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## A Flash Photolysis-Resonance Fluorescence Kinetics Study of the Reaction $S(^3P) + OCS$

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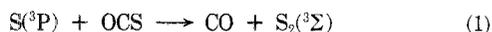
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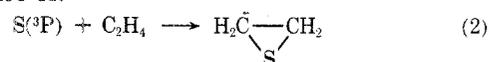
Using the technique of flash photolysis-resonance fluorescence, the reaction of ground-state atomic sulfur with carbonyl sulfide has been investigated over the temperature range 233–445°K. Over this temperature range, the experimental data were fitted to an Arrhenius equation of the form  $k_1 = (1.52 \pm 0.20) \times 10^{-12} \exp(-3.63 \pm 0.12 \text{ kcal/mol}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . A comparison of these results with previous investigations on this reaction system is presented.

### Introduction

Carbonyl sulfide, OCS, has been employed extensively as a photolytic source of atomic sulfur in kinetic studies of ground-state sulfur atom reactions.<sup>2-19</sup> Nevertheless, there appear to be no direct measurements of the rate constant for the reaction of  $S(^3P)$  with the parent molecule, *i.e.*



In a spectroscopic study reported by Basco and Pearson,<sup>14</sup> an effort was made to evaluate  $k_1$  by measuring the rate of formation of  $S_2(^3\Sigma)$ , following the flash photolysis of OCS. However, the value obtained for  $k_1$  was ambiguous since evidence was found which indicated that both bimolecular and termolecular reactions could have been involved in the formation of  $S_2(^3\Sigma)$ . In a recent product analysis study at 298°K, Breckenridge and Taube<sup>13</sup> estimated a lower limit for  $k_1$  of  $1.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , but suggested that the actual value of the rate constant could be ten times larger ( $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ). There have also been two recent relative measurements of the rate constant for reaction 1 in which reaction 2 was taken as the reference reaction. Gunning and Strausz<sup>6</sup> obtained a value of 25 for  $k_2/k_1$ , while Jakubowski, *et al.*,<sup>12</sup> have reported a value of 83 for the rate constant ratio at 298°K.



The activation energy for reaction 1 has been estimated as  $\sim 6 \text{ kcal/mol}$  by Kondratiev<sup>18</sup> in a study of the photooxidation of OCS. However, reaction 1 was not

studied directly, but as part of a complex mechanism and some assumptions were made in obtaining the quoted activation energy for  $k_1$ .

In this paper we report a direct determination of the rate parameters for the reaction of  $S(^3P)$  with OCS using the flash photolysis-resonance fluorescence technique. Rate measurements were made over a temperature range 233–445°K and over a wide range in the experimental parameters. These included an eight- to tenfold variation in the OCS pressure, the flash intensity, and the total pressure.

### Experimental Section

The experimental technique has been described in detail previously;<sup>2-4</sup> and hence, only a brief summary will be given here. This method involves the flash photolysis of OCS to produce atomic sulfur and subsequent monitoring of the kinetic decay of the sulfur atom concentration *via* atomic fluorescence. Typical sulfur atom concentrations were in the range of  $10^{10}$ – $10^{11}$  atoms/cc.<sup>4</sup> As before, Suprasil windows were used on both the photolytic flash lamp and the atomic sulfur resonance lamp to exclude radiation of wavelength less than about 1600 Å. A microwave discharge in a mixture of  $H_2S$  (0.1%) in He served as the source of the atomic sulfur resonance radiation.

In these experiments, sulfur atoms were generated in the central region of a reaction cell in an excess of OCS and buffer gas (Ar). Therefore, in addition to reaction with OCS, atomic sulfur was lost due to diffusion out of the reaction sampling zone. Since the OCS concentration was large compared to the initial S atom concentration,

TABLE I: Rate Data for the Reaction of S(<sup>3</sup>P) with OCS

Temp, °K	OCS, mTorr	Ar, Torr	Flash energy, J	First order, $k^* \times 10^{-2}, \text{sec}^{-1}$	Bimolecular rate constant, $k_1, \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$
236	100	20	31	0.29	
235	100	100	45	0.26	
233	400	100	24	0.29	
233	800	100	24	0.42	
231	100	200	29	0.33	
233	800	200	24	0.51	$(5.6 \pm 3.12) \times 10^{-16}$
298	100	20	31	0.37	
298	400	20	22	0.70	
298	800	20	24	1.10	
298	100	100	8	0.35	
298	100	100	20	0.32	
298	100	100	39	0.33	
298	100	100	80	0.35	
298	400	100	14	0.73	
298	800	100	14	1.18	
298	1000	100	14	1.40	
298	100	200	31	0.31	
298	400	200	22	0.71	
298	800	200	22	1.13	$(3.48 \pm 0.39) \times 10^{-15}$
378	100	20	34	0.72	
377	400	20	29	1.48	
378	800	20	24	2.59	
378	100	100	31	0.53	
379	400	100	22	1.34	
379	800	100	36	2.67	
378	100	200	31	0.61	
377	400	200	29	1.44	
378	800	200	24	2.75	$(1.18 \pm 0.08) \times 10^{-14}$
443	100	20	45	1.04	
445	800	20	24	4.67	
443	100	100	45	0.89	
445	400	100	36	2.52	
445	800	100	36	4.68	
443	100	200	45	0.96	
445	800	200	24	4.79	$(2.52 \pm 0.16) \times 10^{-14}$

<sup>a</sup> The uncertainties in these rate constants were obtained by determining the maximum and minimum slopes that could be drawn within the error bars on the individual points in Figure 1.

the decay of S(<sup>3</sup>P) due to reaction 1 is given by

$$\ln [S_0]/[S] = k_1[\text{OCS}]t \quad (\text{I})$$

The rate of diffusion is also given by a first-order law,<sup>20</sup> and thus, for this process

$$\ln [S_0]/[S] = k_d t \quad (\text{II})$$

where  $k_d$  depends on the temperature, the total pressure, and the type of inert gas. Combining the above equations then yields an expression for the observed atom decay given by eq III. The quantity  $\{k_1[\text{OCS}] + k_d\}$  was deter-

$$\ln [S_0]/[S] = \{k_1[\text{OCS}] + k_d\}t \quad (\text{III})$$

mined experimentally as  $k^*$ , the pseudo-first-order rate coefficient. The bimolecular rate constant,  $k_1$ , was derived from the slope of a plot of  $k^*$  vs. [OCS]. The intercept of this plot gave  $k_d$ .

## Results

The results of experiments carried out over a temperature range 233–445°K are given in Table I. It can be seen that, within the experimental uncertainty, the first-order rate constant is independent of the total pressure with the possible exception of the value derived at the lowest temperature studied, 233°K. Figure 1 shows a plot of  $k^*$  as a function of the OCS pressure for the four temperatures studied. The uncertainty in the individual  $k^*$  data was

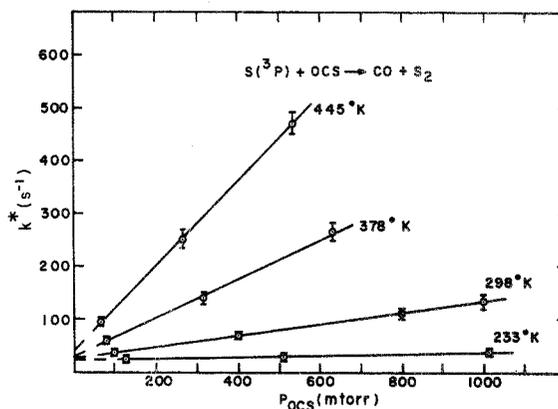


Figure 1. Plot of  $k^*$ , the pseudo-first-order rate coefficient for S(<sup>3</sup>P) + OCS plus diffusion, vs.  $P_{\text{OCS}}$ . In this figure  $P_{\text{OCS}}(T^{\circ}\text{K}) = P_{\text{OCS}}(298^{\circ}\text{K}) \times T^{\circ}\text{K}/298^{\circ}\text{K}$  to facilitate conversion of the derived rate constant to molecular units, e.g.,  $k_1 + \text{OCS}(T) = \text{slope}(T) \times 1/3.21 \times 10^{13} \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ .

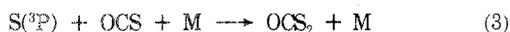
determined to be about  $\pm 10\%$ .<sup>19</sup> The bimolecular rate constants calculated from Figure 1 are also listed in Table I. An Arrhenius plot of these data is shown in Figure 2. A least-squares fit of these data gave the following Arrhenius expression  $k_1 = (1.52 \pm 0.20) \times 10^{-12} \exp(-3.63 \pm 0.12 \text{ kcal/mol}/RT) \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ . The quoted uncer-

tainties are the standard errors<sup>21</sup> calculated from a weighted least-squares treatment of the data over the temperature range 233–445°K. From a consideration of the maximum and minimum slopes which could be drawn through the error bars on each data point in Figure 2, the uncertainty in  $A$  and  $E_{act}$  was determined to be  $\pm 0.55 \times 10^{-12}$  and  $\pm 0.34$  kcal/mol, respectively, for the purpose of extrapolation outside the measured temperature range.

### Discussion and Comparison with Previous Results

In the present study of reaction 1, atomic sulfur was produced by the flash photolysis of OCS in the vacuum uv. The photolytic light source employed for this purpose was of the spark discharge type and, as mentioned in the Experimental Section, the short wavelength cut-off was set at  $\sim 1600$  Å with the use of a Suprasil window. Above this cut-off, several primary photolytic processes are energetically possible leading to the formation of  $S(^3P)$  as well as  $S(^1D)$  and  $S(^1S)$ . It is also energetically possible to produce  $O(^3P) (+CS)$  above 1600 Å; however, the production of atomic oxygen from the vacuum uv photolysis of OCS has been indicated to be of negligible importance even at the LiF cut-off ( $\sim 1050$  Å) in recent studies by Donovan<sup>22</sup> and Stief, *et al.*<sup>23</sup> The fate of the metastable sulfur atoms has been discerned<sup>2a,19</sup> from calculations using recent rate data for the reaction and collisional quenching of these species.<sup>24</sup> For example, in the case of gas mixtures consisting of 100 mTorr of OCS and 100 Torr of Ar, the calculations indicate that the bulk (>95%) of the  $S(^1D)$  and about half of the  $S(^1S)$  formed the flash photolysis of OCS would be deactivated to  $S(^3P)$ .<sup>19</sup> In addition, the lifetimes for these processes are on the order of 10  $\mu$ sec, or less, and, therefore, it may be concluded that under the conditions of the present study only ground-state atomic sulfur,  $S(^3P)$ , was of kinetic significance.

The only previous determinations of the rate constant for reaction 1 were made using either indirect techniques or relative rate measurements. In a flash photolysis-spectroscopic study, Basco and Pearson<sup>14</sup> attempted to determine the value of  $k_1$  from an examination of the rate of formation of  $S_2$ . This system now appears to have been quite complex in that a negative temperature dependence was observed for the rate of formation of  $S_2$ , and the  $S_2$  formation rate data could be fitted to an expression either first or second order in  $[S]$ . They suggested one possibility might be a mechanism involving the termolecular reaction



The results of the present research, however, do not support the importance of reaction 3 since no significant effect on the  $S(^3P)$  decay rate due to total pressure was observed at 298°K or higher temperatures, and the temperature dependence observed in this study was positive. Indeed, Langford and Oldershaw<sup>25</sup> have made several arguments against the importance of reaction 3 in a recent study of  $S_2$  formation from the flash photolysis of OCS in which they present an alternate mechanism that depends on the recombination of  $S(^3P)$  and reactions involving polymeric sulfur but not the  $OCS_2$  species.

In the study of Breckenridge and Taube<sup>13</sup> at 298°K, reaction 1 was assumed to be in competition with the  $S(^3P)$  recombination reaction and a lower limit for  $k_1$  of  $1.7 \times 10^{-16}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$  was thus derived. However, as pointed out earlier, these authors estimated that  $k_1$  was probably much larger, *e.g.*,  $\sim 2 \times 10^{-15}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ . In two other relative rate studies, the rate

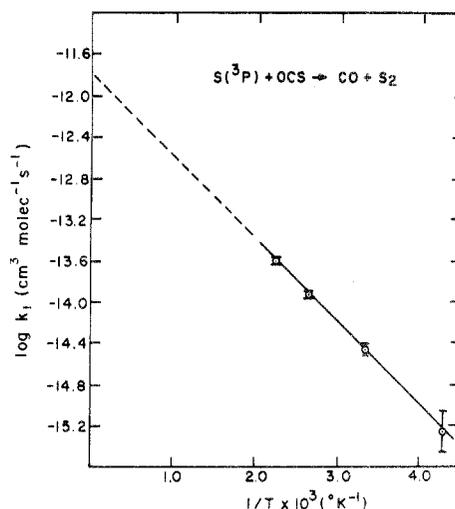


Figure 2. Arrhenius plot of the bimolecular rate constant for the reaction  $S(^3P) + OCS$ .

constant for reaction 1 was measured against that of reaction 2 [ $S(^3P) + C_2H_4$ ]. Combining the value of Donovan, *et al.*,<sup>15</sup> for  $k_2$  ( $1.2 \times 10^{-12}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ ) with the relative rate data of Gunning and Strausz<sup>6</sup> ( $k_2/k_1 = 25$ ), one obtains a value for  $k_1$  of  $4.8 \times 10^{-14}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ . Similarly, taking the relative rate data of Jakubowski, *et al.*<sup>12</sup> ( $k_2/k_1 = 83$ ), a value for  $k_1$  of  $1.4 \times 10^{-14}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$  is obtained. The above values for  $k_1$  are seen to be larger than the present value for  $k_1$  at 298°K by factors of 14 and 4, respectively. On the other hand, combining the value of  $k_2$  obtained by Davis, Klemm, and Pilling<sup>2a</sup> ( $4.97 \times 10^{-13}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ ) with the relative rate of Jakubowski, *et al.*,<sup>12</sup> leads to a value for  $k_1$  that is within a factor of 2 of the present value. Finally, in a shock tube study by Hay and Belford,<sup>26</sup> the value of  $k_1$  was estimated to be  $\sim 1 \times 10^{-12}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$  at 2570°K. Interestingly, this value is seen to agree to within 25% with the value of  $k_1$  extrapolated from the Arrhenius expression derived in the present work.

The Arrhenius parameters obtained in the present study of reaction 1 are  $1.52 \times 10^{-12}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$  for the  $A$  factor and 3.63 kcal/mol for  $E_{act}$ . This activation energy is significantly smaller than that reported by Kondratiev<sup>18</sup> ( $\sim 6$  kcal/mol); but the absence of agreement is not unreasonable considering the scheme used to derive the 6 kcal value. Much better agreement is found in the value of the activation energy calculated by Jakubowski, *et al.*,<sup>12</sup> who used the extended bond energy-bond order method<sup>27</sup> to obtain a value of  $\sim 4$  kcal/mol for  $E_{act}(k_1)$ . The same authors also calculated the "minimum" preexponential factor to be about  $10^{-11}$   $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$  using Benson's method.<sup>28</sup> However, since this method depends upon a number of assumptions concerning the geometry of the transition complex, the results of such calculations are usually considered to be "order-of-magnitude" predictions.

In summary, we have reported the first direct measurement of the activation energy for the reaction of  $S(^3P)$  with the reactant molecule OCS. The measured value of 3.6 kcal/mol differs significantly from the previous experimental estimate of  $\sim 6$  kcal/mol. There is, however, reasonable agreement between approximate theoretical calculations, which give  $\sim 4$  kcal/mol, and the present value for  $E_{act}$  (1).

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## Comparison of the Fluorinations of Uranium Dioxide by Bromine Trifluoride and Elemental Fluorine

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Uranium dioxide powder was fluorinated by gaseous  $\text{BrF}_3$  and  $\text{F}_2$ , separately, in order to compare the characteristics of the two fluorinating agents. The  $\text{BrF}_3$ - $\text{UO}_2$  reaction proceeds under lower temperatures and a lower concentration of the reacting gas than the  $\text{F}_2$ - $\text{UO}_2$  reaction. The temperature dependence of its rate is very small; the apparent activation energy is only 1.6 kcal/mol. In the  $\text{F}_2$ - $\text{UO}_2$  reaction, the production of  $\text{UF}_6$  was not observed below  $390^\circ$ . The rate of this reaction increases remarkably with an increase in temperature; the apparent activation energy for this reaction is 26.0 kcal/mol. In both of these reactions,  $\text{UO}_2\text{F}_2$  is formed as an intermediate, and the further uptake of fluorine in the solid is not observed in either case. The solution from the residue of  $\text{BrF}_3$ - $\text{UO}_2$  reaction contains trace amounts of bromine, which possibly arises by hydrolysis of the  $\text{BrF}_3$  chemisorbed on the solid. Oxygen fluorides were not detected in the  $\text{F}_2$ - $\text{UO}_2$  reaction. The diffusion rate of the reacting gas onto the solid surfaces influences the rates of both reactions. The results indicate that the physical adsorption of  $\text{BrF}_3$  functions as the precursor to its chemisorption, and that the adsorption of fluorine is activated and dissociative.

### Introduction

Bromine trifluoride (mp  $8.8^\circ$ , bp  $127.6^\circ$ ) is readily prepared by direct combination of bromine and fluorine, and has been used as a liquid fluorinating agent or a solvent by many other workers.<sup>1-4</sup> Extensive data on its physical and chemical properties are available.<sup>1-4</sup>

Recently, gaseous  $\text{BrF}_3$  has been used in the author's laboratory for the fluorination of nuclear fuels and fission products. In the series of studies,<sup>5,6</sup> the author has noticed that gaseous  $\text{BrF}_3$  has higher reactivity with such inorganic materials as uranium compounds than  $\text{F}_2$ . For example, gaseous  $\text{BrF}_3$  fluorinates  $\text{UF}_4$  even at  $55^\circ$ ,<sup>5</sup> whereas

Labaton and Johnson have reported that the fluorination of  $\text{UF}_4$  by  $\text{F}_2$  does not proceed below  $220^\circ$ .<sup>7</sup> The reason for this has not been made clear yet. Moreover, details of their reactivities are not obtained from the literature available, because the experimental data are not sufficient or each worker used specimens with different histories of preparation.

The purpose of the present study is to obtain information on the reactivities of  $\text{BrF}_3$  and  $\text{F}_2$ . Uranium dioxide powder was fluorinated by gaseous  $\text{BrF}_3$  and  $\text{F}_2$ , separately, and the reaction rates and processes were studied. On the basis of the results, the difference in reactivity between the two fluorinating agents is discussed.