# Formation of Sulfuric Acid and Sulfur Trioxide/Water Complex from Photooxidation of Hydrogen Sulfide in Solid O<sub>2</sub> at 15 K

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The photooxidation of H<sub>2</sub>S in solid O<sub>2</sub> at 15 K by UV light ( $\lambda$  < 300 nm) gives H<sub>2</sub>O, SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> as stable products which are identified by FTIR spectroscopy. The molecular complexes,  $H_2OSO_2$  and  $H_2OSO_3$ , are also present in significant amounts. The key facile intermediates in photooxidation are probably HS, HO<sub>2</sub>, SO, and HO, but not O atoms. Unlike the photooxidation of H<sub>2</sub>CO in solid O<sub>2</sub>, the H<sub>2</sub>S/O<sub>2</sub> system gives no (HO<sub>2</sub>)<sub>2</sub>, because of the photochemical recoil of the H atom out of the photolysis cage and because HO<sub>2</sub> acts as a strong oxidizer of S-containing species. We observe all of the stable molecular product sets formed in reactions with exothermicity greater than ~90 kcal/mol. A tentative mechanism of  $H_2S$  photooxidation is given.

### Introduction

Homogeneous and heterogeneous oxidation of simple sulfurcontaining compounds has been a subject of much recent interest,<sup>1-4</sup> because of environmental concern for aerosol formation and acid rain. Rapid reaction of H<sub>2</sub>O with SO<sub>3</sub> to form H<sub>2</sub>SO<sub>4</sub> and subsequent hydration of H<sub>2</sub>SO<sub>4</sub> have been suggested as the primary mechanism of nucleation.<sup>2</sup> Another suggested mechanism of nucleation involves free-radical reactions, such as that of HO with SO<sub>2</sub>.<sup>3-5</sup> The present study was initiated with the intention of forming  $SO_2$  and  $SO_3$  complexes of  $H_2O$  from the photo-oxidation of  $H_2S$  in solid  $O_2$  at a cryogenic temperature, since it has been shown in photooxidation studies of matrix-isolated simple polyatomic molecules such as  $H_2CO$  and  $(HCO)_2$  in solid  $O_2$  that the oxidation products formed in the photolysis cage can be predicted largely on the basis of chemical stoichiometry involving the consumption of one and two molecules of  $O_2$ .<sup>6,7</sup> The initial photodissociation products of  $H_2S$  in the gas phase are  $H(^2S)$ and  $HS(^{2}\Pi)$  radicals, and the thermochemical threshold for dissociation is 82 kcal/mol (or  $\lambda < 317$  nm).<sup>8</sup> Hence, the expected photooxidation products from matrix-isolated  $H_2S/O_2$  samples are shown by the following set of reactions.

$$H_2S + O_2 \rightarrow H_2 + SO_2 \tag{1}$$

$$\rightarrow$$
 HS + HO<sub>2</sub> (2)

$$\rightarrow$$
 HSO + HO (3)

$$\rightarrow H_2O + SO(X^3\Sigma^{-})$$
 (4)

$$+ 2O_2 \rightarrow H_2O_2 + SO_2 \tag{5}$$

$$\rightarrow H_2O + SO_3 \tag{6}$$

$$\rightarrow H_2 SO_4 \tag{7}$$

$$H_2S + 3O_2 \rightarrow 2HO_2 + SO_2 \tag{8}$$

$$\rightarrow$$
 HO<sub>2</sub> + HO + SO<sub>3</sub> (9)

$$\rightarrow H_2O + SO_2 + O_3 \tag{10}$$

We have observed all of the above products with the exception of SO, HS, HO, and HSO radicals and H<sub>2</sub>, when the products of the photolyzed sample are analyzed by Fourier transform

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 $H_2S$ 

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infrared (FTIR) spectroscopy. Since nearly all products except some HO<sub>2</sub> (via hot H atoms) and O<sub>3</sub> (via site migration caused by secondary photolyses of ozone) are formed inside the photolysis cage,<sup>6,9</sup> we observe significant amounts of  $H_2SO_4$  as well as  $SO_3$ ·H<sub>2</sub>O and  $SO_2$ ·H<sub>2</sub>O molecular complexes. We find that the ratio of  $SO_3/SO_2$  from the  $H_2S/O_2$  matrix system is several times greater than that from the OCS/O<sub>2</sub> and CS<sub>2</sub>/O<sub>2</sub> matrix photolysis systems described in the accompanying paper.<sup>10</sup> The cause for this difference will be discussed later. Furthermore, we have not observed HSOH in our matrix-isolated  $H_2S/O_2$  photolysis at 15 K, although Smardzewski and Lin observed HSOH as the nearly exclusive photolysis product in their  $O_3/H_2S/Ar$  matrix experiments at 8 K.<sup>11</sup> The contrast between the two experiments will be discussed in light of the importance of the O atom reactions with  $H_2S$  in their experiments but not in ours.

## **Experimental Section**

H<sub>2</sub>S (Matheson, CP grade, minimum purity 99.5%) was used after "freeze-pump-thaw" purification in a vacuum line. A small amount of OCS was present as an impurity, but it did not interfere with the experiment.  $O_2$  (Liquid Carbonic, 99.999% state purity) as matrix gas (M) was used directly without purification. Two values of a matrix/reactant ratio (M/R) were used:  $O_2/H_2S =$ 700 or 1500. The gas mixture of  $H_2S$  and  $O_2$  was made in a 1-L bulb by standard manometric techniques, and it was pulse deposited onto the cold CsI sample window (inside the cold head) maintained within 1 K by a closed-cycle helium refrigerator (Air Products Displex Model 202B). Approximately  $3-10 \mu mol \text{ of } H_2S$ was deposited. Photolysis as carried out at  $\sim 15$  K using a high-pressure mercury arc lamp (Osram HBO-500 w/2). The light was collimated by a fused silica lens, passed through a 10-cm water filter, and imaged onto the cold sample in the vacuum shroud of the cryostat. In this configuration, the shortest UV wavelength available for the photolysis is  $\sim$  220 nm. If a set of Schott WG 280 and Corning CS-7-54 filters was inserted, a transmission envelope of 260-420 nm was achieved. Likewise, a transmission envelope was achieved between 270 and 420 nm with a WG 295/7-54 set and between 300 and 420 nm with a WG 320/7-54 set. Additionally, cutoff filters such as WG 320 (300-nm cutoff), CS-0-54 (330 nm), CS-4-97 (340 nm), CS-4-96 (350 nm), and CS-0-51 (360 nm) were used for photolysis. The photolysis products were monitored after each preset photolysis time as well as after temperature-controlled warm-up cycle for an annealing/diffusion study.

The sample analysis was carried out with an FTIR spectrometer (Nicolet 7199) equipped with a germanium-coated KBr beam splitter and a HgCdTe detector adequate for the 7000-400-cm<sup>-1</sup> range. In a typical run, 200 scans were signal averaged. The

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TABLE I:	Observ	ed II	R Absorp	tion	Peaks	$(cm^{-1})$	) and	
Assignment	s from	the <b>I</b>	Photolys	is of ]	H <sub>2</sub> S in	Solid	0, (1	5 K) <sup>a</sup>

		-2 ()
assignt	$\nu^b$	assignt
$SO_2 \cdot H_2 O(\nu_3)$	1343.5	$SO_2(v_3)\cdot H_2O$
$SO_3 \cdot H_2O(\nu_3)$	1218.6	$H_2SO_4$
$SO_2 \cdot H_2 O(v_1)$	1155.7 (w) 1151.5	$SO_2(\nu_1)$ ·H <sub>2</sub> O
$H_2SO_4$	1146.1	$SO_2(\nu_1)$
$H_2O_2(v_{1,5})$ ·SO <sub>2</sub> ?	1101.1 (w)	$HO_2(\nu_3)$
$SO_3 \cdot H_2O(v_1)$	1038.0 942.9 (vw)	$O_3(\nu_3)$ ?
$H_2O_2(v_{1,5})$ ·SO <sub>2</sub> ?	889.5	$H_2SO_4$
$HO_2(\nu_1)$	842 (w)	H₂SO₄
$H_2S(\nu_3)$	834 (vw)	2 4
$H_2 S(v_1)$	778 (vw)	?
$SO_{(n, \pm n)}H_{0}$	702.7 (w)	$O_3(v_2)$
$^{12}CO_2$ impurity	578) 560)	$H_2SO_4$
<sup>13</sup> CO <sub>2</sub> impurity ?	549.41	$[SO_3(\nu_4) \cdot H_2O]?$
$SO_x \cdot H_2 O(\nu_2)$	528.0 (w)	$SO_3(v_4)$
? H.SO	525.6) 523.8	$SO_2(\nu_2) \cdot H_2O$
$\Pi_2 \cup U_4$	519.4	<b>50</b> ()
$SU_{3}(\nu_{3}) \cdot \Pi_{2}U$	517.9 (W)	$SO_2(\nu_2)$
$SO_{2}(\nu_{2})$	490.8 (w)	$SO_2(v_2)$
$SO_{2}(\nu_{3})$	488.5 (br)	$SO_{3}(\nu_{2})$ ·H <sub>2</sub> O
	$\frac{\text{assignt}}{\text{SO}_2 \cdot H_2 O(\nu_3)}$ $SO_2 \cdot H_2 O(\nu_3)$ $SO_2 \cdot H_2 O(\nu_3)$ $SO_2 \cdot H_2 O(\nu_1)$ $H_2 SO_4$ $H_2 O_2(\nu_{1,5}) \cdot SO_2?$ $SO_3 \cdot H_2 O(\nu_1)$ $H_2 O_2(\nu_{1,5}) \cdot SO_2?$ ? $HO_2(\nu_1)$ $H_2 S(\nu_3)$ $H_2 S(\nu_1)$ $SO_2(\nu_1 + \nu_3) \cdot H_2 O$ $^{12}CO_2 \text{ impurity}$ $^{13}CO_2 \text{ impurity}$ ? $H_2 SO_4$ $SO_3(\nu_3) \cdot H_2 O$ $HO_2(\nu_2)$ $SO_3(\nu_3)$ $SO_2(\nu_3)$	$\begin{array}{c ccccc} \hline & assignt & \nu^b \\ \hline \\ \hline & assignt & \nu^b \\ \hline \\ SO_2 \cdot H_2 O(\nu_3) & 1343.5 \\ SO_3 \cdot H_2 O(\nu_3) & 1218.6 \\ SO_2 \cdot H_2 O(\nu_1) & 1155.7 & (W) \\ 1151.5 & 1\\ H_2 O_2(\nu_{1,5}) \cdot SO_2? & 1101.1 & (W) \\ SO_3 \cdot H_2 O(\nu_1) & 942.9 & (vW) \\ H_2 O_2(\nu_{1,5}) \cdot SO_2? & 889.5 \\ ? & 884.6 \\ \hline \\ HO_2(\nu_1) & 842 & (W) \\ H_2 S(\nu_3) & 834 & (vW) \\ H_2 S(\nu_3) & 834 & (vW) \\ H_2 S(\nu_1) & 778 & (vW) \\ SO_2(\nu_1 + \nu_3) \cdot H_2 O & 578 \\ ? & 502 \\ (V_1 + \nu_3) \cdot H_2 O & 578 \\ ? & 502 \\ H_2 O_2 & impurity & 560 \\ 1^{13}CO_2 & impurity & 560 \\ 1^{13}CO_2 & impurity & 549.4 \\ ? & 545.8 \\ SO_x \cdot H_2 O(\nu_2) & 528.0 & (W) \\ ? & 525.6 \\ H_2 SO_4 & 519.4 \\ SO_3(\nu_3) \cdot H_2 O & 517.9 & (W) \\ HO_2(\nu_2) & 516.6 & (W) \\ SO_2(\nu_3) & 488.5 & (br) \\ \end{array}$

<sup>a</sup>Broad peaks typically 5–10 cm<sup>-1</sup> wide were not listed above, because they appear as the matrix surface condensation: 3685, 2280, 2235, 2153, 1434, 1255–65, 1118–23, 1050, 850, 805, 790, 732, 704, and 490 cm<sup>-1</sup>. All except the first four peaks are probably due to the condensed form of H<sub>2</sub>SO<sub>4</sub> from the vacuum system, since liquid H<sub>2</sub>SO<sub>4</sub> has broad peaks at 1378, 1187, 972, 908, and 558 cm<sup>-1</sup> (see ref 16). <sup>b</sup>The accuracy is probably  $\pm 0.2$  cm<sup>-1</sup>.

truncated length of the travel of the moving mirror in the interferometer was set at 4.14 cm. The use of a full aperture size of IR radiation source and the Hang-Genzel apodization function gave a resolution of  $\sim 0.37$  cm<sup>-1</sup>. The absolute error in frequency reported here is probably  $\pm 0.2$  cm<sup>-1</sup>. In this paper, we present the *difference* spectrum with the ordinate as the difference of absorbances, i.e., the absorbance of the photolysis sample of interest minus the absorbance of the preceding photolysis sample, since it is more informative to examine the product yield for each successive photolysis period. In typical experiments, impurity H<sub>2</sub>O peaks are not observed. However, sometimes a very broad absorption peak appears near 3700 cm<sup>-1</sup> (see Figure 1).

### **Results and Discussion**

IR Absorption of  $H_2S$ . The IR absorption peaks were weak in both samples with  $H_2S/O_2 = 1/700$  and 1/1500. We observed two S-H stretch peaks in solid  $O_2$ , 2635.0 and 2585.3 cm<sup>-1</sup>, the latter peak being slightly more intense than the former. These peaks correspond to 2629.1-cm<sup>-1</sup> ( $\nu_3$ , weak) and 2582.5-cm<sup>-1</sup> ( $\nu_1$ , strong) peaks observed in solid Ar by Barnes and Howells.<sup>12</sup> The  $\nu_2$  peak corresponding to 1179.0 cm<sup>-1</sup> (weak) in solid Ar was too weak to be observed in solid  $O_2$  in the present experiment. Since  $\nu_3$  (very strong) and  $\nu_1$  (strong) peaks in solid  $N_2$  have been observed at 2632.6 and 2619.5 cm<sup>-1</sup>, respectively, <sup>12,13</sup> it appears that the  $H_2S$  monomer interaction with the  $O_2$  matrix is intermediate between those with solid Ar and  $N_2$  but more similar to that with solid Ar than that with solid  $N_2$ . The readers are referred to earlier papers<sup>12,13</sup> for detailed discussions of the matrix effects.

*Photolysis of H*<sub>2</sub>*S*. The first electronic absorption band of H<sub>2</sub>*S* in the gas phase commences near 270 nm and reaches a broad maximum near 190 nm.<sup>8</sup> The thermochemical threshold of the

TABLE II: IR Absorption Frequencies  $(cm^{-1})$  of Monomeric HO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, SO<sub>2</sub>, and SO<sub>3</sub> in Solid O<sub>2</sub>

	13 K <sup>b</sup>			16 K <sup>c</sup>	20 K <sup>d</sup>		16 K <sup>c</sup>	
	HO <sub>2</sub>	H <sub>2</sub> O	O <sub>3</sub>	SO <sub>2</sub>	SO <sub>3</sub> <sup>a</sup>		SO <sub>3</sub>	
$v_1$	3400.3	3635.4		1146.1	$\nu_1$	1070 (R)		
							490.8	
$\nu_2$	1392.1	1612.8	702.6	516.6	$\nu_2$	465	488.8	
-					-	1399	1385.6	
V <sub>6</sub>	1102.8	3731.0	1038.0	1348.8	$v_{3}$ (e)	1385	1384.8	
Ŭ					$\nu_4$ (e)		528.0	

<sup>*a*</sup>Radio-frequency or microwave discharge on pure SO<sub>2</sub>. <sup>*b*</sup>Reference 9. <sup>*c*</sup>Reference 10. <sup>*d*</sup>Reference 15.

TABLE III: Comparison of the IR Absorption Frequencies  $(cm^{-1})$  of  $H_2SO_4$  Observed in Solid  $O_2$  (12 K) and in the Vapor (~500 K)

۰.	,				
	vib descripn	O <sub>2</sub>	vapor <sup>d</sup>	vapor <sup>e</sup>	
	OH, str	3591.6ª	3610 (Q)	3610 (Q)	_
SO <sub>2</sub> , asym str		{1455.5 (w)	1450	1456	
	SO <sub>2</sub> , sym str	1218.6	1223 (Q)	1224 (Q)	
	SOH, bend	b	1159, 1138	1160, 1141	
	S(OH) <sub>2</sub> , asym str	{889.5 (w) {884.6	883 (O)	882 (O)	
	S(OH) <sub>2</sub> , sym str	(842.3 (834.0 (w)	834	831	
	SO <sub>2</sub> , rock	{578 (vw) {560 (vw)	568	570	
	SO <sub>2</sub> , bend	{549.4 (vw) {545.8 (vw)	550	550	

<sup>*a*</sup> There should be two OH stretches, symmetric and asymmetric. We tentatively assign one of these to be at 3591.6 cm<sup>-1</sup>.  ${}^{b}$  SO<sub>2</sub>( $\nu_1$ ) absorbs in this region, and it is difficult to make an unambiguous assignment. <sup>*c*</sup> This work. <sup>*d*</sup> Reference 16. <sup>*e*</sup> Reference 17.

dissociation giving the ground electronic states of the H atom and HS radical corresponds to 317 nm. In order to determine the photochemical reaction threshold of  $H_2S$  in solid  $O_2$  (M/R = 1500), we have carried out photolyses using several filter combinations with different UV cutoff wavelengths between 260 and 360 nm. A 0.5-h photolysis with a 270-nm cutoff filter gave appreciable amounts of products, but a 1-h photolysis with 300-360-nm cutoff filters gave no measurable product yield. Therefore, the photochemical reaction threshold in solid  $O_2$  is below 300 nm, and the wavelengths of mercury lines effective for photolysis are 275, 280, 289, and 297 nm in order of decreasing importance. If we neglect the matrix effect on the initial photodissociation, most of the excess energy (22 kcal/mol at 275 nm and 14 kcal/mol at 297 nm) should appear as the translational recoil energy of H atoms, since the photodissociation of  $H_2S$  gives hot H atoms.<sup>14</sup>

Photolysis Products. The photolysis results from the 260-nm cutoff using the WG 280/7-54 filter combination and M/R = 700 were similar to those from the 270-nm cutoff using the WG 295/7-54 filter combination and M/R = 1500. Important spectral features from the former are shown in Figure 1: photochemical formations of H<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>O·SO<sub>x</sub> complexes as well as HO<sub>2</sub> and O<sub>3</sub>. Spectral features illustrating the variation of SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>O·SO<sub>x</sub>, and O<sub>3</sub> yields due to the use of unfiltered, "white" light ( $\lambda < 220$  nm) are shown in Figure 2. A significant amount of 250-nm radiation is available for photolysis with white light. The observed IR absorption frequencies and assignments of HO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, SO<sub>2</sub>, and SO<sub>3</sub> peaks are based on the monomer assignments (in solid O<sub>2</sub>) given by other studies tabulated in Table II. The assignment of H<sub>2</sub>SO<sub>4</sub> peaks are based on the gas-phase values,<sup>16,17</sup>

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Figure 1. FTIR spectrum of the photolysis product yields from an  $O_2/H_2S$  sample (M/R = 700) at 15 K by using an Hg arc lamp with a filter set (WG 280/7-54) for 260-420-nm transmission. For the 600-480-cm<sup>-1</sup> region, the result from an  $O_2/H_2S$  sample (M/R = 1500) is shown: (a) 20-min photolysis; (b) the subsequent 130-min photolysis.

and the agreement shown in Table III is quite good.

The assignment of the 3400.2-cm<sup>-1</sup> peak to  $HO_2(\nu_2)$  is based on the previous assignment from the photolysis of H<sub>2</sub>CO and  $(HCO)_2$  in solid  $O_2$ .<sup>6,9</sup> In the  $O_2/H_2CO$  photolysis system (and not in the  $O_2/(HCO)_2$  photolysis system), a minor peak appears at 3410 cm<sup>-1</sup> which might be  $HO(\nu) \cdot CO_2$  or the  $HO_2(\nu_2) \cdot HC$ -(O)OO complex.<sup>9</sup> The absorptions by HO in solid Ar at 4.2 (and 20.4) K occur at 3452.5 and 3428.2 cm<sup>-1</sup>,<sup>18</sup> and it is  $\sim 129$  cm<sup>-1</sup> red-shifted from the gas-phase value. The absorptions by HO<sub>2</sub> in solid Ar occur at 3414, 1389, and 1101 cm<sup>-1.19</sup> Since OH shows an abnormally large value of gas-matrix shift in solid Ar,  $\sim 3.5\%$ , compared to numerous other transient molecules,<sup>20</sup> the HO absorption frequency at  $3450-3410 \text{ cm}^{-1}$  in solid O<sub>2</sub> is expected, but no absorption attributable to HO or the HO O<sub>2</sub> complex is found. The absorptions by  $H_2O_2$  in solid Ar occur at 3597.4 and 3593 cm<sup>-1</sup> for  $\nu_1/\nu_5$  fundamentals and 1270.6 cm<sup>-1</sup> for the  $\nu_6$  fundamental,<sup>21,22</sup> and we tentatively assign the weak peaks observed at 3568 and 3548 cm<sup>-1</sup> in solid O<sub>2</sub> to  $H_2O_2(\nu_1,\nu_5)$ ·SO<sub>2</sub> complex, as for the  $H_2O_2(\nu_1,\nu_5)$ ·CO complex<sup>6,9</sup> observed in the  $H_2CO/O_2$ photolysis system.

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Figure 2. FTIR spectrum of the photolysis product yields from an  $O_2/H_2S$  sample (M/R = 1500) at 15 K by using an Hg arc lamp with a filter set (WG 295/7-54) for 270-420-nm transmission. Only the spectral regions for SO<sub>3</sub>( $\nu_3$ ), SO<sub>2</sub>( $\nu_3$ ), and O<sub>3</sub>( $\nu_3$ ) are shown: (a)-(c) photolysis time variation for 0.5, 3.0, and 9.5 h, respectively; (d) and (e) effect of white light photolysis at 4.0 and 6.5 h, respectively. Note the consumption of O<sub>3</sub> on prolonged photolysis and also the higher ratio of  $SO_3/SO_2$  with white light photolysis.

Three transient species (HS, SO, and HSO) were searched for but not found (see Figure 1): their absorptions in an Ar matrix occurs at 2540.8 cm<sup>-1</sup> for HS in Ar,<sup>23</sup> 1136.7 cm<sup>-1</sup> for SO in Ar,<sup>24</sup> and 1063 cm<sup>-1</sup>  $(\nu_2)^{25}$  and 1009.36 cm<sup>-1</sup>  $(\nu_3)^{26}$  for HSO in the gas phase.

 $H_2OSO_x$  Complexes. The assignments of five absorption peaks between 3730 and 3560 cm<sup>-1</sup> to  $H_2O(\nu_1,\nu_3)$ . SO<sub>x</sub> complexes and to  $H_2SO_4$  (O-H stretch) are based on (i) temperature-controlled warm-up experiments after photolysis and (ii) relative frequency shifts for the  $H_2O(\nu_1,\nu_3)$ ·SO<sub>2</sub> and  $H_2O(\nu_1,\nu_3)$ ·SO<sub>3</sub> complexes from the monomeric  $H_2O(v_1, v_3)$ . We have observed a slight decrease of the intensity of the 3591.6-cm<sup>-1</sup> absorption peak upon a short warm-up to 37 K, whereas a significant increase of the intensities and a distinct sharpening of the peak shape were observed with the other four peaks. The warm-up cycle also reduced the  $SO_2(\nu_3)$ monomer peak and increased the  $SO_2(\nu_3) \cdot H_2O$  peak. Therefore, we assign the 3591.6-cm<sup>-1</sup> peak as one of the two H-O stretch fundamentals of  $H_2SO_4$  and we attribute the latter observation to thermally induced annealing and formation of H<sub>2</sub>O·SO, complexes by diffusion near the photolysis cage.<sup>27</sup> SO<sub>2</sub> and SO<sub>3</sub> are expected to behave as Lewis acids with respect to H<sub>2</sub>O as a Lewis base, SO<sub>3</sub> being a stronger acid than SO<sub>2</sub> due to a greater positive atomic charge on the S atom of  $SO_3$  than that on  $SO_2$ .<sup>28</sup> If the electrostatic interaction is dominant in the molecular complex formation<sup>29,30</sup> for the SO<sub>2</sub>–H<sub>2</sub>O and SO<sub>3</sub>–H<sub>2</sub>O pairs, the binding energy for the  $H_2O$ ·SO<sub>3</sub> complex should be greater than that for the  $H_2O$ ·SO<sub>2</sub> complex. In the gas phase at room temperature,  $SO_2$  does not hydrate as easily as  $SO_3$  does. This is indicative of a stronger binding energy of the  $H_2O \cdot SO_3$  complex than that of the  $H_2O \cdot SO_2$  complex.

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A recent calculation<sup>2a</sup> indicates a binding energy of 15.2 kcal/mol for the most favored structure of H<sub>2</sub>O·SO<sub>3</sub> with the O atom of H<sub>2</sub>O sitting on top of the central S atom of "near"-planar  $SO_3$ . For the H<sub>2</sub>O·SO<sub>2</sub> complex, the largest noncovalent intermolecular interaction was obtained with a close approach of the O atom of H<sub>2</sub>O to the S atom of  $SO_2$ .<sup>30</sup> If one assumes that the nature of the donor-acceptor interactions  $(H_2O - SO_x)$  in the two complexes are similar but that H2O·SO3 has a substantially greater binding energy than  $H_2O \cdot SO_2$ , the frequency shifts of the  $H_2O$ fundamentals in the  $H_2O \cdot SO_3$  complex from monomeric  $H_2O$ fundamentals are expected to be greater than those in the H2O·SO2 complex. The  $v_1$  and  $v_3$  fundamentals of H<sub>2</sub>O isolated in solid  $O_2$  have been measured to be 3635.4 and 3731.0 cm<sup>-1,9</sup> respectively, as shown in Table II. Hence, we assign  $X = SO_2$  and Y = SO<sub>3</sub> in Figure 1, i.e.,  $H_2O(\nu_3)$ ·SO<sub>2</sub> at 3719.3 cm<sup>-1</sup>,  $H_2O(\nu_3)$ ·SO<sub>3</sub> at 3678.2 cm<sup>-1</sup>,  $H_2O(v_1)$ ·SO<sub>2</sub> at 3632.2 cm<sup>-1</sup>, and  $H_2O(v_1)$ ·SO<sub>3</sub> at 3562.8 cm<sup>-1</sup>. At the present time, we can only *tentatively* assign the 1597.7- and 1589.9-cm<sup>-1</sup> peaks to  $H_2O(\nu_2)\cdot Z$  and  $H_2O(\nu_2)\cdot Z'$ complexes, respectively, where Z and Z' are  $SO_x$ . The H<sub>2</sub>O( $\nu_2$ )·Z' peak disappears with white light photolysis. The intensity ratios of the absorption peaks for the two partners  $(H_2O \text{ and } SO_3)$  in the H<sub>2</sub>O·SO<sub>3</sub> complex remained constant with the variation of photolysis time. Those for the two partners  $(H_2O \text{ or } SO_2)$  in the H<sub>2</sub>O·SO<sub>2</sub> complex also remained constant.

The S–O asymmetric stretch peaks of  $SO_2(v_3)$ ·V and  $SO_3(v_3)$ ·W complexes shown in Figures 1 and 2 can be assigned to those of  $H_2O$  complexes, i.e.,  $V = H_2O$  and  $W = H_2O$ , since the amount of H<sub>2</sub>O produced is far greater than that of H<sub>2</sub>O<sub>2</sub> formed as indicated by the H<sub>2</sub>O<sub>2</sub> absorption near the 3570-3550-cm<sup>-1</sup> (H-O stretch) and 1280-1260-cm<sup>-1</sup> (OOH bend) regions.<sup>6,9</sup> The monomer SO<sub>2</sub> and SO<sub>3</sub> frequency assignments in solid O<sub>2</sub> are described in the accompanying paper.<sup>10</sup> It is interesting to note that  $SO_2(\nu_3)$ ·H<sub>2</sub>O is a doublet with a ~6-cm<sup>-1</sup> lower frequency than SO<sub>2</sub>( $\nu_3$ ), whereas SO<sub>3</sub>( $\nu_3$ )·H<sub>2</sub>O is a doublet with a ~10-cm<sup>-1</sup> higher frequency than SO<sub>3</sub>( $\nu_3$ ). Both SO<sub>2</sub>( $\nu_1$ )·H<sub>2</sub>O and SO<sub>2</sub>- $(\nu_2)$ ·H<sub>2</sub>O peaks appear at higher frequencies (6 and 9 cm<sup>-1</sup>) from the corresponding monomer SO<sub>2</sub> peaks. The  $SO_3(\nu_2)$ ·H<sub>2</sub>O peak is at slightly lower frequencies  $(-2 \text{ cm}^{-1})$  than the  $SO_3(\nu_2)$  outof-plane bend. However, the location of the  $SO_3(v_4)$ ·H<sub>2</sub>O absorption is uncertain, and we believe that it may overlap with the four peaks of H<sub>2</sub>SO<sub>4</sub> (SO<sub>2</sub>, rock and bend) as a broad peak near 560 cm<sup>-1</sup> as seen in Figure 1. If this were the case, the  $SO_3$ - $(\nu_4)$ ·H<sub>2</sub>O peak is at ~30-cm<sup>-1</sup> higher frequency than SO<sub>3</sub> $(\nu_4)$ , a doubly degenerate in-plane bend (e'). The overlapping of the  $H_2SO_4(SO_2, \text{ rock and bend})$  with the  $SO_3(v_4) \cdot H_2O$  fundamentals probably reflects the similarity of their geometric structures. A recent structure determination of H<sub>2</sub>SO<sub>4</sub> by microwave spectroscopy<sup>31</sup> shows that it has a conformation with  $C_2$  symmetry, not  $C_{2v}$ . Holland and Castleman<sup>2a</sup> have shown in their CNDO/2 calculation, however, assuming  $C_{2v}$  symmetry for H<sub>2</sub>SO<sub>4</sub>, that the energy barrier for the H<sub>2</sub>O·SO<sub>3</sub> adduct rearrangement to H<sub>2</sub>SO<sub>4</sub>

$$H_2O \cdot SO_3 \rightarrow H_2SO_4$$
 (11)

is only  $\sim$  3.3 kcal/mol. This minimum-energy path involves the hopping of an H atom of H<sub>2</sub>O to one of the oxygens of SO<sub>3</sub>. We were unable to prepare good matrix samples for calibrating  $SO_3 \cdot H_2O$  and  $SO_2 \cdot H_2O$ . We believe that rapid conversion of the  $SO_3 H_2O$  complex to  $H_2SO_4$  during the mixed-sample preparation by conventional manometric techniques is responsible for the failure. Because H<sub>2</sub>O and SO<sub>2</sub> are both strongly dipolar molecules and form self-dimers very easily, conventional sample preparation techniques used are unsatisfactory for observing the SO<sub>2</sub>·H<sub>2</sub>O complex without overshadowing effects of the self-dimers. For this reasons, we prefer the photochemical method of generating mixed dimers and provide relatively unambiguous spectral assignments.

Photooxidation Processes. A direct detection of neither  $H_2$ nor H2.SO2 complex was possible under our experimental conditions. However, a minor amount of the SO<sub>2</sub> monomer is ob-



Figure 3. Energetics of oxidation processes starting with  $H_2S + nO_2$ . The standard enthalpies of the reactions at 300 K ( $\Delta H_{rx}^{\circ}$ ) giving various final products are shown. The numbers in parentheses are estimated values.  $^{\rm 33b}$ 

served with the major amount being the  $SO_2 \cdot H_2O$  complex. Therefore, it is likely that SO<sub>2</sub> is formed directly by process 1 or indirectly via a disproportionation reaction of HS and HO<sub>2</sub> formed in process 2 and H<sub>2</sub> could have diffused away from the photolysis cage. The energetics of these processes and other reactions are illustrated in Figure 3, with use of the standard enthalpy values from ref 32. We observe all of the stable product combinations with exothermicity greater than  $\sim 90$  kcal/mol.

We consider the comparison of the  $SO_3/SO_2$  product ratios observed in the photooxidation of H<sub>2</sub>S, OCS, and SOCl<sub>2</sub> in solid O<sub>2</sub> to be the key for understanding photooxidation processes of  $H_2S$  in solid  $O_2$ . At the present time, the lack of reliable integrated IR absorption intensities for  $SO_3$  in solid  $O_2$  prevents the determination of the molar ratios of  $SO_3/SO_2$  for these systems from the observed  $SO_3/SO_2$  intensity ratios. A rough estimate (±40%) of the integrated absorption coefficient of  $SO_3(v_3)$  in the gas phase (courtesy of Dr. J. G. Calvert) is 1.5 times that of  $SO_2(\nu_3)$ . The application of these gas-phase values to the product yields shown in Figure 1 gives the mole ratio of  $SO_3/SO_2$  to be approximately 1/2. It has been found in our recent work that the  $SO_3/SO_2$ product ratios obtained from the  $H_2S/O_2$  and  $SOCl_2/O_2$  systems<sup>33</sup> are similar and that they are several times greater than the ratio obtained from the  $OCS/O_2$  system.<sup>10</sup> Near 250 nm, the photodissociation process on the absorption continuum should give an S atom from OCS and also an SO from SOCl<sub>2</sub>. The higher ratio of  $SO_3/SO_2$  appears to be a characteristic of the SO reaction in solid  $O_2$ , and the lower ratio of  $SO_3/SO_2$  appears to be a characteristic of the S atom reaction in solid O2. We shall proceed to discuss the results with this premise.

The disproportionation and recombination of the HS and HO<sub>2</sub> radicals formed via (2) in the photolysis cage could give HSO and OH via (3) and  $H_2O + SO$  via (4).

$$HS + HO_2 \longrightarrow \begin{bmatrix} H - S \\ H & 0 \end{bmatrix} \longrightarrow HSO + OH (3)$$
$$SO + H_2O (4)$$

It is not surprising that no IR absorption peaks of appreciable intensity attributable to OH, HSO, and SO were observed under our experimental conditions which do not favor the stabilization

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Figure 4. Schematics of a tentative mechanism of photooxidation for H<sub>2</sub>S in solid O<sub>2</sub>.

of these species. Processes 2 and 3 are considerably more endothermic than process 4 or others shown in Figure 3. We have not observed  $(HO_2)_2$  from process 8 in the  $H_2S/O_2$  system, in contrast to the  $H_2CO/O_2$  system.<sup>6,9</sup> This difference probably results from the escape of an H atom from the photolysis cage due to the greater photochemical recoil effect in the H<sub>2</sub>S photodissociation than in the H<sub>2</sub>CO photodissociation. Therefore, either initially produced, hot H atoms from the H<sub>2</sub>S photodissociation escape with ease from the cage, preempting process 8, or  $H_2O$  + SO are formed efficiently via process 4 with a 51 kcal/mol exothermicity.

Now, SO may react further with  $O_2$  to give SO<sub>3</sub> with a 96 kcal/mol exothermicity or SO<sub>2</sub> with a 38 kcal/mol exothermicity.

$$SO + O_2 \rightarrow SO_3$$
 (12)

$$SO + 2O_2 \rightarrow SO_2 + O_3$$
 (13)

The combination of (4) and (12) then gives an  $SO_3 \cdot H_2O$  complex. The observation of  $O_3$  is consistent with process 13. The mechanism giving rise to process 13 may be

$$SO + O_2 \rightarrow SO_2 + O(^3P)$$
 (14)

followed by

$$O + O_2 \rightarrow O_3 \tag{15}$$

Reactions 14 and 15 are both exothermic by 13 and 25 kcal/mol, respectively. The actual process may not even involve O atoms but require an additional UV photon to excite SO( $\bar{X}^3\Sigma$ ) to SO- $(\tilde{A}^{3}\Pi)$ ,<sup>34</sup> because the gas-phase reaction involving the ground electronic states is extremely slow.<sup>35,36</sup> Since there is  $H_2O$  in the cage, the sequence of (14) and (15) gives SO<sub>2</sub> and O<sub>3</sub> which complexes with  $H_2O$ . The overall process corresponds to (10). If an O atom from (14) reacts with  $H_2O$ , rather than with  $O_2$ ,  $H_2O_2$  is formed.

$$O + H_2 O \to H_2 O_2 \tag{16}$$

A photochemical conversion mechanism which would oxidize  $SO_2$ to  $SO_3$  in solid  $O_2$  should be unimportant here, since it has been shown in a study  $3^{\overline{7}}$  in our laboratory that such conversion requires

photolysis of  $(SO_2)_2$  with white light. However, it should be noted that white light gives a somewhat higher  $SO_3/SO_2$  ratio and more  $O_3$  than 280-nm light (see Figure 2)

The gas-phase values of integrated IR absorption coefficients of  $H_2SO_4$  and  $SO_2$  are available in the literature: 120 atm<sup>-1</sup> cm<sup>-2</sup> for the 1222-cm<sup>-1</sup> band of  $H_2SO_4$ ;<sup>38</sup> 95.6 atm<sup>-1</sup> cm<sup>-2</sup> for the 1151-cm<sup>-1</sup> band ( $\nu_1$ ) and 780 atm<sup>-1</sup> cm<sup>-2</sup> for the 1362-cm<sup>-1</sup> band  $(\nu_3)$  of SO<sub>2</sub>.<sup>39</sup> As mentioned before, the integrated absorption coefficient of SO<sub>3</sub>( $\nu_3$ ) is ~1.5 times the value for SO<sub>2</sub>( $\nu_3$ ) from the gas-phase data of Calvert.<sup>10</sup> On the assumption that the gas-phase absorption coefficients are directly applicable to the O2 matrix results, one can obtain a reasonable estimate of relative species concentrations of SO<sub>2</sub> (plus SO<sub>2</sub>·H<sub>2</sub>O), SO<sub>3</sub> (plus SO<sub>3</sub>·  $H_2O$ , and  $H_2SO_4$  from the inspection of the IR absorption peak sizes shown in Figure 1: all three species are present in approximately equal amounts after 130-min photolysis (Figure 1b), but  $H_2SO_4$  is certainly in an amount, 1/3-1/2 of  $SO_2$  (or  $SO_3$ ) after 20-min photolysis (Figure 1a). It is also interesting to note that the high-resolution IR spectrum of the 1222-cm<sup>-1</sup> band of H<sub>2</sub>SO<sub>4</sub> in the gas phase has a wider bandwidth of at least 5 cm<sup>-1</sup>  $(fwhm)^{38,40}$  as compared to the value of 1–2 cm<sup>-1</sup> that we observe in solid O<sub>2</sub>.

We have not observed  $(HO_2)_2$  in the  $H_2S/O_2$  system in contrast to the  $H_2CO/O_2$  system,<sup>6,9</sup> because of the escape of an H atom from the photolysis cage (due to the greater photochemical recoil effect in the H<sub>2</sub>S photodissociation), leaving HS in the photolysis cage. The elementary reactions of HS with O<sub>2</sub> give two sets of products.

$$HS + O_2 \rightarrow HO + SO$$
 (17)

$$HS + 2O_2 \rightarrow HO_2 + SO_2 \tag{18}$$

 $H_2O_2$  in our system may come from the reaction of the HO<sub>2</sub> produced in reaction 18 with nearby HO2. The gas-phase kinetics of (17) has been well established with an upper limit value of the rate constant being  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>35,36</sup> The cage reactions of SO in solid  $O_2$  can give SO<sub>3</sub> and SO<sub>2</sub> by processes 12 and 13, respectively, and further reactions of  $SO_3$  and  $SO_2$  with HO can give HOSO<sub>3</sub> and HOSO<sub>2</sub> radicals.

$$HO + SO_3 \rightarrow HOSO_3$$
 (19)

$$HO + SO_2 \rightarrow HOSO_2$$
 (20)

The gas-phase reaction of HO addition to  $SO_2$  is considered to be the most important step for the formation of  $H_2SO_4$ .<sup>1,4,5</sup> This

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radical mechanism of  $H_2SO_4$  formation is an alternative to the UV conversion of the  $SO_3$ · $H_2O$  complex to  $H_2SO_4$  for which we have no proof. We are making further attempts to trap and characterize HOSO<sub>3</sub> and HOSO<sub>2</sub> radicals under different experimental conditions.

With the above set of reactions, it is now possible to account for all of the observed photooxidation product including molecular complexes. A tentative mechanism of the photooxidation of  $H_2S$ in solid  $O_2$  is schematically summarized in Figure 4. Future studies should be directed to verify the formation mechanisms of  $H_2SO_4$  from HOSO<sub>2</sub>, HOSO<sub>3</sub>, and  $H_2O$ ·SO<sub>3</sub>, as well as to determine the branching ratio of the  $H_2O$  + SO formation reaction to the HO + HSO formation reaction.

Comparison with the  $O_3/H_2S/Ar$  System.<sup>11</sup> The  $O_3/H_2S/Ar$ matrix photolysis system gives HSOH as the predominant product. The photolysis of  $O_3$  gives  $O_2$  and an O atom which attacks  $H_2S$ to give HO and HS. The photolysis of H<sub>2</sub>S gives an H atom and HS, and the  $H + O_3$  reaction can give HO and  $O_2$ , with the net result of producing HO, HS, and O<sub>2</sub> in the photolysis cage. Therefore, both photolyses give the pair of radicals which recombine to give HSOH. The  $H_2S/O_2$  matrix photolysis system gives mainly SO<sub>2</sub>, SO<sub>3</sub>,  $H_2O$ , and  $H_2SO_4$  as photooxidation products due to the formation of the key transient intermediates HS, HO<sub>2</sub>, SO, and HO. The fact that we did not observe HSOH in the  $H_2S/O_2$  system is indicative of the experimental condition that O atoms play an insignificant role in the H<sub>2</sub>S photooxidation in solid  $O_2$  even though  $O_3$  is formed during the photolysis. Also,  $HO_2$  and  $O_3$  are consumed on prolonged photolysis, because of a slow conversion of  $SO_2$  to  $SO_3$ .  $HO_2$  is a strong oxidizer of S-containing intermediates. Additional studies with  $Ar/O_2/H_2S$  using more monochromatic light may help elucidate the photo-oxidation mechanism with a greater certainty.

Note Added in Proof. We became aware of the recent work of Bondybey and English<sup>41</sup> in which IR spectra of SO<sub>3</sub> and its aggregates formed in rare gas matrices are examined. Some of the observed peaks have been assigned to SO<sub>3</sub>, SO<sub>3</sub>·H<sub>2</sub>O, and H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O. Their assigned values of the absorption frequencies of H<sub>2</sub>SO<sub>4</sub> in Ne at 5 K are similar to our values obtained in solid O<sub>2</sub> at 12 K (Table III), except for the very weak peaks at 578–545.8 cm<sup>-1</sup> which they did not report; their values are higher by  $\leq 0.5\%$ . Their assigned frequency values of SO<sub>3</sub>·H<sub>2</sub>O are 3803.9, 3612.9, 1591.4, 1401.3, and 490.9 cm<sup>-1</sup>, and the first two values are considerably different from our values shown in Table I. In any case, they conclude that H<sub>2</sub>O·SO<sub>3</sub> does not rearrange to H<sub>2</sub>SO<sub>4</sub> in the 5 K Ne matrix.

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**Registry No.**  $H_2S$ , 7783-06-4;  $O_2$ , 7782-44-7;  $H_2SO_4$ , 7664-93-9;  $SO_2$ , 7446-09-5;  $SO_3$ , 7446-11-9;  $HO_2$ , 3170-83-0;  $O_3$ , 10028-15-6;  $H_2O$ , 7732-18-5;  $H_2SO_3$ , 7782-99-2.

# Photochemical Oxidation of Carbonyl Sulfide and Carbon Disulfide in Solid $O_2$ at 15 K and the Molecular Complexes of the Photoproducts

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The photooxidation of OCS and CS<sub>2</sub> in solid O<sub>2</sub> at 15 K by UV light ( $\lambda < 300$  nm) has been studied by matrix FTIR spectroscopy. The OCS/O<sub>2</sub> system gives CO and SO<sub>2</sub> as major products and O<sub>3</sub>, SO<sub>3</sub>, and CO<sub>2</sub> as minor products. The product distribution is mostly the result of an S atom reaction with O<sub>2</sub> to give SO<sub>2</sub>. The CS<sub>2</sub>/O<sub>2</sub> system gives OCS, SO<sub>2</sub>, and O<sub>3</sub> as major products and SO<sub>3</sub>, CO, and CO<sub>2</sub> as minor products. The distribution of the major product is *probably* the result of the reactive intermediate formation of CS. More O<sub>3</sub> is formed from CS<sub>2</sub> than OCS. The secondary photolysis of OCS upon prolonged photolysis of the CS<sub>2</sub>/O<sub>2</sub> system gives a more complex product distribution. Probable precursor mechanisms are examined. The IR spectra of SO<sub>2</sub>, SO<sub>3</sub>, OCS, and CO molecular complexes are identified, and some of their structural features are examined. The photooxidation is not driven to completion to the thermochemically most stable set of products.

## Introduction

Photooxidation of SO<sub>2</sub> and its dimer,  $(SO_2)_2$ , in low-temperature matrices has been studied recently in our laboratory.<sup>1</sup> It was shown that  $(SO_2)_2$  in solid O<sub>2</sub> at 12 K was photooxidized readily to SO<sub>3</sub>, but SO<sub>2</sub> was photochemically inactive. In order to study photooxidation of other small sulfur-containing molecules of atmospheric interest and also the infrared spectra of molecular complexes produced by photolysis, we have photolyzed H<sub>2</sub>S, OCS, and CS<sub>2</sub> in solid O<sub>2</sub> at low temperatures. This paper deals with photooxidation of OCS and CS<sub>2</sub> whereas the photooxidation of OCS and CS<sub>2</sub> gives an order of magnitude greater amount of SO<sub>2</sub> than SO<sub>3</sub>, in contrast to the photooxidation of H<sub>2</sub>S which gives nearly twice as much SO<sub>2</sub> as SO<sub>3</sub>. This distinction appears to support a mechanism involving an oxidation of an S atom (or "S atom carrier") from OCS and CS<sub>2</sub> but a different mechanism<sup>2</sup> involving an oxidation of an SO molecule from H<sub>2</sub>S. Our results on the photooxidation of OCS and CS<sub>2</sub> in solid O<sub>2</sub> are distinctly different from the results of the photolyses of O<sub>3</sub> with OCS and CS<sub>2</sub> in low-temperature matrices<sup>3</sup> which give rise to O atom reactions with these molecules. The details of our work are presented here.

### **Experimental Section**

Carbonyl sulfide (Matheson, minimum purity 97.5%) and carbon disulfide (Matheson Coleman and Bell, chromatoquality, 99+ mol%) were used after "freeze-pump-thaw" purification in a vacuum line. O<sub>2</sub> (Liquid Carbonic, 99.999% stated purity) and <sup>18</sup>O<sub>2</sub> (Prochem, 99% atom purity) were used directly without purification. SO<sub>3</sub> was prepared by heating fuming sulfuric acid (20% free SO<sub>3</sub>) to 140–160 °C under O<sub>2</sub> atmosphere on a vacuum line and condensing the vapor fraction as "SO<sub>3</sub>". The gas mixture containing O<sub>2</sub> as the matrix gas (M) and S-containing molecules (R) was made in a 1-L bulb by standard manometric techniques and pulse deposited onto the cold CsI sample window (inside a cold head) maintained within 1 K by a closed-cycle helium re-

<sup>(1)</sup> Sodeau, J. R.; Lee, E. K. C. J. Phys. Chem. 1980, 84, 3358.

<sup>(2)</sup> Tso, T.-L.; Lee, E. K. C. J. Phys. Chem., preceding paper in this issue.

<sup>(3)</sup> Jones, P. R.; Taube, H. J. Phys. Chem. 1973, 77, 1007.