Abstract. The rate of reaction of OH with CS₂ to form OCS by reaction (1) has been measured through observation of 0 k CS following 254 nm photolysis of mixtures of H₂O₂ with ¹⁸CS₂. The OH concentrations have been monitored through simultaneous measurement in the same cell of either (a) the oxidation of CO to CO₂, or (b) the removal of a hydrocarbon such as C₃H₈ or iso-CH₁₀. The upper limit for the formation of OCS based on (a) corresponds to a rate constant k₁ < 0.3 x 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹. Other chemical reactions in the system have led to the formation of both CO and CO₂, indicating the existence of a complex combination of reactions such that the observed OCS need not have been formed by (1).

The rate of reaction (1) is sufficiently slow that it is neither an important atmospheric sink for CS₂ nor an important source for atmospheric OCS. The reaction of OH with OCS has not been measured in these experiments, but by analogy with k₁ it is probably not an important atmospheric sink for OCS nor an important source of SO₂.

Introduction

The discovery that both CS₂ (Sandals and Penkett, 1977) and OCS (Hanst et al., 1975; Maroulis et al., 1977) are present in tropospheric air at the level of ~ 10⁻¹⁰ by volume has produced considerable interest in both their sources and sinks (Crutzen, 1976; Sze and Ko, 1979a, b; Logan et al., 1979; Rowland, 1979; Turco et al., 1980). Neither of these compounds undergoes direct solar photodecomposition in the troposphere, although CS₂ does absorb in the near ultraviolet region between 290-380 nm. However, a recent report of rapid, homogeneous gas phase reactions of these molecules with OH radicals (Kurylo, 1978) would represent an important tropospheric sink for CS₂ and an important source for atmospheric OCS. The reaction of OH with OCS has not been measured in these experiments, but by analogy with k₁ it is probably not an important atmospheric sink for OCS nor an important source of SO₂.

The reported values of the rate constant for OH reaction with CS₂ show little agreement with one another, as summarized in Table 1. Comparable disagreement exists for the measurements of the rate constant for OH reaction with OCS (Kurylo, 1978; Atkinson et al., 1978; Wine, Shah and Ravishankara, 1980). In most of these studies, evidence has been sought only for the rate of disappearance of OH, with no observation of removal of its reaction partner (CS₂ or OCS) or formation of the stable product (OCS or CO₂). No direct evidence exists for rearrangements in the sulfur systems of the kind proposed for (1) and (2) (Kurylo, 1978; Cox and Sheppard, 1980), but a similar rearrangement has been suggested to explain the observed isotopic scrambling of ¹⁸O in the reaction of ¹⁸OH with CO₂ (Kurylo and Lauffer, 1979).

We have sought confirmation of the formation of OCS in the reaction of OH with CS₂, as required by (1), through direct product analysis. Our experiments have been carried out with radioactive ¹⁴CS₂, assaying for OCS by radio gas

<table>
<thead>
<tr>
<th>Authors</th>
<th>Rate Constant</th>
<th>cm³ molecule⁻¹ sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atkinson et al., 1978</td>
<td>&lt; 7</td>
<td>x 10⁻¹⁴</td>
</tr>
<tr>
<td>Kurylo, 1978</td>
<td>18.5±3.4</td>
<td>x 10⁻¹⁴</td>
</tr>
<tr>
<td>Cox and Sheppard, 1980</td>
<td>43 ±16</td>
<td>x 10⁻¹⁴</td>
</tr>
<tr>
<td>Wine et al., 1980</td>
<td>&lt; 0.15</td>
<td>x 10⁻¹⁴</td>
</tr>
<tr>
<td>This work</td>
<td>&lt; 0.3</td>
<td>x 10⁻¹⁴</td>
</tr>
</tbody>
</table>

TABLE 1. Measurements of the Rate Constant for the Reaction of OH with CS₂ to Form OCS.
H$_2$O$_2$ were cooled to 77K, and CO (plus O$_2$ formed during photolysis) were diverted through a glass bead trap at 77K to prevent the formation of CO$_2$, OCS, and CS$_2$ in that order. After photolysis, the samples containing CO, CS$_2$ and separated CO$_2$, OCS and CS$_2$ in that order. The rate constants for these reactions are

\[
\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \quad (5)
\]

\[
\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R} \quad (6)
\]

all convenient for relative measurements of reactions competing with (1) if the latter is proceeding at the rapid rates reported by Kurylo (1978) or by Cox and Sheppard (1980). Our analytical technique is capable of detecting the formation of about 1 part in $10^5$ of $^{13}$CS in $^{13}$CS$_2$, and of course OCS formed from any other carbon source would not be labeled with $^{13}$C. Earlier laboratory experiments have shown that the molecule OCS can be readily formed under experimental conditions in which both S atoms and CO are present in minuscule concentrations (Lee et al., 1964).

## Experimental

### Chemicals.

Hydrogen peroxide was concentrated to > 95% by room temperature distillation of 90% aqueous H$_2$O$_2$ (FMC Corporation), followed by storage at 77K. The radioactive $^{13}$CS$_2$ was obtained from Amer sham with a specific radioactivity of 55 mCi/m mole, and diluted with chromatography CS$_2$ (Matheson, Coleman and Bell) to a specific activity of 24 mCl/m mole. This mixture contained $^{13}$CS as an impurity (0.07% of total $^{13}$C activity) and was therefore purified by preparative gas chromatography. The CS$_2$ + $^{13}$CS$_2$ mixture (designated below as $^1$CS$_2$) used in photolysis contained $< 0.001$% of the total $^{13}$C in the forms of $^{13}$CO, $^{13}$CO$_2$ and $^{13}$OCS. Carbon dioxide (Matheson Research grade) was purified by passage through a glass bead trap at 77K. The other gases were used as furnished: C$_3$H$_0$, Matheson, Instrumental Grade; iso-CH$_10$, Phillips Research Grade.

### Light Sources and Photolysis Cells.

Two photolysis arrangements were used. The initial experiments were carried out in a 170 cm$^3$ quartz photolysis cell withsuprasil windows, and a 1000-watt Xenon Mercury arc lamp operated through a Bausch & Lomb monochromator for irradiation at 254 nm. All of the experiments listed in Table 2 were performed with a 207 cm$^3$ Vycor 791 cell and an Ultraviolet Products Mineralight R-52 lamp for higher intensity at 254 nm.

### Analytical Procedure.

After 3-6 hours of photolysis, the samples containing CO, $^1$CS$_2$ and H$_2$O$_2$ were cooled to 77K, and CO (plus O$_2$ formed during photolysis) were transferred to a silica gel chromatographic loop at 77K. The fraction condensable at 77K was then analyzed by radio gas chromatography (Lee et al., 1962; Iyer and Rowland, 1973) on a 5-foot Chromosorb-102 column which separated CO$_2$, OCS and CS$_2$ in that order. After the elution of the OCS peak, the flow stream was diverted through a glass bead trap at 77K to prevent proportional counter contamination from the very highly radioactive $^1$CS$_2$. The $^{13}$CS$_2$ content was separately assayed with a small aliquot, normally containing only about $1/20$ of the sample. The contents of the silica gel loop were analyzed on a 20-foot charcoal column which separates CO from O$_2$ and N$_2$. Similar procedures were used for samples containing iso-C$_3$H$_6$ or C$_3$H$_0$ in place of CO. The Chromosorb column was operated at 333K for the separation of OCS from C$_3$H$_0$, and at 358K for the separation of iso-C$_3$H$_6$ and OCS.

A typical filling of the cell to 50 torr pressure of $^1$CS$_2$ corresponded to approximately $4 \times 10^3$ counts min$^{-1}$ measured at a flow rate of 30 ml per minute through the counter.

### Results

For each experiment, a percentage conversion of $^{13}$CS$_2$ to $^1$CS$_2$ can be measured and compared with the percentage change of CO to OCS or percentage removal of CS$_2$. Typical data for one of three of these types of experiments are summarized in Table 2. In each case, the presence of other oxidized forms of $^{13}$C ($^{13}$CO and $^{13}$CO$_2$) demonstrates that a variety of chemical reactions are occurring in these photolysis systems, and the observation of $^{13}$CS$_2$ therefore does not demonstrate that reaction 1 must be occurring, since other reaction routes could be forming $^1$CS$_2$ as well as $^{13}$CO and $^{13}$CO$_2$. Macromolecular amounts of CO$_2$ and OCS were always observed as well. The experimental observations of yields of $^{13}$CS$_2$ are converted into upper limits for the absolute rate constant for k$_1$ through the known reaction rate constants for k$_5$ (NASA, 1979) and k$_6$ (Gorse and Volman, 1974; Butler et al., 1978).

### Discussion

Our experiments have consistently shown that $^{13}$CS$_2$ is not formed by the reaction of OH with CS$_2$ at any rate comparable to the rates reported by Kurylo (1978) and by Cox and Sheppard (1980). A conservative upper limit from six separate experiments with CO as the monitor at 298K is $k_1 < 0.3 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, with one experiment at 313K putting the limit at 0.1 $\times 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

Equivalent results were obtained with both light sources. The experiments with C$_3$H$_0$ and iso-C$_3$H$_6$ as monitors also show $k_1$ to be much less than measured by Kurylo (1978) and by Cox and Sheppard (1980). In all cases, other chemical processes than (1) are possible leading to the formation of $^{13}$CS$_2$, so that there is no requirement that $k_1$ be other than zero. Since reaction (4) is endothermic, our upper limit on $k_1$ is also an upper limit for the overall reaction rate of OH with CS$_2$. The insertion of this upper limit into various atmospheric models leads to the conclusions that:

(a) CS$_2$ is not an important precursor for OCS in the atmosphere; and (b) reaction with OH is not an important route for the removal of CS$_2$ from the earth's atmosphere.

Several of the experimental measurements summarized in Table 1 are based upon comparative OH removal rates in the absence and presence of added CS$_2$ during the flash photolysis of H$_2$O, without measurement of concentration changes for
TABLE 2. Typical Experimental Results in the 254 nm Photolysis of H$_2$O$_2$-CS$_2$ Mixtures

<table>
<thead>
<tr>
<th>Pressure, torr</th>
<th>0</th>
<th>0.9(a)</th>
<th>1.4</th>
<th>1.8</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>0</td>
<td>0.53</td>
<td>0.56</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>*S$_2$CO</td>
<td>0</td>
<td>0.2</td>
<td>0.21</td>
<td>0.15</td>
<td>0.166</td>
</tr>
<tr>
<td>CO</td>
<td>20.1</td>
<td>18.6</td>
<td>20.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$H</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{10}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Oberved Radioactivity in Product, % of Total $^{14}$C

<table>
<thead>
<tr>
<th>14CO</th>
<th>0.084</th>
<th>0.936</th>
<th>2.09</th>
<th>(n.m.)</th>
<th>0.589</th>
</tr>
</thead>
<tbody>
<tr>
<td>14CO$_2$</td>
<td>0.006</td>
<td>0.069</td>
<td>0.63</td>
<td>0.118</td>
<td>0.053</td>
</tr>
<tr>
<td>13CO</td>
<td>0.009</td>
<td>0.021</td>
<td>0.15</td>
<td>0.106</td>
<td>0.066</td>
</tr>
<tr>
<td>$%$CO + CO$_2$</td>
<td>1.2</td>
<td>3.1</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$%$RH removed</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.3</td>
<td>17.4</td>
</tr>
<tr>
<td>$\Delta$(Monitor)/$\Delta$(OCS)</td>
<td>k$_5$/k$_1$</td>
<td>-</td>
<td>150</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>k$_1$ x 10$^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>170</td>
<td>260</td>
</tr>
</tbody>
</table>

(a) Temperature 313 K for this experiment; others at 296 K.

We believe that plausible alternate mechanisms exist for the increased disappearance rate for OH found by Kurylo (1978) and for CS$_2$ by Cox and Sheppard (1980), including the possibility of OH reaction with fragments from CS$_2$ photolysis, i.e., OH + S and OH + CS. The latter combination may be the pathway by which OCS is formed in our experiments, and for the OCS found by Cox and Sheppard.

The use of a very different kinetic measurement technique in our experiments has the advantage that our sensitivities to impurities are unlike those encountered in flash-photolysis OH-disappearance measurements. In particular, the reaction of OH with trace levels of H$_2$S has no important consequence in our system, except a lowering of the concentration of OH radicals available for reactions (1), (5) and (6). Since no $^{14}$C is involved in that reaction, no $^{14}$CS can be formed. On the other hand, the reaction of OH with H$_2$S with a rate constant of 3 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ (NBS, 1977) is sufficiently rapid that an H$_2$S/CS$_2$ ratio of 10$^{-3}$ in a flashed CS$_2$/H$_2$O$_2$ mixture can explain an apparent rate constant of 3 x 10$^{-15}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for the disappearance of OH in a CS$_2$ system.

While we have not performed any experiments here which relate to the reaction of OH with OCS, the positive evidence for reaction (2) and/or (3) with OCS has been obtained by Kurylo (1978) by the same technique used for gathering the CS$_2$ data of Table 1. With OCS as the reactant for OH, Cox and Sheppard have reported that essentially no reaction is observed, in marked contrast to their results with CS$_2$. We conclude that the reaction of OH with OCS in all probability does not proceed at a rapid rate, and therefore that: (a) reaction with OH is not an important tropospheric sink for OCS; and (b) OCS is not an important tropospheric precursor of SO$_2$. The ultraviolet photolysis of OCS in the stratosphere can be a source of SO$_2$ through the subsequent reactions of the atomic S released during photodecomposition (Crutzen, 1976).

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References


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