# RATE COEFFICIENTS FOR CS REACTIONS WITH O2, O3 AND NO2 AT 298 K

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CS radicals have been produced by photodissociation of CS<sub>2</sub> at 193 nm and their disappearance monitored by LIF. The vibrationally excited CS radicals rapidly relax to CS(v = 0). At 298 K, the rate coefficients for CS(v = 0) reactions with O<sub>2</sub>, O<sub>3</sub> and NO<sub>2</sub> are (2.9 ± 0.4) × 10<sup>-19</sup>, (3.0 ± 0.4) × 10<sup>-16</sup> and (7.6 ± 1.1)× 10<sup>-17</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> respectively. The quenching of CS(A <sup>1</sup>11)<sub>v=0</sub> by He has a rate coefficient of (1.3 ± 0.2) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

## 1. Introduction

Crutzen [1] was the first to recognize the possible importance of OCS and  $CS_2$  as precursors of sulfuric acid aerosols in the stratosphere. The recent detection [2] of these gases in the stratosphere has prompted much discussion of the role of these gases in the global sulfur cycle. The degradation of these molecules by O. OH or photodissociation produces the odd-sulfur radicals CS, SO and HS. Unfortunately, very little kinetic information exists on the reactions of these radicals with atmospheric species. This paper is concerned with the reactions of CS with O<sub>2</sub>, O<sub>3</sub> and NO<sub>2</sub> at 298 K.

No previous work could be found on the reactions of CS with  $O_3$  or  $NO_2$ , but the reaction with  $O_2$  has been examined in a number of previous studies. The work prior to 1975 has been summarized elsewhere [3] and established an upper limit (Callear and Dickson [4], quoted in ref. [5]) of  $3 \times 10^{-18}$  cm<sup>3</sup> molecule $^{-1}$  s $^{-1}$  for the reaction of CS with O<sub>2</sub> at room temperature. In 1975, the reaction of CS with O<sub>2</sub> was studied [6] at both 293 and 495 K and the rate coefficient expression  $k = A \exp(-E/RT) \text{ cm}^3$  $mol^{-1} s^{-1}$  with  $log A = 8.2 \pm 0.5$  and  $E = (3.7 \pm 0.9)$ kcal/mol determined. In this study [6] the  $O_2$  addition was limited to ≪1 Torr and the CS decay was too slow to observe directly. Instead, the production of OCS was measured, and it was assumed that the OCS was produced in the reaction

$$CS + O_2 \rightarrow OCS + O$$
,  $\Delta H = -38.5$  kcal/mole, (1)

and that this was the dominant path in the  $CS-O_2$  interaction and that the alternative pathway

$$CS + O_2 \rightarrow SO + CO$$
,  $\Delta H = -90$  kcal/mole (2)

was of minor importance. Previously Wood and Heicklen [7] had concluded that these two channels occurred in parallel and that their rates were approximately equal over the temperature range 298–415 K. In light of these uncertainties, we have remeasured the rate coefficient for the CS $-O_2$  reaction using  $O_2$ pressures up to 760 Torr with direct monitoring of the CS disappearance by LIF.

#### 2. Experimental

The apparatus for these measurements has been fully described elsewhere [8]. Briefly, it involves the use of an excimer laser to produce CS by 193 nm photodissociation of CS<sub>2</sub> ( $\sigma \approx 2 \times 10^{-16}$  cm<sup>2</sup>) [9]. Only  $\leq 1$  mJ of 193 nm radiation traversed the photolysis cell. The CS was monitored by LIF using an Nd : YAG-dye laser system with rhodamine 610 (basic solution) whose output, after doubling, was Raman shifted in H<sub>2</sub>. The first anti-Stokes output was used to excite fluorescence from the v'' = 0 level of CS using the (0, 0) band of the CS(A <sup>1</sup>Π  $\leftarrow$  X <sup>1</sup>Σ<sup>+</sup>) system at 257.7 nm. Total available laser energy was Volume 102, number 1

0.1-0.2 mJ/pulse in a pulse of  $\approx 5 \text{ ns}$  duration with a bandwidth of  $\approx 0.5 \text{ cm}^{-1}$ . The resulting fluorescence was detected with an RCA C31034 photomultiplier attached to a 1/4 m monochromator. The photomultiplier output passed to a boxcar and then to a chart recorder. The time delay between the two lasers could be varied in order to determine the temporal behavior of the CS produced by the excimer laser. Fluorescence in the (0,0), or (0,1) band at 266.4 nm, was used to monitor the CS decay. For some of these measurements, because of the very long lifetime of CS, the lasers were operated at 5 Hz.

The CS<sub>2</sub> ("Baker Analyzed" Reagent) was either used directly from a reservoir containing the liquid (vapor pressure 350 Torr at 298 K) or, for the high pressure experiments, used as an  $\approx 5\%$  mixture in helium. O<sub>3</sub> concentration was measured by 253.7 nm absorption in a 10 cm cell prior to the gases entering the photolysis cell. The other gases were supplied by Matheson Gas Products and were used without further purification. In all experiments gases were flowed through the cell which was evacuated with either a small rotary pump (gas residence time  $\approx 20$  s) or a diffusion pump.

## 3. Results and discussion

Fig. 1 shows a typical laser-excitation spectrum of the CS A  $^{1}\Pi$ -X  $^{1}\Sigma^{+}$  (0,0) transition recorded with  $\approx$ 5 mTorr of CS<sub>2</sub> in the photolysis cell. A very similar spectrum has been reported previously [10]. Similar spectra were recorded for the (1,1), (2,2) and (3,3)bands. The vibrational energy distribution of the CS produced by 193 nm photodissociation of CS<sub>2</sub> has been studied previously [11,12] and excitation up to at least v'' = 7 has been observed [11]. In order to study kinetics of CS in its ground vibrational state it was necessary to understand the effect of these vibrationally excited states. Measurements on the v'' = 1level (and a few observations on higher v'' levels) determined that they disappeared in <2 ms and correlated with an increase in the CS(v''=0) population over the same time interval. Such fast vibrational relaxation (much faster than the infrared emission lifetime) has been observed before [13] and attributed to interaction with atomic sulfur giving vibrational relaxation about every collision. Support for that



Fig. 1. Laser excitation spectrum of CS A  ${}^{1}\Pi - X {}^{1}\Sigma^{+}(0,0)$  transition with fluorescence monitored on the (0,0) band with a bandpass of  $\approx 2$  nm. Dye laser bandwidth  $\approx 0.5$  cm<sup>-1</sup>, 2  $\mu$ s between excimer and dye laser pulses, CS<sub>2</sub>  $\approx 5$  mTorr.

viewpoint came from two observations. Firstly, the decay rate of CS(v'' > 0) was increased by increasing the excimer energy (and hence the concentration of the photolytic products CS and S), and, secondly, the addition of  $O_2$  gave some increase in the lifetime. This latter observation can be explained by the removal of S atoms by the fast reaction ( $k = 2.2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) [3]

$$S + O_2 \rightarrow SO + O$$
,  $\Delta H = -5.5$  kcal/mole. (3)

Even with the S atoms removed, the short lifetime of CS(v'' > 0) indicates that other species are efficient at vibrational relaxation.

After this initial increase in the CS(v'' = 0) level was complete in a few milliseconds, the CS decay was observed to have two stages. An initial (persisting for  $\approx 20$  ms) stage of more rapid decay followed by a very slow decay. The initial faster section was attributed to diffusion and possible interaction with other transient species and all the kinetic data to be discussed was determined from the effect of added gas on the decay of the CS in the 20–200 ms time interval.



Fig. 2. Decay rate of the CS radical versus  $O_2$  and He addition.  $CS_2 \approx 5$  mTorr.

The CS decay rate as a function of added  $O_2$  is shown in fig. 2. These measurements were made with two different grades of  $O_2$ , 99.6 and 99.99% to be sure that the observed CS removal was due to reactions (1) and (2) and not an impurity in the  $O_2$ . Fig. 2 also shows the decay in the absence of  $O_2$  with only He as the buffer gas. The CS decay does not show any dependence on the He pressure. The slope of the line through the oxygen data gives a rate coefficient of  $(2.9 \pm 0.4) \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the combination of reactions (1) and (2) at 298 K where the error bar is  $\pm 2\sigma$  from the least-squares fitting procedure. Within the combined experimental errors this is in agreement with the only previous measurement [6] which predicts a rate coefficient of



Fig. 3. Decay rate of the CS radical versus O<sub>3</sub> addition at various helium pressures. CS<sub>2</sub>  $\approx$  5 mTorr.

 $(4.8 \pm 1.8) \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. Furthermore, this agreement verifies that reaction (1) is the dominant path and (2) must be of minor importance.

Similar measurements with  $O_3$  are shown in fig. 3. In this case  $O_3$  additions were limited to <1 Torr because of absorption of the dye laser beam by  $O_3$ . The results were made at a number of helium buffer pressures and show no dependence over the 50–300 Torr range. The slope of the line in fig. 2 gives a rate coefficient of  $(3.0 \pm 0.4) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> where the error bar is  $\pm 2\sigma$  from the least-squares fitting procedure. Presumably the reaction is

$$CS + O_3 \rightarrow OCS + O_2$$
,  $\Delta H = -132 \text{ kcal/mole.}$  (4)

A few measurements were also made with NO<sub>2</sub> and are shown in fig. 4. The slope of the line gives a rate coefficient of  $(7.6 \pm 1.1) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> where the error limits are  $\pm 2\sigma$  from the leastsquares fitting procedure. The likely reaction is

$$CS + NO_2 \rightarrow OCS + NO$$
,  $\Delta H = -107 \text{ kcal/mole.}(5)$ 

In the course of this study the effect of He on the  $CS(A^{1}\Pi)_{\nu'=0}$  emission lifetime was also measured. The results are shown in fig. 5 and give  $(1.3 \pm 0.2) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $\pm 2\sigma$  error bar) for the removal of  $CS(A^{1}\Pi)_{\nu'=0}$  by He. This must involve collisional transfer into the neighboring triplet levels



Fig. 4. Decay rate of the CS radical versus NO<sub>2</sub> addition with He = 24 Torr. CS<sub>2</sub>  $\approx$  5 mTorr.

[14]. This mechanism has also been used [15] to explain observations of long-lived CS(A <sup>1</sup>\Pi) emission in electron beam excited CS<sub>2</sub> and OCS. Electronic quenching of CS(A <sup>1</sup>\Pi) by He has also been invoked by Marcoux et al. [16]. Their results can be used to infer that 9 Torr of He give  $\approx 10\%$  quenching of



Fig. 5. Decay rate of CS A  ${}^{1}\Pi(v'=0)$  versus He addition. CS<sub>2</sub>  $\approx$  5 mTorr.

 $CS(A^{1}\Pi)_{\nu'=0}$  and hence  $k(He) \approx 1.7 \times 10^{-12} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> in good agreement with the present measurement.

Because of the very slow rate coefficients found for the removal of CS by  $O_2$ ,  $O_3$  and  $NO_2$  consideration must be given to the possibility that other species, generated by the initial photodissociation or in subsequent reactions, are contributing to the removal of CS. In particular, the fast reaction with atomic oxygen

$$CS + O \rightarrow CO + S$$
,  $\Delta H = -84$  kcal/mole,

$$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [3,5]$$
 (6)

could be involved. This can be ruled out in all three systems because of the fast removal of  $O({}^{3}P)$  by  $O + O_2 + O_2$  in the oxygen system and by its reaction with NO<sub>2</sub> and O<sub>3</sub> in the other two systems.

Reaction with any SO formed can also be excluded CS + SO  $\rightarrow$  CO + S<sub>2</sub>,  $\Delta H = -62$  kcal/mole,

$$\rightarrow$$
 OCS + S,  $\Delta H = -33$  kcal/mole, (7)

because of the short lifetime of SO in all these systems. It appears, therefore, that transient species generated in the initial photodissociation or in subsequent reactions can be ruled out as contributors to the observed reactions.

Although the rate of the CS- $O_2$  reaction has only been measured at 298 K in this study, if the temperature dependence measured previously [6] is correct, then the major loss of CS in the lower stratosphere (15-25 km) will be by reaction with  $O_2$  rather than  $O(^{3}P)$ . Using model atmosphere information [17] and the earlier kinetic expression [6], the CS lifetime increases from 30 to 90 s over the 15-25 km region.

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