

Laboratory Studies on the Reactions between Chlorine, Sulfur Dioxide, and Oxygen: Implications for the Venus Stratosphere¹

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The title reaction was studied by photolyzing mixtures of Cl_2 and SO_2 with and without O_2 present in an atmosphere of N_2 , using Fourier transform infrared spectrophotometry to monitor reactants and products. In the absence of oxygen, sulfur dioxide is quantitatively converted to sulfonyl chloride. With 10 to 150 Torr O_2 present H_2SO_4 is produced as well as SO_2Cl_2 . When a number of speculative reactions inferred from these experiments are added to a published model for Venus stratospheric chemistry, it emerges that SO_2Cl_2 is a key reservoir species for chlorine and that the reaction between Cl and SO_2 provides an important cycle for destroying O_2 and converting SO_2 to H_2SO_4 . The modified model could provide a possible solution to the photochemistry of the Venus stratosphere if the mixing ratio of chlorine on Venus were as high as 8 ppm.

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INTRODUCTION

It is now widely accepted that in the stratosphere of Venus some of the key catalytic cycles for reversing the photolysis of carbon dioxide involve chlorine species and/or sulfur dioxide (Prinn, 1971; Sze and McElroy, 1975; Winick and Stewart, 1980; Yung and DeMore, 1982; von Zahn *et al.*, 1983). A recent measurement of the rate constant for the reaction between chlorine atoms and sulfur dioxide (Strattan *et al.*, 1979; Eibling and Kaufman, 1983) has indicated that the sulfur and chlorine cycles are interconnected.

As part of a program to obtain further insights into the ways in which these spe-

cies influence the Venus stratospheric chemistry, we have undertaken a stoichiometric study of the reaction between chlorine atoms and sulfur dioxide both in the presence and in the absence of oxygen. The possible consequences of some of the reactions suggested by our experiment were qualitatively explored using the model of Yung and DeMore (1982).

EXPERIMENTAL

Mixtures of chlorine and sulfur dioxide with and without added oxygen in an atmosphere of nitrogen were photolyzed using either Philips Black Light or Cool White fluorescent lamps surrounding a cylindrical pyrex reaction vessel (17 cm i.d. \times 60 cm long). The vessel is fitted internally with White Cell optics aligned to give an overall path length of approximately 12 m for the beam from a Bomem Model 3.002 Fourier transform infrared spectrophotometer which operated with a global light source, a

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KCl beamsplitter, and a liquid nitrogen-cooled MCT detector, a combination which allowed measurements in the region 800–4000 cm^{-1} . Concentrations of various reactants and products were monitored before and during photolysis, generally by averaging 20 scans and by using an apodized resolution of 1.0 cm^{-1} (Bartle apodization). A PDP-11/23 computer and accessories were used to collect, process, and display data. For quantification, integrated band areas were used in conjunction with spectra of pure samples of reactants and products recorded using conditions as close as possible to those used during photolysis experiments.

N_2 (Matheson, 99.9995%) and O_2 (Matheson, 99.99%) were used directly from the gas cylinders. Cl_2 (Matheson, 99.96%), SO_2 (Matheson, 99.98%), NO_2 (Matheson, 99.5%), HCl (Union Carbide, 99.99%), and SO_2Cl_2 (J. T. Baker) were further purified by vacuum distillation at a liquid nitrogen trap. The photochemical reactor was always evacuated to $\leq 1 \times 10^{-4}$ Torr by a vacuum system consisting of a liquid nitrogen trap, a 2-in. diffusion pump, and a rotary pump before the experiments. Several experiments were performed after gently heating the reactor to $\approx 70^\circ\text{C}$ under vacuum over a period of 12 hr in order to reduce the water vapor.

The spectral distribution of Philips Black Light fluorescent lamps (FS40BLB) was measured by a monochromator (Bausch and Lomb)/photomultiplier tube (EMR 510N)/picoammeter (Keithley) assembly over the wavelength range of 200 to 400 nm. It was found that the lamps emitted at 370 nm with $\text{FWHM} = 20$ nm. The light flux was calibrated using the well-known procedure with NO_2 gas as an actinometer. With four lamps and an initial NO_2 concentration between 0.011 and 0.057 Torr at 1 atm of N_2 , the average photolysis rate was measured to be $1.7 \times 10^{-3} \text{ sec}^{-1}$. Because of the very weak absorption of SO_2 at 370 nm ($\sigma \approx 2 \times 10^{-22} \text{ cm}^2$) and the fast quenching rate of the excited SO_2 (3B_1) ($k \approx 1 \times 10^{-13}$

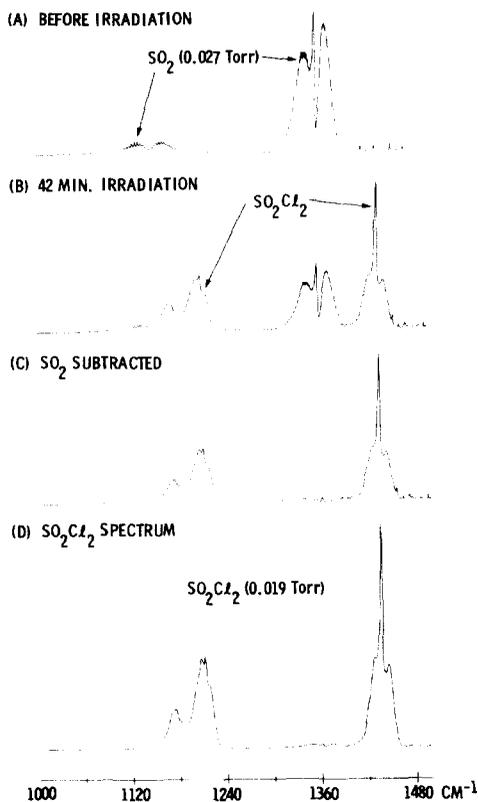


FIG. 1. Photolysis of 2.04 Torr Cl_2 and 0.027 Torr SO_2 in 760 Torr N_2 using Black Light fluorescent lamps. Spectrum (C) is (B) with 0.012 Torr SO_2 subtracted, while (D) is the spectrum of a pure sample of SO_2Cl_2 in 760 Torr N_2 .

$\text{cm}^3 \text{ sec}^{-1}$) by N_2 (Okabe, 1978), the contribution of this excited molecule to the mechanism was found to be negligible. Assuming unit efficiency for reactions of $^3\text{SO}_2$ with Cl_2 , the calculated yield of SO_2Cl_2 was less than 1% of the observed yield. Therefore we attribute the SO_2Cl_2 formation to photolysis of Cl_2 and not SO_2 .

RESULTS

(A) In the Absence of Oxygen

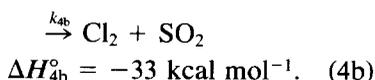
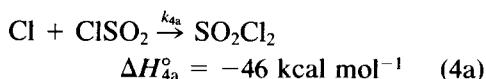
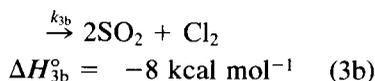
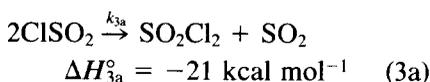
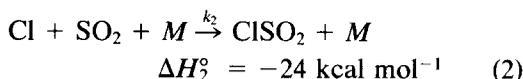
(i) *Stoichiometry.* When mixtures of sulfur dioxide and chloride made up to 1 atmosphere with nitrogen were photolyzed at $300 \pm 5^\circ\text{K}$, the only detectable product was sulfuryl chloride, SO_2Cl_2 , as is shown in Fig. 1. In 14 experiments listed in Table I

TABLE I
STOICHIOMETRY FOR CONVERSION OF SO₂ INTO
SO₂Cl₂ AT 300°K

Expt	[Cl ₂]	[SO ₂]	Reaction time	Δ[SO ₂]	$\frac{\Delta[\text{SO}_2\text{Cl}_2]}{\Delta[\text{SO}_2]}$
3	2.04 Torr	0.027 Torr	22 min	0.0096 Torr	0.95
			35	0.0125	0.94
4	1.02	0.063	42	0.0139	0.93
			20	0.011	0.90
			52	0.027	0.92
5	2.05	0.049	72	0.032	0.93
			4	0.0133	1.07
			8	0.0251	1.01
6	0.545	0.0252	11	0.030	0.99
			20	0.0058	0.97
			26	0.0076	0.98
42	1.06	0.074	9	0.011	1.09
			20	0.027	1.04
			29	0.036	1.00

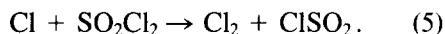
the ratio of the concentration of sulfuryl chloride formed to the concentration of sulfur dioxide consumed, $\Delta[\text{SO}_2\text{Cl}_2]/\Delta[\text{SO}_2]$, was measured: the average value was 0.98 ± 0.1 . It appears then that SO₂ is converted quantitatively to SO₂Cl₂.

(ii) *Reactions involved.* Possible reactions in this system follow:



Reaction enthalpies have been calculated using data tabulated by Takacs (1978). These data are firmly established for all relevant species with the possible exception of

ClSO₂, for which the heat of formation relies upon a fairly old indirect estimate of ΔH° (Szabo, 1964) for the reaction

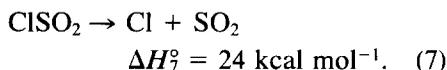
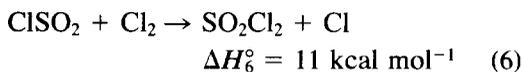


Reaction (5) could play a role in the laboratory experiment if k_5 is comparable to k_2 . Unfortunately, to the best of our knowledge k_5 is unknown.

The photoabsorption cross section of SO₂Cl₂ was measured by Uthman *et al.* (1978) and by us using a 10-cm quartz cell and a Cary 14 spectrophotometer. The cross section at 370 nm was found to be less than $3 \times 10^{-21} \text{ cm}^2$ at 298°K. Consequently, the loss of SO₂Cl₂ by photolysis is negligible.

For reaction (2), Strattan *et al.* (1979) reported a rate constant of $(2.3 \pm 0.5) \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$ at 295°K for $M = \text{N}_2$: their measurements were made in the pressure range 3 to 13 Torr. If reaction (2) is in the third-order region up to atmospheric pressure, then its apparent second-order rate constant $k_2' = k_2[M] = 5.7 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. Alternatively, taking their actually measured second-order rate constant $7 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ at 10 Torr and assuming that the high pressure limit is only a factor of 2 or 3 greater, we would have $k_2' \approx 2 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$. These values should represent lower and upper limits of k_2' for this study.

Because they appear to be endothermic, the following two reactions can probably be eliminated:



The above scheme, 1–4 is qualitatively consistent with our stoichiometric measurements.

(B) In the Presence of Oxygen

(i) *Product identification.* When mixtures of Cl₂, SO₂, O₂, and N₂ were photolyzed with Black Light tubes, both sulfuryl chlo-

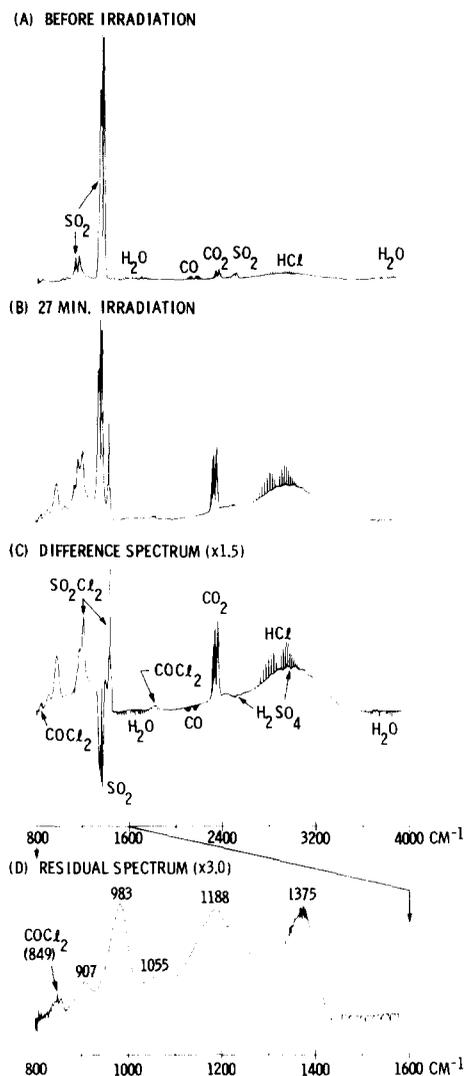


FIG. 2. Photolysis of 1.06 Torr Cl_2 , 0.074 SO_2 , 50 Torr O_2 made to 760 Torr with N_2 . Spectrum (C) is (B) with (A) subtracted from it, while (D) is portion of (B) with 0.012 Torr SO_2Cl_2 and 0.048 Torr SO_2 stripped out: the peak at 849 cm^{-1} is due to phosgene formed from impurity CO.

ride and sulfuric acid were produced. The former was identified by its bands at 1212 and 1437 cm^{-1} , while the latter was characterized first by subtracting SO_2Cl_2 and SO_2 from the product spectrum and then by comparing the result with the spectrum of sulfuric acid reported by in the literature (Stopperka, 1966). Figure 2 shows spectra

from a typical experiment. (A) is the initial measurement in the dark (predominantly SO_2 with traces of CO, CO_2 , HCl, and H_2O impurities, mainly from the atmosphere of N_2); (B) is the spectrum after 27 min irradiation, and (C) is a difference spectrum showing consumption of SO_2 and H_2O and production of SO_2Cl_2 and HCl and showing a set of broad bands later assigned to H_2SO_4 : impurity CO is converted to phosgene and CO_2 , a well-known reaction. (D) is the product spectrum (B) with 0.012 Torr SO_2Cl_2 and 0.048 Torr SO_2 subtracted out: this spectrum plus the broad band centered on 3050 cm^{-1} [clearly visible in (B) and (C)] is virtually identical to the H_2SO_4 spectrum reported by Stopperka (1966) and other workers. The peak maxima found in (D) and in analogous spectra from similar experiments are listed in Table II along with those reported by previous measurements.

The reported infrared spectra were of thin liquid films. Because of the similarity of our spectra with those of previous data and of the broadness of the bands, it is concluded that the sulfuric acid is present as an aerosol in our experiments: the facility with which H_2SO_4 forms aerosols is well known.

(ii) *Dependence on oxygen pressure.* A series of experiments was performed using varying pressures of oxygen and measuring both $[\text{SO}_2]$ and $[\text{SO}_2\text{Cl}_2]$. In the absence of any other sulfur containing products it was assumed that

$$[\text{H}_2\text{SO}_4] = \Delta[\text{SO}_2] - [\text{SO}_2\text{Cl}_2]. \quad (8)$$

TABLE II

IR BAND MAXIMA FOR REACTION PRODUCT AND SULFURIC ACID

Chachalackal and Stafford	Stopperka	Giguere and Savoie	Reaction product (this work)
910 cm^{-1}	908 cm^{-1}	910 cm^{-1}	$907 \pm 3\text{ cm}^{-1}$
973	976	973	983 ± 3
1170	1187	1195	1188 ± 5
	1210		
1368	1378	1368	1375 ± 2
2450	2450	2450	2440 ± 5
2970	3050	2970	3030 ± 10

TABLE III
PHOTOLYSIS OF Cl₂, SO₂, O₂, AND N₂ MIXTURES

[O ₂]	Δ[SO ₂]	[H ₂ SO ₄]/[SO ₂ Cl ₂]
0	0.036 Torr	0
10	0.024	0.46
50	0.026	1.2
151	0.026	3.3

Note. [Cl₂] = 1.0 Torr, [SO₂] = 0.074 Torr, temperature 300 ± 3°K. Total pressure made to 760 Torr with N₂. Light source: four Black Light tubes. Duration of irradiation = 27 min.

Results are shown in Table III. With only 10 Torr of oxygen the amount of H₂SO₄ formed was about 50% of the amount of SO₂Cl₂, and as oxygen pressure was increased the ratio of H₂SO₄ to SO₂Cl₂ increased also.

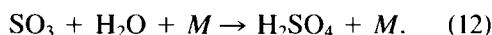
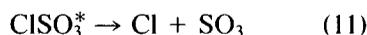
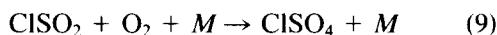
It has not been possible to perform a direct calibration for H₂SO₄ in order to confirm Eq. (8), but it was noted that the H₂SO₄ band areas increased proportionately as [H₂SO₄], calculated from Eq. (8), increased. The quantitative measurements involving H₂SO₄ aerosols are notoriously difficult.

Whether sulfur trioxide was the precursor of sulfuric acid in these experiments could not be determined because of an inability to establish sufficiently dry operating conditions. Although water vapor was consumed early in each experiment, there seemed to be adequate sources of adsorbed moisture to ensure that any SO₃ formed would be rapidly converted to H₂SO₄. Because the only SO₃ absorption band (1391 cm⁻¹) in the infrared region used in this study (800–4000 cm⁻¹) overlaps a sulfuric acid band (1375 cm⁻¹), the only way of detecting SO₃ would be to see this band grow relative to the other H₂SO₄ bands; no such relative growth was observed.

It is necessary to determine whether the HCl production observed in Fig. 2 and in similar experiments is a result of the reactions under investigation or merely of impurity reactions. Photolysis of mixtures of Cl₂

and N₂ alone caused some HCl production: photolysis of Cl₂, SO₂, N₂ mixtures caused approximately similar production of HCl. In both cases this HCl production could be attributed to impurity reactions—probably reaction of Cl with a variety of hydrocarbons desorbing from the surfaces of the reaction cell and the quite extensive metallic hardware and O rings of the White Cell optical mounts. In the Cl₂, SO₂, O₂, and N₂ experiments $d[\text{HCl}]/dt$ was somewhat higher than in these earlier experiments but not sufficiently greater to conclude with any confidence that there was a source of HCl other than impurity reactions.

(iii) *Mechanism.* The detailed mechanism of H₂SO₄ formation is unknown. A possible pathway from ClSO₂ to H₂SO₄ is the following sequence:



An alternative to reaction (10), namely,

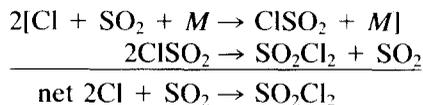


followed by (11), is unsatisfactory because it implies complete regeneration of Cl atoms which should cause the overall rate of reaction, $-d[\text{SO}_2]/dt$, to increase as oxygen pressure increases. Such an increase was not observed. However, other pathways cannot be rule out.

IMPLICATIONS FOR THE VENUS STRATOSPHERE

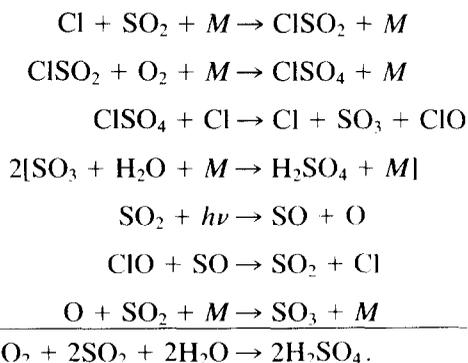
Our experiments have demonstrated the ease with which chlorine atoms can convert SO₂ into sulfuryl chloride and sulfuric acid. There are two main results from incorporating this new chlorine-sulfur chemistry into the model of Yung and DeMore (1982):

(i) Sulfuryl chloride acts as a reservoir species for chlorine in the lower stratosphere. SO₂Cl₂ is considered to be formed by



and it is removed primarily by photolysis. The lifetime of SO_2Cl_2 is of the order 10^4 sec; the role it plays in the chlorine chemistry of Venus is analogous to that of chlorine nitrate in the terrestrial stratosphere.

(ii) A new chemical cycle has been introduced for destroying O_2 and oxidizing SO_2 to SO_3 , eventually leading to sulfuric acid:



This provides an additional mechanism for removing O_2 in the lower stratosphere. Note that chlorine atoms are used only as a catalyst for the combination of SO_2 and O_2 .

Model C of Yung and DeMore (1982) predicts the ratio of CO to O_2 column abundances to be 16. This is in conflict with the lower limit of 170 based on the value for CO of Connes *et al.* (1968), and the upper limit for O_2 of Trauger and Lunine (1983). One way to bring the model results into better agreement with the observations is to postulate more chlorine. On the basis of a large number of runs we concluded that the most reasonable way to bring more chlorine into the model without violating the observational constraints is via SO_2Cl_2 . The results of a model with $f(\text{SO}_2\text{Cl}_2) = 4 \times 10^{-6}$ and $f(\text{HCl}) = 4 \times 10^{-7}$ at the lower boundary. Note that models containing more chlorine than this one would grossly violate the data of Hoffman *et al.* (1980). Discussions of the quantitative aspects of this model are not warranted here, and will be referred to a future publication.

CONCLUSIONS

The results of our laboratory experiments and atmospheric modeling suggest that SO_2Cl_2 may be a major reservoir of chlorine on Venus, and that chlorine atoms can catalyze the oxidation of SO_2 to H_2SO_4 . A photochemical model of Venus is proposed that is characterized by 4 ppm (4×10^{-6}) of SO_2Cl_2 . This model predicts the O_2 abundance and provides substantial opacity in the near UV (300–400 nm). The high-chlorine model has a number of interesting predictions, such as the phase angle dependence for the UV absorber and its time constant for variability, the diurnal variations of CO, and the partitioning of atmospheric chlorine reservoirs. However, we must emphasize the speculative and qualitative nature of this work. Much remains to be explored by further laboratory experimentation, modeling, and comparison with Pioneer-Venus chemical and optical data.

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