

## ELEMENTARY REACTIONS OF ATMOSPHERIC SULFIDES

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The presence of  $\text{SO}_2$  and sulfate aerosols in the earth's troposphere and stratosphere is of great concern due to their impact on human health, agriculture, materials degradation etc. This recognition has focused attention on the photolytic and kinetic processes which mechanistically describe their formation. In the latter category are included reaction rate studies of the oxidative conversion of atmospheric sulfides to  $\text{SO}_2$  since such reactions can be rate determining in the global sulfur cycle.

The suggestion that dimethyl sulfide (DMS) plays an important role in the natural transport of sulfur to the atmosphere has prompted an investigation of its rate of reaction with hydroxyl radicals. Similarly, the detection of carbonyl sulfide (OCS) at appreciable mixing ratios in both troposphere and stratosphere has suggested a kinetic study of the  $\text{OH} + \text{OCS}$  reaction. An investigation of the reaction of OH radicals with carbon disulfide ( $\text{CS}_2$ ) was deemed necessary to test the validity of speculation regarding production of OCS via  $\text{CS}_2$  oxidation. This latter compound has been detected in wide distribution in coastal and ocean waters but not as yet in the ambient atmosphere. Finally, calculations of the atmospheric lifetime of OCS indicate it to be the principle stratospheric sulfur compound and have solicited interest in its potential coupling with the  $\text{ClO}_x$  cycle via Cl atom reaction.

Studies of the aforementioned reactions were performed using the flash photolysis resonance fluorescence (FPRF) technique (apparatus schematized in Fig. 1). The flash photolysis of water vapor provided the source of OH radicals while  $\text{CCl}_4$  served as photolytic precursor of Cl atoms. A microwave flow discharge resonance lamp (1 torr He saturated with water vapor for OH detection; 1 torr Ar containing 0.1%  $\text{Cl}_2$  for Cl measurement) was used to excite a small fraction of the radicals or atoms. The radical or atomic emission resonantly scattered was detected photometrically utilizing standard pulse counting and multichannel scaling data accumulation techniques. Reactant concentrations were always much larger than the radical or atom concentration to insure pseudo-first-order kinetic behavior. Experiments involving flash energy variation tested the presence of secondary reactions for radical or atom production and/or removal. Mixtures containing the OH or Cl precursor, the reactant, and an inert diluent were slowly flowed through the temperature controlled reaction cell to insure minimal reactant depletion or product buildup.

The  $\text{OH} + \text{DMS}$  study (performed over the temperature range 273 to 400 K) exhibited no complications due to secondary reactions or reactant photolysis over a wide range of experimental conditions. Experiments conducted at 296 K with both Ar and  $\text{SF}_6$  diluents should no evidence for a pressure dependence of the rate constant. The data (combined with the results of another recent study) can be fit to the Arrhenius expression

$$k_{\text{OH}+\text{DMS}} = (6.08 \pm 2.54) \times 10^{-12} \exp[(134+135/T) \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}]$$

This fit is indistinguishable from an Arrhenius expression with a zero activation energy on  $T^{-1/2}$  pre-exponential factor. The present study affords no direct evidence for a mechanistic assignment of this reaction. Inference drawn from thermochemical arguments or rate constant comparisons is indecisive regarding OH addition vs H atom abstraction and direct mechanistic studies are needed.

Early experiments on the OH + OCS system were complicated by secondary chemistry stemming from OCS photolysis. By increasing the  $[\text{H}_2\text{O}]/[\text{OCS}]$  ratio and lowering the flash intensity, such complications were overcome and the OH decay exhibited the expected pseudo-first-order behavior. The rate constant thereby obtained at 296 K was

$$k_{\text{OH}+\text{OCS}} = (5.66 \pm 1.21) \times 10^{-14} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

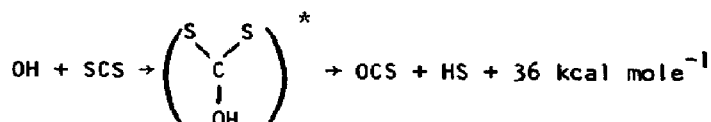
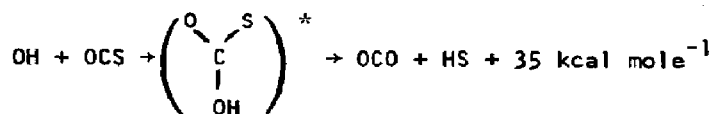
The OH + CS<sub>2</sub> investigation was conducted under the final experimental conditions of the OCS study. No complications due to secondary chemistry were observed and a 296 K rate constant was measured.

$$k_{\text{OH}+\text{CS}_2} = (1.85 \pm 0.34) \times 10^{-13} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

Assuming a uniform tropospheric OH concentration of  $4.1 \times 10^5 \text{cm}^{-3}$  we can calculate reaction lifetimes of 3, 150, and 500 days for DMS, CS<sub>2</sub>, and OCS respectively. Thus, it is expected that DMS (and to a lesser extent CS<sub>2</sub>) will be oxidized during tropospheric transport. The slower rate of oxidation for OCS should permit its transport to and participation in the chemistry of the stratosphere.

The rate constants measured for OCS and especially CS<sub>2</sub> are thermochemically inconsistent with an endothermic S atom abstraction process ( $\Delta H_{\text{OH}+\text{OCS}} \sim +2 \text{ kcal mole}^{-1}$ ;  $\Delta H_{\text{OH}+\text{CS}_2} \sim +23 \text{ kcal mole}^{-1}$ ).

However an exothermic addition path can be written for each reaction



To test this addition hypothesis we performed experiments on a system containing <sup>18</sup>O and unlabeled CO<sub>2</sub>. Substantial amounts of <sup>18</sup>OCO were detected (between 10 and 20% of the <sup>18</sup>O) thereby establishing the

validity of the addition/exchange hypothesis.  $\text{CO}_2$  was chosen in these experiments to avoid complications due to  $\text{OCS}$  or  $^{13}\text{CS}_2$  photolysis. Extrapolation of these results to the sulfide systems indicate possibility of direct carbon oxidation with subsequent  $\text{SO}_2$  and sulfate formation via SH reaction chains. Moreover this mechanism provides for direct oxidative conversion of  $\text{CS}_2$  into  $\text{OCS}$  thereby yielding an additional source for this ubiquitous atmospheric species.

At the time of this writing kinetic experiments on the  $\text{Cl} + \text{OCS}$  reactions are in progress. Results should be available at the time of this presentation.

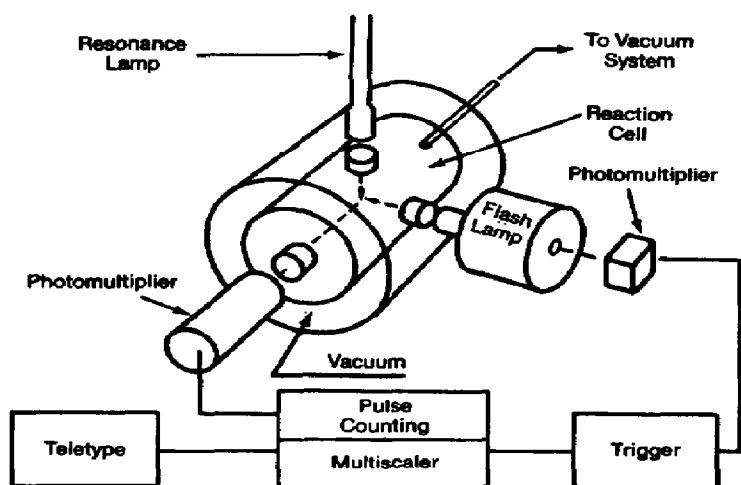


Figure 1. Flash Photolysis Resonance Fluorescence Apparatus