Mechanistic Studies of the OH-Initiated Oxidation of CS₂ in the Presence of O₂

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We have investigated production of carbon- and sulfur-containing end products of the OH-initiated oxidation of CS_2 in the presence of O_2 , an important atmospheric chemical reaction which is known to proceed via the following three elementary steps: OH + CS₂ + M \leftrightarrow CS₂OH + M; CS₂OH + O₂ \rightarrow products. Two different experimental approaches were employed. In one set of experiments (CP-FTIR studies) continuous photolysis of CH₃ONO/NO/CS₂/Air mixtures at 298 K and 700-Torr total pressure was combined with product detection by Fourier transform infrared spectroscopy; these studies measured moles of products formed per mole of CS₂ consumed. In a second set of experiments (LFP-TDLAS studies) 248-nm laser flash photolysis of H₂O₂/ $CS_2/N_2O/He/O_2$ mixtures at 298 K and 25–100-Torr total pressure was combined with product detection by time-resolved tunable diode laser absorption spectroscopy; in this case, the quantity measured was moles of product formed per mole of OH consumed. In both studies OCS and CO are observed as carbon-containing products with yields of 0.83 ± 0.08 and 0.16 ± 0.03 , respectively; uncertainties represent estimates of absolute accuracy at the 95% confidence level. The LFP-TDLAS experiments demonstrate that the above yields represent "prompt" product formation; i.e., OCS and CO are formed either as primary products of the $CS_2OH + O_2$ reaction or as products of a fast $(k > 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ secondary reaction of a primary product with O2. The CP-FTIR experiments show that, under atmospheric conditions, SO2 is produced with a yield of 1.15 \pm 0.10; in this case, the LFP-TDLAS results strongly suggest that only about three-fourths of the SO₂ is formed as a prompt product, with the remainder generated via slow reaction of SO (generated as a prompt product of the $CS_2OH + O_2$ reaction) with O_2 . The implications of our results for understanding the detailed mechanism of the very complex $CS_2OH + O_2$ reaction are discussed, as are their implications for understanding the atmospheric cycles of CS_2 and OCS.

Introduction

Because of its importance in atmospheric chemistry and its chemical complexity, the $OH + CS_2$ reaction has been studied extensively.¹⁻²³ Early direct studies of OH + CS₂ kinetics, carried out with millisecond time resolution and in the absence of O_{2} ,⁴⁻⁷ suggested that OH was unreactive toward CS₂. However, CW photolysis-end product analysis studies^{3,8-10} provided evidence that the $OH + CS_2$ reaction rate increases from a very low value in the absence of O₂ to a value greater than 1×10^{-12} cm³ molecule⁻¹ s⁻¹ in 1 atm of air at room temperature (296 \pm 4 K). Jones et al.⁸ were the first to suggest that OH reacts with CS₂ to form a weakly bound adduct which, under atmospheric conditions, reacts with O2 in competition with decomposition back to reactants:

$$OH + CS_2 + M \rightarrow CS_2OH + M$$
(1)

$$CS_2OH + M \rightarrow OH + CS_2 + M \qquad (-1)$$

$$CS_2OH + O_2 \rightarrow products$$
 (2)

Direct kinetic studies coupling OH production by laser flash

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photolysis with OH detection by pulsed laser induced fluorescence^{12,13,16,17,21,22} have verified the above mechanism and shown that the adduct is bound by 10-11 kcal mol⁻¹,^{12,17,21} that the adduct lifetime toward unimolecular decomposition in 1 atm of N₂ at 298 K is 4.5 μ s,¹² and that K₂(298 K) \approx 3 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹.^{12,17,21} Experimental¹⁴ and theoretical^{20,23} studies suggest that although the HO-CS₂ isomer is about 25 kcal mol⁻¹ more stable than the SCS-OH isomer,^{20,23} it is the SCS-OH isomer which is produced under atmospheric conditions^{14,23} due to the existence of a large potential energy barrier inhibiting OH addition to the carbon atom.23

The importance of the $OH + CS_2$ reaction in atmospheric chemistry stems from its role as a source for OCS, the most ubiquitous sulfur compound in the atmosphere and a potentially important contributor to the stratospheric sulfate aerosol layer.24,25 Hence, the OCS yield from reaction 2 is a parameter of great interest to atmospheric chemists. Reaction 2 is also a process of considerable fundamental chemical interest. There are well over 20 sets of products which are energetically feasible, and calculation of potential energy barriers for various possible pathways is becoming a theoretically tractable problem as computing power continues to improve; hence, high-quality product yield data could potentially help to refine theoretical procedures for calculating potential energy surfaces.

A number of studies of the products of the $OH + CS_2 + O_2$ reaction are reported in the literature,^{8-10,16,18,19} and the results are somewhat conflicting. End product analysis studies by Jones et al.^{8,9} and Barnes et al.¹⁰ suggest that OCS and SO₂ are formed with unit yield. However, similar studies by Becker et al.¹⁶ and Iver et al.¹⁹ suggest that $CO_{16,19}^{16,19}$ and CO_{2}^{19} as well as OCS are formed as carbon-containing products of reaction 2. Becker et al.¹⁶ have pointed out that rate coefficients for the $OH + CS_2 +$ O₂ reaction obtained by direct observation of OH decay

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kinetics^{12,16} are lower than some of those evaluated by following CS_2 removal or OCS formation in continuous photolysis experiments;^{10,16} they interpret this observation as suggesting that OH is "regenerated" from reaction 2 with a yield of about 30%; i.e., they suggest that an important reaction channel is not observable in experiments which directly follow OH decay kinetics. The only study where reaction products have been observed in "real time" is that of Lovejoy et al.¹⁸ These investigators employed the discharge flow technique with laser magnetic resonance and chemical ionization mass spectrometric detection and the laser flash photolysis technique with pulsed laser-induced fluorescence detection. Their principal findings were that HO₂ and SO₂ are produced with unit yield and that a majority of SO₂ is produced "directly", i.e., not via an SO intermediate; they also found that HSO is not produced in significant yield from reaction 2.

In this paper we report the results of an investigation where two different experimental methods were employed to investigate the mechanism of the OH + CS₂ + O₂ reaction. In one set of experiments (carried out at Ford Motor Co.), continuous photolysis (CP) of suitable reaction mixtures was coupled with product detection by Fourier transform infrared spectroscopy (FTIR). In a separate study (carried out at Georgia Tech), laser flash photolysis (LFP) of $H_2O_2/CS_2/O_2/He/N_2O$ mixtures was coupled with product detection by time-resolved tunable diode laser absorption spectroscopy (TDLAS). The two studies are in quantitative agreement concerning the yields of carbon-containing products. In addition, temporal profiles for product formation observed in the LFP-TDLAS studies allow some interesting inferences to be made concerning the possible production of OH, S, and/or SO as products of reaction 2.

Experimental Section

All studies were conducted at room temperature, 297 ± 4 K. As mentioned above, two different types of experiments were carried out. The CP-FTIR and LFP-TDLAS experiments are discussed separately below.

The CP-FTIR Experiments. The apparatus and experimental techniques employed in the CP-FTIR studies are described in detail elsewhere.^{26,27} All experiments were performed in a 140-L Pyrex reactor surrounded by 22 fluorescent blacklamps (GE F15T8BL). Hydroxyl radicals were generated by photolysis of methyl nitrite in air at 700-Torr total pressure with and without added NO:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
 (3)

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
 (4)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (5)

$$OH + CS_2 \rightarrow \rightarrow products$$
 (6)

The loss of CS₂ and the formation of products were monitored using Fourier transform infrared spectroscopy. The path length for the analyzing infrared beam was 26.6 m. The spectrometer was operated at a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32–64 co-added interferograms. Reference spectra were obtained by expanding known volumes of the reference material into the long-path length cell. Products were identified and quantified by fitting reference spectra of the pure compounds to the observed product spectra using integrated absorption features over the following wavelength ranges (in cm⁻¹); ¹²CS₂, 1490–1560; ¹³CS₂, 1450–1520; O¹²CS, 2025–2090; O¹³CS, 1975– 2025; SO₂, 1320–1390; ¹³CO, 2000–2200; ¹³CO₂, 2200–2350. We do not have a calibrated reference spectrum of O¹³CS. Instead, the integrated absorption over the region 1975–2025 cm⁻¹ in the product spectrum was compared to the corresponding feature at 2025–2090 cm⁻¹ in our calibrated O¹²CS reference. The isotopic shift factor for this IR feature was 1.026. The intensity of this feature is not expected to be significantly different (<5%) in the two isotopically labeled OCS molecules.

Initial concentrations of the gas mixtures were 3–25 mTorr of ${}^{12}CS_2$ or 3–20 mTorr of ${}^{13}CS_2$, 11–64 mTorr of CH₃ONO, and 0–15 mTorr of NO. CH₃ONO was synthesized at Ford.²⁶ All other reagents were purchased from commercial vendors at purities of >99% and used without further purification. Experiments were performed in 700 Torr of ultrapure synthetic air.

The LFP-TDLAS Experiments. A schematic diagram of the LFP-TDLAS apparatus is shown in Figure 1. The reaction cell was a Pyrex cylinder 25 mm in diameter and 118 cm in length with angled calcium fluoride windows attached to the ends using high vacuum epoxy (Torr Seal). Calcium fluoride flats coated for IR transmission and UV reflection combined and separated the 248-nm photolysis beam and the infrared probe beam, which made two passes through the reaction cell. Care was taken to ensure that the UV beam completely enclosed the probe beam throughout the length of the reaction cell. Probe frequencies for OCS, CO, and SO₂ were 2070.860, 2115.629, and 1347.002 cm⁻¹, respectively, as listed in the ATMOS data base.²⁸

Hydroxyl radicals were produced by 248-nm laser flash photolysis of H₂O₂. A Lambda Physik Model 200 EMG KrF excimer laser served as the photolytic light source. The photolysis laser could deliver up to 8×10^{17} photons per pulse at a repetition rate of up to 10 Hz; the pulse width was 20 ns. A 20-mm-diameter aperture selected the central, most intense, and most spatially uniform portion of the photolysis beam. The fluence in the reaction cell was typically 30 mJ cm⁻², although it varied by \sim 15% down the length of the cell due to beam divergence. The laser fluence for each shot was monitored by two silicon photodiodes (positioned near the two ends of the reaction cell) which sampled small fractions of the beam reflected off uncoated quartz plates. Corning 7-54 filters and Teflon diffusers were employed to obtain photodiode signals which varied linearly as a function of laser power. The photodiode outputs were monitored on separate channels of a gated charge integrator (GCI). Absolute calibration was achieved by comparison of GCI readings from the "entrance" photodiode with laser powers measured by a Scientech disk calorimeter positioned at the center of the reaction cell. (The central section of the reaction cell could be removed for this measurement.) The absolute calibration was further confirmed by measuring the amount of CO generated from phosgene photolysis:

$$Cl_2CO + h\nu (248 \text{ nm}) \rightarrow 2Cl + CO$$
 (7)

The CO yield from phosgene photolysis (known to be unity²⁹) was measured periodically during the course of this investigation and was always found to lie in the range 0.95-1.05; the estimated accuracy of the measurements is $\pm 10\%$. Because the excimer laser would not run reliably at the low repetition rate (~0.05 Hz) required to ensure a fresh reaction mixture for each flash, the laser was pulsed at a rate of 0.5 Hz and a mechanical shutter was employed to allow only every tenth flash to traverse the reaction cell. The pulse immediately preceding each photolysis flash was used for background subtraction.

The infrared probe beam was generated by a lead salt diode laser (Laser Analytics) housed in a helium cooled cryostat. The diode output was collimated by a gold-coated off-axis paraboloid and merged with a helium-neon alignment laser using a glass flat coated for infrared reflection and visible transmission. The infrared beam diameter was reduced to 4 mm by two concave gold-coated reflectors configured as a reducing telescope. The "tightened" beam passed through the reaction cell, entered a 0.5-m grating monochromator where a single mode was selected, and then impinged on a HgCdTe infrared detector (the signal detector), which was cooled to 77 K. As a spectral reference, a



Figure 1. Schematic of the LFP-TDLAS apparatus: AMP = amplifier, BPF = band-pass filter, DM = dichroic mirror, IRD = infrared detector, MFM = mass flow meter, PM = photomultiplier, PR = parabolic reflector, Pres. = pressure gauge, REF. = reference, and vib. = vibrational.

small fraction of the probe beam was directed through a sealed 10-cm cell containing about 0.5 Torr of OCS, CO, or SO2 and then monitored by a second HgCdTe infrared detector (the reference detector). The output from the signal detector was amplified and applied to an 8-bit analog-to-digital transient recorder card in an MS-DOS compatible microcomputer. For each laser flash, 4096 samples were recorded. The sampling frequency was adjustable by factors of 2 from 20 MHz to 156.25 kHz. Results from repeated flashes were summed in the computer to obtain an acceptable signal-to-noise ratio; typically, 32 or 64 shots were averaged. The free-running diode laser output frequency was not sufficiently stable to remain centered on a low-pressure absorption feature for the time required to complete a yield measurement (typically 30 min). Hence, the laser frequency was modulated and the reference cell signal was applied to a lock-in amplifier adjusted to provide a feedback signal which kept the laser tuned to the reference absorption.

Since this was our first investigation using the TDLAS detection technique, methodology for signal acquisition evolved during the course of the study. During the early part of the investigation, two different approaches were employed depending on the time scale of interest. In one approach (the triangle waveform (TW) method), a sawtooth current ramp was applied to the diode causing the laser output frequency to be swept approximately linearly back and forth through an absorption feature of interest. A polynomial fit to the base line on either side of each absorption peak was employed to interpolate a base line; then the signal was computed from the peak area. The TW method worked reasonably well for some yield measurements but had two major disadvantages. The time resolution (hundreds of microseconds) was insufficient to allow analysis of product formation rates, and the peak-by-peak method of data analysis was extremely tedious. The second approach for data acquisition used during the early part of the study employed square wave (SW) modulation of the diode current, such that the diode lasing frequency was alternately on and off resonance with an absorption feature. The principal advantages of the SW method compared to the TW method were an order of magnitude improvement in time resolution and a similar improvement in the time required for data analysis. Absolute calibration of data obtained by the SW method was tricky, however, because small drifts in the "on-resonance" frequency could have a significant effect on the observed signal. During the latter part of the study a third approach was developed which combines the advantages of the TW (ease of calibration) and SW (good time resolution, ease of data reduction) methods. In this approach, labeled the second harmonic (SH) method, the diode laser output frequency was varied up and down through an absorption feature of interest via 40-kHz sinusoidal modulation of the drive current. The signal appeared at twice the frequency of the drive current modulation and, therefore, could be retrieved as the second harmonic component from a Fourier analysis of the digitized intensity versus time data.

One major source of noise in TDLAS systems results from mechanical vibrations induced by the compressor in the closed cycle refrigeration system; this mechanical perturbation results in noise spikes in the diode laser output signal which occur approximately every 0.15 s. To alleviate the mechanical noise problem, the approach of Sams and Fried³⁰ was employed. A microphone was attached to the cryostat housing, and the resulting signal was processed to produce a logic-level indication of the compressor phase, i.e., quiet or noisy. A variable delay was adjusted to produce a gate correlated with quiet phases of the refrigerator cycle. This "acoustic" gate was electronically ANDed with the diode laser modulation signal to provide a trigger for the excimer laser and the transient recorder. The laser trigger was delayed relative to the start of the transient record to provide a preflash base line.

All LFP-TDLAS experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was typically 10-15 cm s⁻¹, and as mentioned above, the repetition rate was typically 0.05 Hz; hence, the contents of the reactor were nearly completely replaced between laser shots. The calibration gases OCS, CO, and SO2 were flowed into the reaction cell from 12-L Pyrex bulbs containing dilute mixtures in N_2 , while the buffer gases N_2 and O_2 as well as the vibrational relaxers He and N₂O were flowed directly from their high-pressure storage tanks. Flows of CS_2 and H_2O_2 were established by passing the appropriate buffer gas (N_2 in the case of CS_2 and O_2 in the case of H_2O_2) through bubblers filled with liquid samples. The CS_2 bubbler was positioned on the high-pressure side of the flow control valve while, due to the low vapor pressure of H2O2 and its tendency to decompose on metal surfaces, the hydrogen peroxide bubbler was positioned on the low-pressure side of the flow control valve. All components in the reaction mixtures were premixed before entering the reaction cell. Concentrations of most components in the reaction mixtures were determined from measurements of the appropriate mass flow rates and the total pressure. However, the concentrations of H_2O_2 and CS_2 were measured directly in the slow flow system by UV photometry. The monitoring wavelengths were 228.8 nm for H_2O_2 (Cd pen ray lamp light source) and 313.3 nm for CS_2 (Hg pen ray lamp light source). Absorption cross sections used to convert measured absorbances into concentrations were 1.88×10^{-19} cm² for H₂O₂ at 228.8 nm³¹ and 7.0 \times 10⁻²⁰ cm² for CS₂ at 313.3 nm.¹²

The pure gases used in the LFP-TDLAS experiments had the following stated minimum purities: N_2 and He, 99.999%; O_2 , CO, and N_2O , 99.99%; SO_2 , 99.98%; Cl_2CO , 99.0%; OCS, 97%. N_2 , O_2 , He, CO, and N_2O were used as supplied while SO₂, Cl_2CO , and OCS were degassed at 77 K before use. The liquid CS₂ sample was Aldrich gold label with a stated purity of 99+%; it was transferred into the bubbler under nitrogen atmosphere and was kept shielded from light at all times. The liquid H₂O₂ sample was 70 wt % in H₂O; it was further concentrated by bubbling N₂ through it for several days before experiments were undertaken and constantly during the course of the experiments.

Results

The CP-FTIR Studies. The products of the reaction of OH with CS_2 were investigated by the irradiation of mixtures of ¹²- CS_2 or ${}^{13}CS_2$ with CH_3ONO in air, with and without added NO. Following irradiation, SO₂, OCS, CO, and a trace amount of CO_2 were determined to be products resulting from the reaction of OH radicals with CS₂. The use of isotopically labeled CS_2 enabled the yields of CO and CO_2 from the reaction of OH radicals with CS₂ to be determined free from any interference caused by products of CH₃ONO photolysis. For example, Figure 2A shows a typical spectrum in the region 2020-2100 cm⁻¹ acquired before a 6-min irradiation of a mixture of 20.0 mTorr of ¹³CS₂ and 57 mTorr of CH₃ONO in 700 Torr of air. Figure 2B shows the spectrum after irradiation (35% loss of ${}^{13}CS_2$). Figure 2C is the residual spectrum after features attributable to ¹²CO have been subtracted from Figure 2B. Comparison of Figure 2C with a reference spectrum of 3.90 mTorr of ¹³CO (Figure 2D) shows the formation of 1.09 mTorr of ¹³CO. The product at 2020 cm⁻¹ is 013CS.

Observed product yields are given in Table I and are plotted as a function of the CS₂ loss in Figure 3. There was no discernible difference in the OCS or SO₂ yields from the OH-initiated oxidation of either ¹²CS₂ or ¹³CS₂. Linear least-squares analyses of the data given in Figure 3 give the following observed product yields (errors are 2σ , precision only): O¹²CS, 0.84 ± 0.07; O¹³-CS, 0.83 ± 0.04; SO₂ from ¹²CS₂ + OH, 0.97 ± 0.06; SO₂ from ¹³CS₂ + OH, 1.02 ± 0.04; ¹³CO, 0.15 ± 0.03; ¹³CO₂, 0.012 ± 0.007. All yields are expressed in terms of moles of product observed per mole of CS₂ consumed.

The above product yields are those actually observed. As in all product studies, careful consideration must be given to possible secondary reactions in the chamber. Potential complications in the present work include loss of CS_2 , or any of the observed products, either by photolysis or heterogeneous processes. To



Figure 2. Infrared spectra taken before (A) and after (B) a 6-min irradiation of a mixture of ${}^{13}CS_2$ and ${}^{12}CH_3ONO$ in 700 Torr of air. Figure C is the residual spectrum obtained after subtracting ${}^{12}CO$ features from (B). Figure D is a reference spectrum of ${}^{13}CO$.

test for such, mixtures of CS_2 , OCS, SO_2 , CO, and CO_2 in synthetic air were introduced into the chamber, allowed to sit in the dark for 10 min, then irradiated for 20 min (in the absence of CH₃-ONO). In all cases there was no observable (<2%) loss of these species. To test for a nonphotolytic reaction between CS_2 and CH₃ONO, mixtures of these compounds were allowed to stand in the dark for 20 min; there was no observable loss of either compound.

An additional complication in our experiments is the potential consumption of products by reaction with OH radicals:

$$OH + OCS \rightarrow products$$
 (8)

$$OH + SO_2 + O_2 \xrightarrow{M} \rightarrow SO_3 + HO_2$$
(9)

$$OH + CO + O_2 \xrightarrow{M} HO_2 + CO_2$$
(10)

The rate coefficient for reaction 8, $k_8 = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} ,³¹ is a factor of 500–1000 times slower than k_6 in 700 Torr of air, so reaction 8 will be of negligible importance. The ratelimiting steps in reactions 9 and 10 have rate coefficients in units of cm³ molecule⁻¹ s⁻¹ of 8.6×10^{-13} and 2.3×10^{-13} , respectively (in 700 Torr of air),³¹ which are of comparable magnitude, although somewhat slower than, k_6 ; hence, reactions 9 and 10 may be of significance in the present work. To assess the importance of secondary consumption of SO₂ and CO in the present work, the chemistry in the chamber was simulated using the Acuchem chemical kinetics modeling program³² in conjunction with a chemical mechanism consisting of reactions 6 and 8-10. Four different sets of kinetic parameters were considered. First, the recommended³¹ values for k_9 and k_{10} were used with k_6 varied over the range $(1.2-2.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, which is consistent with experimental values.^{12,16,31} Second, the values of k_9 and k_{10} were varied by $\pm 20\%$ and used in conjunction with k_6 values expected to give the likely maximum and minimum necessary corrections. In all cases, simulations were performed for each individual data point in Figure 2, and the appropriate corrections were calculated. The data were then replotted and

TABLE I: Results of the CP-FTIR Product Studies (All Concentrations in mTorr)

irradiation								
time (min)	[CS ₂] ₀	[CH ₃ ONO] ₀	[NO]₀	Δ [CS ₂]	Δ [OCS]	$\Delta[SO_2]$	Δ[¹³ CO]	Δ [¹³ CO ₂]
				¹² CS ₂				
0	3.22	11.1		-				
1				0.42	0.42	0.42		
2.25				0.63	0.58	0.63		
4				0.82	0.79	0.82		
0	11.93	37.0						
0.75				1.07	0.84	1.05		
2.75				2.15	2.43	2.52		
5.0				3.94	3.18	3.57		
0	24.7	63.5	3.33					
0.75				2.96	2.71	3.15		
2				4.94	4.39	5.15		
3				5.93	4.86	5.57		
				13CS2				
0	17.24	45.3	15.0	2				
10				1.72	1.31	2.00	0.35	nda
0	3.07	12.4						
2				0.74	0.71	0.79	0.12	nd
6				1.07	1.01	1.05	0.19	nd
10				1.26	1.10	1.26	0.25	nd
0	13.8	53.1						
2				3.59	3.14	3.78	0.39	0.030
4				4.14	3.81	4.31	0.55	0.044
7				4.84	4.39	5.25	0.78	0.059
10				6.21	4.90	6.30	1.17	0.12
0	20.0	57.0						
0.75				3.20	2.62	3.26	0.39	nd
1.5				4.00	3.37	4.20	0.51	0.030
3				5.40	4.58	5.57	0.74	0.044
6				7.00	5.80	6.83	1.09	0.056

^a nd: not detected, <0.03 mTorr.



Figure 3. Plot of the observed yields of SO_2 (circles), OCS (triangles), CO (diamonds), and CO₂ (inverted triangles) versus the loss of CS₂ following the irradiation of CS₂/CH₃ONO mixtures. Filled symbols were obtained using ¹³CS₂; open symbols are data for ¹²CS₂. The solid lines are linear least-squares fits.

new linear least-squares analyses performed. The effect of including corrections to account for secondary loss of SO_2 and CO is shown in Table II.

The LFP-TDLAS Studies. The LFP-TDLAS experiments were carried out under pseudo-first-order conditions with CS₂ and O₂ in large excess over OH. Concentration ranges in units of 1013 molecules cm⁻³ were as follows: CS₂, 1000–16 000; H_2O_2 , 47– 780; $OH_{t=0}$, 0.36-3.9. Total pressures of O₂ ranged from 25 to 100 Torr. In experiments where CO (OCS) production was observed, several Torr of N_2O (He) was added to the reaction mixture to facilitate rapid deactivation of any CO (OCS) which was formed in excited vibrational levels.^{33,34} A few experiments where vibrational relaxers were omitted from the reaction mixtures gave results essentially identical to those obtained with vibrational relaxers present; i.e., no evidence for production of vibrationally excited OCS or CO was observed. In experiments where SO₂ production was observed, it was assumed that O_2 , CS_2 , and H_2O_2 were efficient at facilitating SO₂ vibrational relaxation; the near resonances of CS₂, H₂O₂, and SO₂ stretching frequencies are the

primary justifications for this assumption. In experiments where CS_2/O_2 mixtures were photolyzed in the absence of H_2O_2 , no product formation was observed.

As mentioned in the Experimental Section, OH radicals were generated by 248-nm laser flash photolysis of H_2O_2 .

$$H_2O_2 + h\nu (248 \text{ nm}) \rightarrow OH + OH$$
 (11a)

$$\rightarrow O + H_2O$$
 (11b)

$$\rightarrow$$
 H + HO₂ (11c)

$$\rightarrow$$
 H₂ + O₂ (11d)

In our data analysis, we assume a quantum yield of 2 for OH production, as currently recommended by the NASA panel for evaluation of chemical kinetics and photochemical data for use in stratospheric modeling.³¹ It should be noted, however, that a somewhat lower OH quantum yield of 1.58 ± 0.23 has recently been reported.³⁵ The rationale for choosing a quantum yield of 2 is elaborated on below in the Discussion section.

The relatively high ($\sim 10^{13}$ per cm³) OH concentrations which were required in order to obtain readily measurable product absorbances resulted in two kinetic complications. First, it was necessary to employ relatively high concentrations of H₂O₂ in order to photolytically generate the required concentration of OH. Hence, the reaction

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{12}$$

competed with reaction 1 for OH radicals. As a result, accurate values for k_1 , k_{-1} , k_2 , and k_{12} must be known in order to determine the fraction of photolytically generated OH which ultimately participates in the CS₂OH + O₂ reaction. While k_{12} is well-established,³¹ uncertainties in $k_1(P)$, $k_{-1}(P)$, and $k_{-2}(P)$ at 297 K are substantial.^{12,17,21} A second complication which results from the use of relatively high radical concentrations is that

TABLE II:	Effect of Secondary	Reactions of OH Radicals	on Product	Yields in the CP-FTIR Studies ^a
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	kinetic data used to model system and make appropriate corrections for secondary chemistry						
product yields (%) ($\pm 2\sigma$)	no corrections	$k_6 = 1.2E - 12^b$ $k_9 = 8.6E - 13$ $k_{10} = 2.3E - 13$	$k_6 = 2.2E-12$ $k_9 = 8.6E-13$ $k_{10} = 2.3E-13$	$k_6 = 2.2E-12$ $k_9 = 6.9E-13$ $k_{10} = 1.8E-13$	$k_6 = 1.2E-12$ $k_9 = 10.3E-13$ $k_{10} = 2.8E-13$		
SO ₂ from ¹² CS ₂	97 ± 6	108 ± 6	103 ± 6	102 ± 6	109 ± 6		
SO_2 from ¹³ CS ₂	102 ± 4	119 ± 5	111 ± 4	109 ± 4	123 ± 6		
SO_2 from ${}^{12}CS_2$ and ${}^{13}CS_2$	100 ± 4	116 ± 5	109 ± 4	107 ± 4	119 ± 6		
¹³ CO from ¹³ CS ₂	15 ± 3	16 ± 3	16 ± 3	16 ± 3	16 ± 3		
$^{13}CO_2$ from $^{13}CS_2$	1.2 ± 0.7	0.4 ± 0.6	0.8 ± 0.6	0.8 ± 0.6	0.2 ± 0.4		

 $a(6) = OH + CS_2$, (9) = OH + SO₂, (10) = OH + CO. ^b Read as 1.2×10^{-12} .



Figure 4. Representative OCS, CO, and SO₂ appearance temporal profiles observed in the LFP-TDLAS experiments. Species concentrations in the OCS experiment were P = 25.2 Torr, 6.42×10^{17} O₂ cm⁻³, 3.8×10^{16} CS₂ cm⁻³, 1.6×10^{15} H₂O₂ cm⁻³, and 1.0×10^{13} OH cm⁻³ at t = 0. Species concentrations in the CO experiment were P = 25.4 Torr, 5.53×10^{17} O₂ cm⁻³, 5.0×10^{16} CS₂ cm⁻³, 4.3×10^{15} H₂O₂ cm⁻³, and 1.7×10^{13} OH cm⁻³ at t = 0. Species concentrations in the SO₂ experiment were P = 24.0 Torr, 6.19×10^{17} O₂ cm⁻³, 4.9×10^{16} CS₂ cm⁻³, 1.6×10^{15} H₂O₂ cm⁻³, and 1.0×10^{13} OH cm⁻³ at t = 0. Solid lines are simulations using the model outlined in the text and in Table III and using the parameters in column "100/3" of Table V. Dashed lines are obtained from the same simulations as the solid lines, but with an optimal linear scaling factor applied to compensate for absolute calibration error. For clarity, OCS and SO₂ concentrations are offset from zero by 2×10^{12} and 4×10^{12} molecules cm⁻³, respectively.

radical-radical side reactions can influence observed product temporal profiles.

Representative OCS, CO, and SO₂ product temporal profiles observed in the LFP-TDLAS studies are shown in Figure 4. The OCS and CO appearance data (examples of which appear in Figure 4) lead to a number of *qualitative* conclusions: (a) in agreement with the CP-FTIR results, the yield of OCS is 4–5 times larger than the yield of CO; (b) the shapes of the OCS and CO appearance temporal profiles are very similar and are nonexponential; (c) the pseudo-first-order rate coefficients for the fast components of the nonexponential appearance temporal profiles are approximately those expected for OH decay via reactions 1, -1, and 2;^{12,17,21} and (d) the slow components of the OCS and CO appearance temporal profiles become faster as $[OH]_0$ increases, thus suggesting the importance of at least one radical-radical reaction in the appearance chemistry.

One possible explanation for the slow increase in [OCS] and [CO] observed at long times after the laser flash is secondary chemistry involving S or SO. If either S or SO is generated as a product of the $CS_2OH + O_2$ reaction, then under the experimental conditions employed in the LFP-TDLAS experiments, the following secondary reactions would occur:

$$S + O_2 \rightarrow SO + O$$
 (13)

$$SO + O_2 \rightarrow SO_2 + O$$
 (14)

$$O + CS_2 \rightarrow CS + SO \tag{15}$$

$$CS + O_2 \rightarrow OCS + O$$
 (16a)

$$CS + O_2 \rightarrow CO + SO$$
 (16b)

$$SO + HO_2 \rightarrow OH + SO_2$$
 (17a)

$$SO + HO_2 \rightarrow HSO + O_2$$
 (17b)

Kinetic data are available in the literature for all reactions listed above except reaction 17, and k_{17a} has been estimated³⁶ to be 3 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (by analogy with the ClO + SO reaction for which kinetic data are reported³⁷). The occurrence of reactions 13–17 could explain the slow components of the CO and OCS temporal profiles and would also predict large secondary (chain) production of SO₂. The LFP-TDLAS studies of SO₂ production were carried out primarily to see whether observed SO₂ temporal profiles are consistent with the occurrence of reactions 13–17. The solid lines in Figure 4 are Acuchem³² simulations of the experiments. The simulations employ a 37 reaction scheme which is detailed in Table III. Reactions 13–17 are the secondary reactions of primary importance, although a number of other secondary reactions are included in the mechanism. The mechanism assumes three product channels for reaction 2:

$$CS_2OH + O_2 \rightarrow OCS + HOSO$$
 (2a)

$$\rightarrow$$
 HCO + SO₂ + S (2q)

$$\rightarrow$$
 other products (2')

The mechanism also allows for the possibility of OH regeneration via rapid decomposition of HOSO:

$$HOSO + M \rightarrow OH + SO + M$$
(18a)

$$\rightarrow$$
 H + SO₂ + M (18b)

The above reactions represent one of a number of possible sets of elementary reactions which are consistent with a vast majority of experimental observations on this complex chemical system. The solid lines in Figure 4 are generated assuming $\Phi_{OCS} \equiv k_{2a}/k_2$ = 0.83, $\Phi_{CO} \equiv k_{2r}/k_2 = 0.17$, and $\Phi_{OH} \equiv k_{18a}/k_{18} = 0.05$; as discussed below, these values represent the overall best fit parameters for a data set consisting of 100 appearance temporal profiles. Comparison of the observed and simulated temporal profiles demonstrates that it is possible to reproduce both the time dependencies and absolute magnitudes of the concentrations of OCS, CO, and SO₂ reasonably well using the chemical model described above.

Quantitative "prompt" yields of OCS, CO, and SO₂ were extracted from the LFP-TDLAS data in three stages. (By "prompt" we mean either a primary product of the CS₂OH + O₂

TABLE III: Mechanism Assumed To Simulate OCS, CO, and SO₂ Temporal Profiles Observed in the LFP-TDLAS Experiments

	reactants	products	$k (10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
A	$OH + CS_2 + M$	CS ₂ OH + M	a
B	$CS_2OH + M$	$OH + CS_2 + M$	a
С	$OH + H_2O_2$	$HO_2 + H_2O$	170
D	OH + HO2	$H_2O + O_2$	11000
E	$CS_2OH + O_2$	Х	2.75
F	X	OCS + HOSO	ь
G	X	$HCO + SO_2 + S$	Ь
н	Х	other products	ь
I	HOSO + M	OH + SO + M	с
J	HOSO + M	$H + SO_2 + M$	с
K	$HCO + O_2$	$HO_2 + CO$	550
L	$H + O_2 + M$	HO ₂ + M	5.7×10^{-18} [M]
Μ	$S + O_2$	SO + O	230
Ν	S + OH	SO + H	6600
0	S + O ₃	$SO + O_2$	1200
Р	$SO + O_2$	$SO_2 + O$	0.0084
Q	SO + OH	$SO_2 + H$	8600
R	SO + O3	$SO_2 + O_2$	9.0
S	$O + O_2 + M$	O3 + M	6.0 × 10 ⁻²⁰ [M]
Т	O + HO ₂	$OH + O_2$	5900
U	$O + CS_2$	CS + SO	320
V	$O + CS_2$	OCS + S	34.6
W	$O + CS_2$	CO + S ₂	5.4
X	O + OH	$O_2 + H$	3300
Y	$O + H_2O_2$	$OH + HO_2$	0.17
Ζ	O + CS	CO + S	2000
AA	OH + OH	H ₂ O + O	190
BB	OH + OH + M	$H_2O_2 + M$	d
CC	$HO_2 + HO_2$	$H_2O_2 + O_2$	170
DD	$HO_2 + HO_2 + M$	$H_2O_2 + O_2 + M$	4.9 × 10 ^{−18} [M]
EE	SO + HO ₂	$SO_2 + OH$	3000
FF	$HSO + O_3$	$SH + O_2 + O_2$	10
GG	$CS + O_2$	OCS + O	2.6×10^{-5}
HH	$CS + O_2$	CO + SO	2.6 × 10 ⁻⁶
Π	$CS + O_3$	$OCS + O_2$	0.03
JJ	SH + O	H + SO	16000
KK	$SH + O_3$	$HSO + O_2$	350

^a Obtained as a fit parameter. ^b Very fast; branching ratio for production of OCS and CO obtained as fit parameters. ^c Very fast; branching ratio for OH production obtained as fit parameter. ^d k(P) obtained from falloff parameters given in Table II of ref 31.

reaction or a product formed via rapid secondary reaction of a primary product with O₂; in order for the secondary reaction of a primary product with O₂ to occur as rapidly or more rapidly than the primary reaction, the rate coefficient for the secondary reaction would have to be at least 1×10^{-15} cm⁻³ molecule⁻¹ s⁻¹ under our experimental conditions.) Initially, the entire data set of 163 individual experiments (23 monitoring CO, 84 monitoring OCS, and 56 monitoring SO₂) was analyzed by extrapolating the slow component of the product appearance temporal profile back to t = 0 (the time of the photolysis laser flash) and comparing the resulting concentration to $f[OH]_0$, where $[OH]_0$ is the concentration of flash generated OH and f is the fraction of OH which is removed via reaction with CS_2 . Values for $f[OH]_0$ were derived from a simple model which included only those reactions which were expected to occur on the fast time scale for removal of flash-generated OH; these were reactions 1, -1, 2, 12, and 19:

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{19}$$

Values for k_1 , k_{-1} , and k_2 used in this preliminary analysis were based on our earlier study of OH + CS₂ kinetics,¹² while values for k_{12} and k_{19} were taken from ref 31. This procedure resulted in values for [X]/f [OH]₀ of 0.83 ± 0.30 for X = OCS, 0.17 ± 0.06 for X = CO, and 0.82 ± 0.45 for X = SO₂ (errors are 2σ and represent precision only). The results are in excellent agreement with the CP-FTIR results, although the uncertainties in measured yields are quite large. It should be noted that the LFP-TDLAS yields are computed as moles of product formed

TABLE IV:	Exothermic	Channels	for	the	Reaction
$CS_2OH + O_2$	\rightarrow Products				

reaction no.	products	$-\Delta H (\text{kcal mol}^{-1})^a$
2a	OCS + HOSO	105
2b	HOCO + S ₂ O	93
2c	$CO + SH + SO_2$	89.8
2đ	$CO_2 + SH + SO$	85.2
2e	$CO_2 + H + S_2O$	82
2f	$OH + CO_2 + S_2$	80.5
2g	$OCS + H + SO_2$	79.3
2h	$OCS + HSO_2$	73.4
2i	$OH + CO + S_2O$	57
2j	$CO_2 + HSO + S$	55.3
2k	CO + HSO + SO	52.5
21	$CS + HOSO_2$	51.4
2m	HCS + SO ₃	50.5
2n	OH + OCS + SO	49.8
2o	CO + HOSO + S	31.6
2p	$OCS + SH + O_2$	26.4
2q	$HCO + SO_2 + S$	21.1
2r	$OH + CS + SO_2$	21.1
2s	$HO_2 + CO + S_2$	19.1
2t	HCO + SO + SO	13.8
2u	HOCO + SO + S	11.9
2v	$CO + H + SO_2 + S$	5.5
2w	$CS + H + SO_3$	1.9
2x	OCS + HSO + O	1.8
2у	$CO_2 + H + SO + S$	0.9
2z	$CO + HSO_2 + S$	-0.4

^a Heats of formation used to compute ΔH values were obtained from the following sources: HOSO and HSO₂ from ref 45; S₂O from ref 46; HCS from ref 47; all others from ref 31.

per mole of OH reacted in contrast to the CP-FTIR values, which relate products to CS_2 consumption.

The second stage of analysis involved least-squares fitting of the model presented in Table III to a selected data set of 100 experiments. The selection involved removing most of the earliest OCS data, which were of generally lower quality than data acquired after some experience with the system, and a few other experiments which were excessively noisy or subject to large calibration errors. The remaining data were divided among the three observed product molecules as follows: 20 observations of CO, 33 of OCS, and 47 of SO₂. As shown in Table IV, we have identified 26 possible exothermic product channels for reaction 2. The product channels used in our model (Table III) were selected from the possible exothermic channels to allow for production of the observed species, the possible regeneration of OH, and the production of S or SO radicals to explain the observed slow product generation.

A Powell type iteration³⁸ was used to minimize the relative root-mean-square (rms) deviation between the data and the corresponding Acuchem simulations by varying the five parameters: Φ_{CO} , Φ_{OCS} , Φ_{OH} , k_1 , and K_c ($\equiv k_1/k_{-1}$). The function minimized was

$$Q = \frac{1}{100} \sum_{j=1}^{100} \left[\frac{1}{N_j} \sum_{i=1}^{N_j} \left\{ \frac{C_{ji} - A(\vec{K}, \vec{P}_j, t_{ji})}{A(\vec{K}, \vec{P}_j, t_{ji})} \right\}^2 \right]^{1/2}$$
(I)

where the j index runs over the 100 experiments, the i index runs over the points within each experiment, N_j is the number of points in experiment j, C_{jl} is the concentration observed in experiment j at the time t_i , and $A(\vec{K}, \vec{P}_j, t_l)$ is the corresponding Acuchem result for the given set of rates \vec{K} and the set, \vec{P}_j , of experimental conditions. The fit results are shown in column 1 of Table V. The yields for CO and OCS agree very well with the CP-FTIR values and with the values of [X]/f [OH]₀ obtained from the simpler analysis. The rate coefficients for reactions 1 and -1 obtained using the above procedure are, within experimental uncertainties, consistent with the range of values reported in the literature.^{12,17,21}

Since the yield of SO_2 is not an adjustable parameter in the model, the SO_2 yield was computed as the product of the model

TABLE V:Summary of Results Obtained by FittingLFP-TDLAS Observations of OCS, CO, and SO2 TemporalProfiles Using the Mechanism Given in Table III

	no. of experiments/choice of k_{17a}^{a}				
	100/3	9/1	9/3	9/9	
Φco	0.17	0.17	0.16	0.15	
Φocs	0.83	0.83	0.78	0.75	
Фон	0.05	0.05	0.05	0.07	
k_1^{b}	3.0	2.7	3.1	2.4	
Kcc	1.8	2.3	1.9	2.7	
rms dev	0.13	0.087	0.086	0.098	

^a Units are 10^{-11} cm³ molecule⁻¹ s⁻¹. ^b Assumed to be in its low-pressure limit; units are 10^{-31} cm⁶ molecule⁻² s⁻¹. ^c Units are 10^{-17} cm³ molecule⁻¹.

yield (i.e., $\Phi_{CO} + \Phi_{OCS} (1 - \Phi_{OH})$) times the ratio of the observed concentration to the model prediction. The yield result of 0.84 is essentially unchanged from the earlier analysis, but the standard deviation is reduced considerably.

The fits to the data set of 100 experiments were quite expensive in terms of computer time, and it was not possible to include the (unknown) SO + HO₂ rate coefficient as a sixth parameter. To evaluate the sensitivity of the analysis to this poorly known rate coefficient, a final simplification was made. For this third stage, nine experiments were selected as representative of the entire data set. These nine included one run for each of the three products from each of three sets of conditions: 25 Torr, low [OH]₀; 25 Torr, high [OH]₀; and 100 Torr, high [OH]₀. The original fitting procedure was then repeated with the reduced data set for k_{17a} values of 1×10^{-11} , 3×10^{-11} , and 9×10^{-11} cm³ molecule⁻¹ s⁻¹. The yield results show little dependence on the k_{17a} value and agree well with the results from the larger data set. Additionally, the rms deviation is smallest for the intermediate value of k_{17a} , suggesting that the correct value lies within the range examined.

The Powell fitting method gives little information about the uncertainties in the results, and a simple grid search revealed a high degree of correlation among the parameters. For example, an increase in Φ_{CO} can be largely offset by a reduction in Φ_{OH} . It is thus difficult to place error bars on the results. However, we feel it is reasonable to make the following estimates based on variations between experiments (uncertainties are 2σ and represent precision only): $\Phi_{CO} = 0.17 \pm 0.03$, $\Phi_{OCS} = 0.83 \pm 0.15$, and $\Phi_{SO_2} = 0.84 \pm 0.20$; it should be reemphasized that these yields are the "prompt" product formation, i.e., formation as a primary product of the CS₂OH + O₂ reaction or via fast reaction of a primary product with O₂.

Discussion

The CP-FTIR and LFP-TDLAS studies are in quantitative agreement concerning the yields of OCS and CO. Combining the results obtained from the two different types of experiments, we report the following yields for production of OCS and CO from the $CS_2OH + O_2$ reaction:

$$\Phi_{\rm OCS} = 0.83 \pm 0.08$$
$$\Phi_{\rm CO} = 0.16 \pm 0.03$$

The LFP-TDLAS experiments demonstrate that the above yields represent OCS and CO production either as primary products of the CS₂OH + O₂ reaction or as products of fast secondary reaction-(s) of a primary product with O₂. Previous observations of carboncontaining end products of the OH + CS₂ + O₂ reaction have all employed continuous photolysis techniques with detection of products by gas chromatography^{8,9,19} or FTIR spectroscopy.^{10,16} Barnes et al.¹⁰ also employed a "dark" reaction scheme where thermal decomposition of peroxynitric acid in the presence of NO was employed as the OH radical source. It is generally agreed that OCS is the predominant carbon-containing product. However, there is poor agreement concerning the yield of CO. Jones et al.^{8,9} did not attempt to detect CO, but their reported OCS yield of unity implies that $\Phi_{CO} \approx 0$. Barnes et al.¹⁰ did attempt to observe CO by FTIR spectroscopy, but with negative results; they reported $\Phi_{CO} < 0.05$. On the other hand, Iyer et al.¹⁹ report observation of CO with significant (though unspecified) yield, and Becker et al.¹⁶ also report observation of CO production with $\Phi_{CO} \approx 0.10$. The results reported in this study represent the first quantitative measurements of Φ_{CO} and the first observations which prove that OCS and CO are generated as "prompt" products of the CS₂OH + O₂ reaction. Our results also demonstrate that $\Phi_{CO_2} < 0.01$, in agreement with most earlier work, but in contrast to the results of Iyer et al.,¹⁹ who report observation of significant CO₂ production, but with unspecified yields.

Consideration of the data in Table II leads to a "best estimate" SO_2 yield from the CP-FTIR studies of 1.15 ± 0.10 ; on the other hand, from the LFP-TDLAS experiments a prompt SO₂ yield of 0.84 ± 0.20 is obtained. The likely difference between these two results centers on the secondary chemistry of SO, which we believe (based on SO₂ temporal profiles observed in the LFP-TDLAS experiments) is generated as a "prompt" product of the CS2OH + O₂ reaction. In the CP-FTIR studies, SO₂ generated via the slow SO + O_2 reaction would be observed; however, in the LFP-TDLAS studied SO₂ produced via SO + O_2 and/or other slow secondary processes is observed in the slow component of the appearance temporal profile and does not contribute to the measured "prompt" yield. Under lower tropospheric conditions, the dominant fate of SO is reaction with O_2 to generate SO_2 + O. Furthermore, both in the CP-FTIR experiments and in the real atmosphere, the dominant fate of O atoms is reaction with O_2 to generate O_3 . Hence, for purposes of atmospheric modeling we report the CP-FTIR result, i.e.

$$\Phi_{\rm SO_2} = 1.15 \pm 0.10$$

The only previous study which addresses the issue of SO production from the $CS_2OH + O_2$ reaction is that of Lovejoy et al.,¹⁸ who observed an SO₂ yield of 0.9 ± 0.2 in a low-pressure flow tube experiment with chemical ionization mass spectrometric detection of SO₂. Under the experimental conditions of Lovejoy et al. ($[O_2] \le 10^{17}$ cm⁻³), the SO + O₂ reaction could not have been a source of their observed SO₂. Lovejoy et al. employed considerably lower radical concentrations than those employed in our LFP-TDLAS studies. Hence, our primary evidence for SO production, the slow components in the OCS, CO, and SO₂ temporal profiles observed in the LFP-TDLAS studies, would not have been observable in the experiments of Lovejoy et al.¹⁸ We conclude that our postulate of SO generation as a "prompt" product of the CS₂OH + O₂ reaction is consistent with all information available in the literature.

On the basis of the comparison of rate coefficients for the overall $OH + CS_2 + O_2$ reaction obtained by absolute and competitive methods, Becker et al.¹⁶ have postulated that OH is produced as a "prompt" product of the $CS_2OH + O_2$ reaction with a yield, Φ_{OH} , of approximately 0.3. Both the shapes and amplitudes of temporal profiles observed in the LFP-TDLAS studies are sensitive to Φ_{OH} , so this parameter was included in the fitting procedure used to extract product yields. As summarized in Table V, the best fit value for Φ_{OH} is 0.05-much lower than the value postulated by Becker et al. However, as discussed briefly above, we consider the low value for Φ_{OH} obtained from our data analysis to be suggestive, but not conclusive, since the value for Φ_{OH} obtained from the data analysis changes significantly when other parameters are fixed at values different from their best fit values and also depends upon the assumed quantum yield for OH production from H₂O₂ photolysis.

The absolute product yields derived from the LFP-TDLAS experiments are based on an assumed yield of 2 for OH production from 248-nm photolysis of H_2O_2 . Two measurements of the quantum yield of interest have recently been reported. Vaghijiani and Ravishankara³⁹ derive a quantum yield of 2.09 \pm 0.36 using

OH production from 248-nm photolysis of $O_3/H_2O/He$ mixtures as an absolute reference; they assumed an OH yield of $1.73 \pm$ 0.09 for the reference photolysis system.⁴⁰ Schiffman et al.³⁵ report a quantum yield of 1.58 ± 0.23 based on infrared flash kinetic spectrometric detection of OH using absolute infrared OH transition moments recently reported by Nelson et al.41 (same research group). The experiments of Vaghjiani and Ravishankara³⁹ also involved attempts to observe oxygen atoms and hydrogen atoms as products of 248-nm photolysis of H_2O_2 ; these experiments were negative, leading to upper limit quantum yields of 0.002 for production of $O(^{3}P) + O(^{1}D)$ and 0.0002 for production of $H(^{2}S)$. In CW photolysis experiments, Glinski and Birks⁴² report a similarly low upper limit for H₂ production from 253.7-nm photolysis of H_2O_2 . The absorption spectrum of H_2O_2 is totally diffuse,³¹ suggesting that the quantum yield for photodissociation is unity. Since no photoproducts other than OH have been observed, we feel that the most probable quantum yield for OH production is 2.0.

Twenty six possible exothermic product channels for the CS2- $OH + O_2$ reaction, i.e., reaction 2, are listed in Table IV. While the results obtained in this study do not allow unequivocal identification of the important product channels, they do significantly constrain the number of possibilities. Our results strongly suggest that there exists at least one major channel which results in production of "prompt" OCS and "prompt" SO2 and also at least one minor channel which results in production of "prompt" CO and "prompt" SO. Candidates for the major pathway include channels 2a, 2g, and 2h while candidates for the minor pathway include channels 2k, 2o, 2q, 2t, 2v, and 2z. It is interesting to note that none of the four channels which involve production of OH as a primary product are included in the above list of possible major and minor pathways. However, the simultaneous occurrence of channels 2g, 2n, and 20 would be consistent with our observations and also allow for significant OH regeneration. Prompt secondary production of OH could also occur via decomposition of HOSO.

As mentioned in the Introduction, experimental¹⁴ and theoretical²³ results suggest that the SCS-OH isomer, which is considerably less stable than the HO-CS₂ isomer, is produced via addition of OH to CS₂ due to the existence of a large potential energy barrier inhibiting OH addition to the carbon atom.²³ Howard⁴³ has suggested a mechanism for the SCS-OH + O_2 reaction which is able to qualitatively account for our observations:

In the above mechanism, sufficiently energized OCS* could decompose to CO + S while sufficiently energized HOSO* could decompose to $H + SO_2$ or OH + SO. Additional experimental and theoretical research will be required to further constrain the detailed mechanism for this complex chemical reaction.

For purposes of understanding the atmospheric cycles of CS_2 and OCS, the key result from this study is the measurement of $\Phi_{\text{OCS}}.$ Chin and Davis have recently reported a detailed study of the global budgets of OCS and \dot{CS}_2 .⁴⁴ Using our measured yield, $\Phi_{OCS} = 0.83$, they conclude that about 30% of atmospheric OCS is generated via CS₂ oxidation. Another parameter of importance for understanding the atmospheric budget and distribution of CS_2 is the effective rate coefficient, k_6 , for the overall $OH + CS_2 + O_2$ reaction (consisting of three elementary steps) in 1 atm of air. As pointed out in the Introduction, it has been suggested that a significant reaction channel involving OH production via the $CS_2OH + O_2$ reaction is not observed in measurements of k_6 which directly follow OH decay kinetics.¹⁶ While results presented here and elsewhere^{8,9,12} suggest that little or no OH production occurs, further studies aimed at quantitatively evaluating the yield for OH production from the CS₂OH

 $+ O_2$ reaction are needed in order to firmly establish the appropriate value of k_6 for use in atmospheric models.

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