and entropy we took the molecular geometry and vibrational frequencies of Laakso et al. The barrier to internal rotation ($V_0 = 7.9 \text{ kJ mol}^{-1}$) was directly taken from Laakso et al.'s computed G2 barrier for cis to trans transition of HOSO.

References


Sulfinyl (HSO$_2$)

$\Delta_H^0 (298.15 \text{ K}) = -178.2 \pm 8.4 \text{ kJ mol}^{-1}$

Vibrational Frequencies (cm$^{-1}$) and Degeneracies:

2269 (1)
1600 (1)
1128 (1)
1065 (1)
810 (1)
431 (1)

Ground State Quantum Weight: 2 ($^2A'$)

Point Group: $C_i$

External Rotational Symmetry Number: $\sigma = 1$

Bond Length (angstrom):

$r(S-O1) = 1.447$
$r(S-O2) = 1.447$
$r(H-O2) = 1.381$

Bond Angle (degree):

$\theta (O1-S-O2) = 123.2$
$\theta (H-S-O2) = 105.6$
$\theta (H-S-O2(01)) = 121.1$

Product of the Moment of Inertia: $l_x l_y l_z = 1.485 \times 10^{-115} \text{ g cm}^2$
Enthalpy of Formation

Benson’s estimate for the enthalpy of formation of HSO$_2$ was $\Delta_f^o H(298.15 \text{ K}) = -177.4 \pm 16.7 \text{ kJ mol}^{-1}$ (42.4 $\pm$ 4 kcal mol$^{-1}$). The corresponding $D^o_{298.15}(\text{H}+\text{SO}_2)=41 \text{ kcal mol}^{-1}$ was compatible with the fast rate coefficients measured in flame studies at $T>1600 \text{ K}$ for the three-body recombination reaction (H+SO$_2$+M=HSO$_2$+M).\textsuperscript{1} Boyd et al. performed ab initio calculations for HSO$_2$ at the HF/STO-3G* level.\textsuperscript{2} Using the calculated $D^o_{\text{H}+\text{SO}_2}=142.1 \text{ kJ mol}^{-1}$ and the $\Delta_f^o H(0 \text{ K})$ values of H and SO$_2$ in the JANAF tables,\textsuperscript{3} $\Delta_f^o H(0 \text{ K})=-220.4 \text{ kJ mol}^{-1}$ (52.7 kcal mol$^{-1}$) was derived for HSO$_2$. Laakso et al. optimized geometry and vibrational frequencies for HSO$_2$ at the MP2=FULL/6-31G* level.\textsuperscript{4} Energies were obtained with G2 theory. For the enthalpy of formation, the change in G2 energy for the reaction, HSO$_2$ → H+SO$_2$ ($\Delta_f^o H(0 \text{ K})=56.8 \pm 10 \text{ kJ mol}^{-1}$) was obtained and then $\Delta_f^o H(0 \text{ K})$ of HSO$_2$ was derived using the measured $\Delta_f^o H(0 \text{ K})$ values of H and SO$_2$ in the JANAF tables. $\Delta_f^o H(298.15 \text{ K})$ of HSO$_2$=-141.4 $\pm$ 10 kJ mol$^{-1}$ (33.8 $\pm$ 2.4 kcal mol$^{-1}$) was recommended. Laakso et al. proved the reliability of their calculation by comparing their G2 level $\Delta_f^o H(0 \text{ K})$ for the reaction, HS+O$_2$ → H+SO$_2$ with that of the experimental value from the JANAF tables. Considering the error limit in the G2 $\Delta_f^o H(0 \text{ K})$ value, the difference in the reaction enthalpy, $\Delta_r H(0 \text{ K})=9.4 \text{ kJ mol}^{-1}$ was considered excellent. Recently, Denis and Ventura investigated the enthalpy of formation of XSO$_2$, X=H, CH$_3$ using the B3LYP and B3PW91 methods with very large basis sets up to cc-pV6Z.\textsuperscript{5} The enthalpy of formation of HSO$_2$, $\Delta_f^o H(298.15 \text{ K})=-178.2 \pm 8.4 \text{ kJ mol}^{-1}$ (42.6 $\pm$ 2 kcal mol$^{-1}$) resulting from B3PW91 method was recommended. We adopted the enthalpy of formation of Denis and Ventura, $\Delta_f^o H(298.15 \text{ K})=-178.2 \pm 8.4 \text{ kJ mol}^{-1}$ for HSO$_2$.

Heat Capacity and Entropy

Vibrational frequencies of HSO$_2$ have not been measured experimentally and only one theoretical calculation is available. For the derivation of heat capacity and entropy we used the vibrational frequencies calculated at the MP2=FULL/6–31G* level by Laakso et al.\textsuperscript{4} The molecular geometry was taken from the theoretical calculation using the B3PW91 method with cc-pV6Z basis set by Denis and Ventura.\textsuperscript{5}

References

Mercapto (SH)

$\Delta_{t}H^\theta(0 \text{ K})=133.03 \text{ kJ mol}^{-1}$

Enthalpy of Formation

The current JANAF recommendations for $\Delta_{t}H^\theta(0 \text{ K})=136.49 \pm 5.0 \text{ kJ mol}^{-1}$ and $\Delta_{t}H^\theta(298.15 \text{ K})=139.33 \pm 5.0 \text{ kJ mol}^{-1}$ are based on the measurements of HS ionization potential and the appearance potential of HS$^+$ from photoionization of H$_2$S. The previous NASA recommendation for $\Delta_{t}H^\theta(298.15 \text{ K})$ was also 139.33 kJ mol$^{-1}$. Continetti and Lee$^3$ performed photodissociation of H$_2$S at 193.3 nm using H-atom photofragment-translational spectroscopy with mass spectroscopic detection. They found $D_{\theta}(\text{H--S})=349.27 \pm 2.89 \text{ kJ mol}^{-1}$ (83.48 $\pm 0.69$ kcal mol$^{-1}$) in the secondary photodissociation of HS radicals, formed in the primary H$_2$S photodissociation experiments. Nicovitch et al.$^4$ measured the forward and reverse reaction rate coefficients of Br($^2P_{3/2}$)+H$_2$S=HS+HBr over the temperature range of 319 to 431 K. Using both the "second law method" and the "third law method," an average value of $\Delta_{t}H^\theta$ at a given temperature was obtained, then the values of $\Delta_{t}H(0 \text{ K})$ and $\Delta_{t}H^\theta(298.15 \text{ K})$ were calculated by applying heat capacity corrections from data in JANAF tables for Br, H$_2$S, HS and HBr. The reported values for the enthalpy of formation and the bond dissociation energy are $\Delta_{t}H^\theta(0 \text{ K})=142.55 \pm 3.01 \text{ kJ mol}^{-1}$ (34.07 $\pm 0.72$ kcal mol$^{-1}$), $\Delta_{t}H^\theta(298.15 \text{ K})=143.01 \pm 2.85 \text{ kJ mol}^{-1}$ (34.18 $\pm 0.68$ kcal mol$^{-1}$) and $D_{\theta}(\text{H--S})=348.23 \pm 3.26 \text{ kJ mol}^{-1}$ (83.23 $\pm 0.78$ kcal mol$^{-1}$), $D_{\theta}(298.15 \text{ K(\text{H--S})})=351.96 \pm 3.10$ kJ mol$^{-1}$ (84.12 $\pm 0.74$ kcal mol$^{-1}$), respectively. We adopted the bond dissociation energy of Continetti and Lee, $D_{\theta}(\text{H--S})=349.27 \pm 2.89 \text{ kJ mol}^{-1}$ (83.48 $\pm 0.69$ kcal mol$^{-1}$) and derived $\Delta_{t}H^\theta(0 \text{ K})=\Delta_{t}H^\theta(0 \text{ S})+\Delta_{t}H^\theta(\text{H})-349.27=270.5126+211.8014-349.27=133.03 \text{ kJ mol}^{-1}$ (31.80 kcal mol$^{-1}$).

References


Hydrogen Sulfur Oxide (HSO)

$\Delta_{t}H^\theta(0 \text{ K})=3.8 \text{ kJ mol}^{-1}$

Vibrational Frequencies (cm$^{-1}$) and Degeneracies:
2480 (1)
1164 (1)
1026 (1)

NASA/CR—2003-212293
Ground State Quantum Weight: 2 (2A''
Point Group: C1
External Rotational Symmetry Number: s=1
Bond Length (angstrom):
\( r(S-O) = 1.494 \)
\( r(S-H) = 1.389 \)
Bond Angle (degree):
\( \theta (H-S-O) = 106.6 \)
Product of the Moment of Inertia: \( I_xI_yI_z = 5.028 \times 10^{-117} \) g\(^3\) cm\(^6\)

Enthalpy of Formation

Schurath et al.\(^1\) measured the chemiluminescence spectrum of the \( X^2A'' \leftarrow A^2A' \) transition of HSO and DSO. The \( \Delta H^0 (298.15 \text{ K}) \) for the reaction \( HS + O_3 \rightarrow HSO + O_2 \) (HS+O3 \rightarrow HSO*+O2, HSO* \rightarrow HSO) was estimated using the observed highest level of HS–O vibration, \( v = 7 \), which corresponds to 19149 cm\(^{-1}\) (54.74 kcal mol\(^{-1}\)). Using \( \Delta_s H^0 (298.15 \text{ K}) \leq 54.74 \) kcal mol\(^{-1}\) and the values of the enthalpy of formation of HS and O\(_3\) available, Schurath et al.\(^1\) set an upper limit of \( \Delta H^0 (298.15 \text{ K}) \leq 14.9 \) kcal mol\(^{-1}\). White and Gardiner\(^2\) reanalyzed the results of Schurath et al. and presented 12.2 \( \Delta H^0 (298.15 \text{ K}) \leq 14.1 \) kcal mol\(^{-1}\). Benson's estimate\(^3\) was \( \Delta H^0 (298.15 \text{ K}) \approx -5 \pm 4 \) kcal mol\(^{-1}\). Slagle et al.\(^4\) suggested \( \Delta H^0 (298.15 \text{ K}) \approx -3 \) kcal mol\(^{-1}\), based upon their kinetic work on the reaction \( O(3P) + H_2S \rightarrow HSO + H \). Davidson et al.\(^5\) studied the reactive scattering of O atoms with H\(_2\)S molecules using a crossed molecular beam mass spectrometric detection of HSO radicals. The value of the enthalpy of formation obtained was \( \Delta H^0 (298.15 \text{ K}) \approx -1.4 \pm 1.9 \) kcal mol\(^{-1}\) (\(-6 \pm 8 \text{ kJ mol}^{-1}\)). Balucani et al.\(^6\) determined \( \Delta H^0 (0 \text{ K}) \approx -0.9 \pm 0.7 \) kcal mol\(^{-1}\) (\(-3.8 \pm 2.9 \text{ kJ mol}^{-1}\)) from the analysis of high resolution crossed beam reactive scattering experiments on the reaction \( O(3P) + H_2S \rightarrow HSO + H \). Here we took Balucani et al.'s value \( \Delta H^0 (0 \text{ K}) \approx -0.9 \pm 0.7 \) kcal mol\(^{-1}\) (\(-3.8 \pm 2.9 \text{ kJ mol}^{-1}\)).

Heat Capacity and Entropy

The molecular geometries and vibrational frequencies of HSO and DSO radicals were determined by Schurath et al.,\(^1\) Kakimoto et al.,\(^7\) and Ohashi et al.\(^8\) Following the measurements of Schurath et al., Kakimoto et al. and Ohashi et al. observed the doppler-limited dye laser excitation spectra of the \( A^2A'(003) \leftarrow X^2A''(000) \) vibronic transition of HSO and DSO. Here we took the structural parameters of HSO from those of Ohashi et al. and Kakimoto et al., instead of the "best fit" values used in vibronic band contour synthesis by Schurath et al. The product of moment of inertia, \( I_xI_yI_z \), was calculated using the directly measured rotational constants, \( B_x, B_y \), and \( B_z \) of Ohashi et al.

The three ground state (2A'') vibrational frequencies, H–SO stretching (\( \omega_1 \)), H–S–O bending (\( \omega_2 \)), and HS–O stretching (\( \omega_3 \)), were presented by Schurath et al.\(^1\). From \( v' = 3 \) progression, \( \omega_3 \) (1013 cm\(^{-1}\)) was measured. The quantity \( \omega_2 \) was estimated (1063 cm\(^{-1}\)) using the measured bending frequency of DSO and the isotope factor. For \( \omega_1 \), the recommended—S–H group frequency (2570 cm\(^{-1}\))\(^9\) was assigned. However, the harmonic force field analysis by Ohashi et al.\(^8\) yielded \( \omega_2 = 1164 \text{ cm}^{-1} \) and \( \omega_3 = 1026 \text{ cm}^{-1} \). The force constant, \( k_1 \), was estimated by applying
Badger's rule using the bond lengths and force constants of HS($^2\Pi$) and HS($^2\Sigma^+$) as references. From this estimated force constant $\omega_1=2271 \text{ cm}^{-1}$ was calculated.

Here we adopted $\omega_2=1164 \text{ cm}^{-1}$ and $\omega_3=1026 \text{ cm}^{-1}$ of Ohashi et al. We believe the $\omega_1$ value from—S–H group frequency is too high and that of Ohashi et al. is too low. Therefore we estimated the $\omega_1$ value in the following manner: Using the known H–O and H–OO stretching frequencies the force constant change from H–O to H–OO was calculated. For H–OO stretching the force constant was reduced by 15% from that of H–O. Since HS and HSO are isovalent radicals of HO and HOO, respectively, we calculated the force constant of H–SO by applying the same 15% reduction to the H–S force constant. The $\omega_1$ value was calculated to be $\omega_1=(1/2 \pi c)(k_1/m_H)^{1/2}=2480 \text{ cm}^{-1}$, where $c$ is the speed of light and $m_H$ is the mass of the terminal H atom.

References

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**Abstract**: Sulfuric acid ($H_2SO_4$), formed in commercial aircraft operations via fuel—$S \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$, plays an important role in the formation of contrails. It is believed that the first step occurs inside the combustor, the second step in the engine exit nozzle, and the third step in the exhaust plume. Thus, measurements of the sulfur oxidation rates are critical to the understanding of contrail formation. Field measurements of contrails formed behind commercial aircraft indicate that significantly greater conversion of fuel-bound sulfur to sulfate aerosol occurs than can be explained by our current knowledge of contrail physics and chemistry. The conversion of sulfur from $S(IV)$ to $S(VI)$ oxidation state, required for sulfate aerosol formation, is thermodynamically favored for the conditions that exist within jet engines but is kinetically disfavored. The principal reaction pathway is $O+SO_2+M \rightarrow SO_3+M$. The rates of this reaction have never been measured in the temperature and pressure regimes available to aircraft operation. In the first year (FY02) of this project, we performed a series of experiments to elucidate the rate information for the $O+SO_2+M \rightarrow SO_3+M$ reaction. The work performed is described below, following the proposed work plan. Because we used the $H_2/O_2$ system for an O-atom source and rate coefficients were obtained via computer simulation, construction of a reaction mechanism and either recalculation or estimation of thermodynamic properties of $H_xSO_y$ species are described first.