$$z_{\rm c} = K_{\rm cB} \; (\mu n^2 r_0^6 / (\sigma bt))^{1/4} + z_{\rm min}$$
 (viii)

where $K_{cB} = (3B/2^9)^{1/4}$

$$z_0 = K_{0B} (b^5 n^2 \mu \Delta \rho g / (\sigma^2 t))^{1/2} + z_{\min}$$
 (ix)

where $K_{0B} = (Z_0 - Z_{min})/4B^{1/2}$. 5b. The constants K_{cB} and K_{0B} are empirically related to Z_{min} by

$$K_{cB} = 0.263 - 0.01519Z_{min} - 0.04908Z_{min}^{2}$$

$$K_{cB} = 0.34585 - 0.19044Z_{c} - 0.02953Z_{c}^{2}$$

$$K_{\rm 0B} = 0.34585 - 0.19044 Z_{\rm min} - 0.02953 Z_{\rm min}$$

6. Setting m = 1 and $\tau_{\rm B} = 0$ reduces these expressions to those for a Newtonian fluid for which $Z_0 = 1.25$ and B = 1/1.22

$$z_{\rm c} = K_{\rm cN} (\mu n^2 r_0^6 / (\sigma bt))^{1/4}$$
(x)

where $K_{\rm eN} = (3/(1.22 \times 2^9))^{1/4}$

$$z_0 = K_{0N} (b^5 n^2 \mu \Delta \rho g / (\sigma^2 t))^{1/2}$$
 (xi)

where $K_{0N} = ((1.25^2 \times 1.22)/2^4)^{1/2}$.

7. The numerical constants differ from those derived by Frankel and Mysels, who incorrectly used the boundary condition d^2Z/dR^2 = 2/B when $R \rightarrow +\infty$ instead of eq v.

8. Comparison of the values of z_c and z_0 experimentally measured by Platikanov with the values predicted by eq x and xi shows better agreement than with the values predicted by the corresponding equations of Frankel and Mysels.

Effects of $(H_2S)_2$ Formation and Added H_2O on Ultraviolet Photooxidation of Hydrogen Sulfide in an O₂ Matrix

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UV photooxidation of H₂S effected by $\lambda = 270-300$ nm in an O₂ matrix at 13 K has been studied for a wide range of the matrix:solute ratios, 200-8000. The $H_2S:O_2 = 1:8000$ sample represents the limiting case of matrix-isolated H_2S monomer and gives the product ratio of $SO_2:SO_3:H_2SO_4 = 1:0.5:0.1$, whereas the $H_2S:O_2 = 1:200$ sample represents the limiting case of $(H_2S)_2$ dimer and gives the product ratio of 1:0.1:0.02. The photochemical formation of the S(VI) products is substantially reduced by the $(H_2S)_2$ dimer formed during the preparation of the concentrated matrix sample, and the H_2S partner in the dimer acts as a reducing agent of a photooxidation precursor. However, it appears that the H₂O partner of the H₂S·H₂O complex formed in the $H_2S/H_2O/O_2$ matrix samples neither enhances nor suppresses the H_2S photooxidation process that gives the S(IV) products in an O_2 matrix.

Introduction

It was reported recently that the in situ UV photooxidation of H_2S in an O₂ matrix at 15 K produced H_2SO_4 , SO₃, SO₂, HO₂, H_2O , H_2O_2 , and O_3 .¹ One of the molecular complexes formed in the matrix photolysis cage was $H_2O \cdot SO_3$, which had been suggested earlier to be a precursor to H₂SO₄ formation in the atmosphere.^{2,3} Recently, a very interesting study of the infrared spectra of the SO₃/H₂O mixture in rare gas matrices was reported by Bondybey and English.⁴ They found $H_2O \cdot SO_3$ and $H_2SO_4 \cdot nH_2O$ but not $(H_2O)_{n+1} \cdot SO_3$, where $n \ge 1$, and they concluded that SO₃ reacts to form hydrated H₂SO₄ in the presence of two or more H₂O molecules. Because of this suggestion concerning the role played by the second molecule of H_2O in the gas-phase conversion of SO_3 (+H₂O) to H₂SO₄, we have carried out a study of the in situ UV photooxidation of the H_2S/H_2O mixture in an O₂ matrix so that we can understand better the mechanism of H₂S photooxidation and formation of S(VI) species such as SO₃ and H₂SO₄. Since molecular complexes such as $(H_2S)_2$ and $H_2O \cdot H_2S$ can be formed in concentrated matrix samples, i.e., at low values of matrix:solute ratios (M/S), we have studied their spectra by Fourier transform infrared spectroscopy.⁵

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In this paper, we report on the photooxidation product distribution obtained in these samples and the mechanism of photooxidation processes of H_2S that is modified by the molecular complex formation with H_2S and H_2O in the matrix samples.

Experimental Section

The same experimental apparatus and procedure as described earlier¹ have been used, except for the ternary component samples. The gas mixtures of H_2S and O_2 and of H_2O and O_2 were prepared to the same total pressure but separately in two 0.5-L glass bulbs by standard manometric techniques. For the deposition of the ternary component samples, each sample bulb was connected to a solenoid valve (for pulse deposition) and then to a common inlet to a small mixing chamber that is connected to the sample deposition tube. The samples were pulse-deposited on a CsI window kept at 13 K and the spectra were taken at an instrumental resolution of 0.36 cm⁻¹ on an FTIR spectrometer (Nicolet Model 7199). The in situ photolysis of the matrix sample was effected by filtered light from a 500-W Hg arc lamp¹ using a filter set (Schott WG 295 plus Corning 7-54) that transmits a broad envelope between 270 and 420 nm (10% values of the envelope maximum are at 290 and 400 nm). It was shown in the previous work that the H₂S photodecomposition is effected in the wavelength range 270-300 nm with the lamp/filter apparatus used. In some experiments, unfiltered light ($\lambda \ge 220 \text{ nm}$) was used. All photolyses and analyses were carried out at 13 K.

Results

The previous study in our laboratory was carried out with the $O_2:H_2S$ ratios of 700 and 1500.¹ In the present study, we have used O_2 :H₂S ratios of 200, 1000, 1350, 2000, 4000, and 8000 in the binary component samples. H₂O was added to make the



Figure 1. Absorption spectra of monomeric H_2O , dimeric $(H_2O)_2$, and H_2OH_2S complex in the O-H stretch region. The $H_2S:H_2O:O_2 = 1:1:1000$ sample shows (b) only absorption of monomeric $H_2O(\nu_3)$ at 3732.3 cm⁻¹ with $H_2O(\nu_1)$ at 3636.7 cm⁻¹ too weak to be seen, and upon a $13 \rightarrow 26 \rightarrow 13$ K warmup (b') it shows appearance of some absorption features due to $(H_2O)_2$ and what might be $H_2OH_2S(A')$. In more concentrated samples (c and d), absorption features due to binary complexes and trimeric $H_2O(T)$ appear strong.

O2:H2O ratio be 100 or 200 in the ternary component samples. Representative FTIR spectra in the O-H stretch and the S-H stretch regions for the ternary component samples before photolysis are shown in Figures 1 and 2, respectively. Since the spectra of the monomeric, dimeric, and trimeric H_2O^6 in solid O_2 and the similar spectra for H_2S species⁵ in solid O_2 already have been studied, the absorption features due to these species can be readily identified. The remaining and new absorption features in the prephotolysis sample can now be characterized as mixed dimers and possibly mixed trimers. We observe new absorption features in the O-H stretch region to be at 3668 (peak A'), 3704 (peak A), 3585 (peak B), and 3557 cm⁻¹ (peak C). Peak A' at 3668 cm⁻¹ appears upon a warmup of the $H_2S:H_2O:O_2 = 1:1:1000$ sample (see Figure 1, b and b'); it may contain two overlapping absorptions due to the trimeric $(H_2O)_3$ (ν_3 , peak T) and the complex $H_2O(\nu_3)$ ·HSH. Peak A at 3704 cm⁻¹ in Figure 1d for the $H_2S:H_2O:O_2 = 5:5:1000$ sample probably contains two overlapping absorptions due to the $H_2O \cdot HOH(v_3)$ and H_2O - (v_3) ·HSH complexes, with the latter dominating. Both peaks A and A' appear near where $H_2O(\nu_1)$. HSH should absorb, because $H_2O(\nu_1)$ as an electron donor to the hydrogen atom of H_2S in the hydrogen bonding complex shows a moderate red-shift from the 3732.2 cm⁻¹ absorption of the monomeric $H_2O(v_3)$.⁶ Such a hydrogen bonding behavior is fairly well-known in the literature.^{5,6} Peak B at 3585 cm⁻¹ in Figure 1d probably contains two overlapping H-bonding absorptions due to $(H_2S)_n \cdot HOH(v_1)$ and $H_2O \cdot HOH(v_1)$, where n may be 1 or 2. We leave peak C unassigned, although it could be the absorption due to a different conformational isomer of $(H_2S)_n \cdot HOH(\nu_1)$.

New absorption features in the S-H region shown in Figure 2 are not sufficiently distinct for *definitive* assignments to mixed dimers, since they overlap somewhat with the self-dimer spectrum produced in the H_2O -free H_2S/O_2 mixture (see Figure 2 of ref



Figure 2. Absorption spectra of monomeric H₂S, dimeric (H₂S)₂, and H₂O·H₂S complex in the S-H stretch region. The binary component sample of H₂S:O₂ = 1:4000 (a) shows only absorption of monomeric H₂S(ν_3) at 2635.0 cm⁻¹. In the H₂S:H₂O:O₂ = 1:1:1000 sample (b), a weak absorption of dimeric H₂S at 2585.3 cm⁻¹ appears, and upon a 13 \rightarrow 26 \rightarrow 13 K warmup (b') it shows the appearance of a broad absorption feature due to what might be H₂O·H₂S complex (E). In more concentrated samples (c and d), absorption features due to binary and trimeric complexes appear.



Figure 3. Absorption spectra in the S=O stretch region after 270–420-nm photolysis of H_2O -free $H_2S:O_2$ matrix samples.

6). The H₂S:H₂O:O₂ = 5:10:2000 sample, although not shown in Figure 2, gives new H-bonding absorptions at 2566 and 2552 cm⁻¹ that are close to the H-bonding absorptions of (H₂S)_n, where n = 2 and 3, at 2585, 2575, and 2566 cm⁻¹; in the ν_3 absorption region, new features occur at 2628 and 2616 cm⁻¹ corresponding to the absorptions of (H₂S)_n⁵ at 2629 and 2621 cm⁻¹.

The results of 270–420-nm photolyses of the H_2S matrix samples are shown in Figures 3 and 4 for the S=O stretch region in which H_2SO_4 , SO_3 · H_2O , HO_2 , SO_2 , and SO_2 · H_2O as photo-oxidation products absorb. The relevant absorption frequencies are listed in Table I in agreement with the previous data.¹ Photolysis was carried out for various lengths of irradiation time for each sample. Only a representative set of the results is shown in Figures 3 and 4. The relative product yields were evaluated by integrating the area under each absorption curve as shown in Table II. A broad absorption feature at 1431 cm⁻¹ (Figure 4d)



Figure 4. Absorption spectra in the S=O stretch region after 270–420-nm photolysis of H_2O containing $H_2S:O_2$ matrix samples.

TABLE I: Absorption Frequencies (ν) of H₂SO₄, SO₃, SO₂, and HO₂ Species in the S=O Stretch Region in an O₂ Matrix (13 K)

		-
species	<i>v</i> , cm ^{−1}	vibrational mode
H ₂ SO ₄	1455.5 (w)	
	1452.0	$S(=O)_2$ antisym str
<i>SO</i> ₃ ·H ₂ O	1397.0	v_3 of SO_3
$HO_{2}(\tilde{M})$	1391.4	ν_2 bend
SO ₃ (M)	1385.8	$v_3(e)$
	1384.8 (sh)	
$SO_{2}(M)$	1348.8	ν_1 antisym str
<i>SO</i> , H,O	1343.6	ν_1 of SO ₂
	1342.5	
	$\frac{\text{species}}{\text{H}_2\text{SO}_4}$ $\frac{SO_3 \cdot \text{H}_2\text{O}}{\text{HO}_2(\text{M})}$ $\text{SO}_3(\text{M})$ $\text{SO}_2(\text{M})$ $\frac{SO_2(\text{M})}{SO_2 \cdot \text{H}_2\text{O}}$	$\begin{array}{c c} $\mathbf{species} & \overline{\nu}, \ \mathrm{cm}^{-1} \\ \hline \mathbf{H}_2 \mathbf{SO}_4 & 1455.5 \ (\mathrm{w}) \\ & 1452.0 \\ \mathbf{SO}_3 \cdot \mathbf{H}_2 \mathbf{O} & 1397.0 \\ \mathbf{HO}_2 (\mathbf{M}) & 1391.4 \\ \mathbf{SO}_3 (\mathbf{M}) & 1385.8 \\ & 1384.8 \ (\mathrm{sh}) \\ \mathbf{SO}_2 (\mathbf{M}) & 1348.8 \\ \mathbf{SO}_2 \cdot \mathbf{H}_2 \mathbf{O} & 1343.6 \\ & 1342.5 \\ \end{array}$

has not been identified. Although it could be a *hydrated* form of H_2SO_4 , this is not proven as will be discussed later.

We have also photolyzed the $H_2O:O_2 = 1:100$ sample for 1.8 h with unfiltered light ($\lambda > 220$ nm), but only small amounts of O_3 (1037.9 cm⁻¹), H_2O_2 (1264.7 cm⁻¹), and H_2O_2 · H_2O (1299.6 cm⁻¹) and a trace amount of HO₂ (1391.5 cm⁻¹) were observed. This result can be explained by a photolysis mechanism in which (i) O(³P) atom is presumably formed by O₂ photolysis (220 < $\lambda < 270$ nm), (ii) O₃ is formed by O(³P) + O₂ reaction, (iii) O(¹D) atom is formed by the secondary photolysis of ozone, and (iv) H_2O_2 is formed by an O(¹D) atom reaction with H_2O near the O₃ photolysis site. Similarly, we have found that N₂O (2232 cm⁻¹) and O₃ are formed when an N₂/O₂ matrix is photolyzed with unfiltered, white light ($\lambda > 220$ nm). We shall discuss these results later in connection with the photolysis results of the H₂S/H₂O/O₂ samples.

Discussion

a. H_2S/O_2 System. The effect of H_2S concentration (or matrix:solute ratio) on the photooxidation product distribution is shown in Figure 3 and Table II. According to the H₂S absorption spectrum taken for the $H_2S:O_2 = 1:4000$ sample (see Figure 2a), most of the H₂S molecules in this matrix sample exist as isolated monomers with a sharp absorption peak, and therefore the product distribution observed represents that due to the photooxidation of the matrix-isolated $H_2S(M)$. On the other hand, the H₂S absorption spectrum of the H₂S:O₂ = 1:200 sample (to be seen in Figure 2 of ref 6 or similar to Figure 2d) is indicative of a substantial degree of aggregation as $(H_2S)_2$ or perhaps trimer, and hence the product distribution observed in Figure 2c represents that due to the photooxidation of the matrix-isolated monomeric H₂S as well as that of dimeric (and trimeric) species. It is difficult to assess quantitatively how much $(H_2S)_2$ and $(H_2S)_3$ are present, but as much as 50% of H₂S may exist as dimeric species, if one can reasonably estimate the amount from the satellite absorptions next to the 2634.3-cm⁻¹ (v_3) absorption. Because the integrated molar absorption coefficients of the species shown in Figure 3 are not known,¹ we can only estimate the relative product yields by

TABLE II: Relative Product Yield Dependence on Matrix:Solute Ratio at $\lambda = 270-420 \text{ nm}^{a}$

mole ratios			rel areas absorpn by prod. ^b		
H_2S	H ₂ O	O ₂	"SO2"c	"SO3"d	H ₂ SO ₄ ^e
1		8000	(1)	0.51	0.07
1		4000	(1)	0.55	0.10
1		1350	(1)	0.39	0.08
1		200	(1)	0.11	≤0.02
1	40	8000	(1)	0.52	0.07
1	80	8000	(1)	0.52	0.07
1	1	1000	(1)	0.29	0.08
1	5	1000	(1)	0.30	0.05
5	5	1000	(1)	0.09	≤0.01
	mc H ₂ S 1 1 1 1 1 1 1 5	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{tabular}{ c c c c c c } \hline mole \ ratios \\ \hline H_2S & H_2O & O_2 \\ \hline 1 & 8000 \\ 1 & 4000 \\ 1 & 1350 \\ 1 & 200 \\ \hline 1 & 80 & 8000 \\ 1 & 80 & 8000 \\ 1 & 1 & 1000 \\ 1 & 5 & 1000 \\ \hline 5 & 5 & 1000 \\ \hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a The photolysis times were in the 4-14-h range. ^bSince the integrated molar absorption coefficients of SO₃ and H₂SO₄ are not known,¹ the relative areas under the absorption curves for the S=O antisymmetric stretch were measured (see Figures 3 and 4). Probably the values are accurate to $\pm 20\%$. ^cAbsorptions by both SO₂(ν_3) and SO₂(ν_3)·H₂O were measured as the reference. ^dAbsorptions by H₂SO₄ at 1452.0 and 1455.2 cm⁻¹ were measured.

assuming the same IR sensitivity of absorptions for the antisymmetric S=O stretch in all of the monomers and molecular complexes. Probably, this approximation is reasonable for the present comparison as shown in Table II. Also, we shall lump together yields of sulfur(IV) and yields of sulfur(VI) in the discussion as follows: "SO₂" = SO₂(M) + SO₂·H₂O; "SO₃" = SO₃(M) + SO₃·H₂O; S(IV) = "SO₂"; S(VI) = "SO₃" + H₂SO₄.

It is clear in Table II that "SO₃" yield decreases from a value of ~0.5 to ~0.1 and the H₂SO₄ yield decreases from a value of ~0.10 to ≤ 0.02 , when the M/S ratio decreases from a value of 8000 to 200, a 40-fold change. The H₂SO₄/"SO₃" ratio appears to be ~0.2 throughout. These results suggest that (H₂S)₂ does not produce S(VI) species in the UV photooxidation, and if so, the mole fraction of H₂S that exists as monomers cannot be greater than ~20%. This is somewhat lower than the earlier estimate of ~50%. Before we discuss the photooxidation mechanism, we should consider the H₂O concentration effect below.

b. $H_2S/H_2O/O_2$ System. The results tabulated in the lower half of Table II compared to those in the upper half show that within the accuracy of the product yield measurements the addition of H₂O holding O₂/H₂S ratio constant (as much as 1.0 mol % of O_2 for O_2 : $H_2S = 1:8000$) has no appreciable effect on the relative product distribution. The examination of the H₂O and H_2S absorptions such as shown in Figures 1 and 2 (see sample c) indicates that when large amounts of H_2O are added to the H_2S/O_2 mixtures the new absorption is dominated by the selfdimer of H_2O , $(H_2O)_2$. The mixed dimer, $H_2O \cdot H_2S$, is expected to be twice as abundant as the self-dimers, if the complex formation during the sample deposition of the $H_2O:H_2S = 1:1$ mixture is statistically controlled, but this is not apparent. On the other hand, the bandwidth of the 2585-cm⁻¹ peak (of H₂S) broadened by the complex formation with H₂O in the H₂S:H₂O:O₂ = 5:5:1000 sample (see Figure 2d) is approximately twice the bandwidth of the 2585-cm⁻¹ peak (of H_2S) broadened by the self-dimer formation in the $H_2S:O_2 = 5:1000$ sample (Figure 2 of ref 6). Therefore, we feel that a significant amount of $H_2O \cdot H_2S$ is present in comparison to $(H_2S)_2$ in our matrix sample. Furthermore, the photolytic product ratio of $SO_3(M)$ vs. $SO_3 \cdot H_2O$ is not affected by the presence of $H_2O \cdot H_2S$.

We have expected that the $H_2O \cdot H_2SO_4$ complex might be formed from the photolysis of the $H_2O \cdot H_2S$ molecular complex. The aerosol particles containing various amounts of H_2SO_4 show strong S=O stretching absorptions below 1350 cm⁻¹ (see Figure 17 of ref 3). Preliminary results from our laboratory show that the gaseous mixture of H_2O and SO_3 in O_2 sprayed on the matrix sample window at 12 K gives no strong absorption near 1431 cm⁻¹, although we expected to deposit some H_2O and H_2SO_4 formed from a rapid gas-phase reaction of H_2O and SO_3 .⁷ Therefore,

(7) Green, M.; Lee, E. K. C., unpublished results from our laboratory.

we do not have a positive identification for the 1431-cm⁻¹ peak observed to the red of the 1452-cm⁻¹ peak of $H_2SO_4(M)$. In the absence of proof that the broad 1431-cm⁻¹ absorption feature is due to $H_2O \cdot H_2SO_4$, we are forced to conclude that there is no photochemical effect of H_2O addition. The lack of the H_2O addition effect on the photooxidation of H₂S in an O₂ matrix indicates that the H₂O complex formation or the presence of H₂O at or near the photooxidation site in an O_2 matrix does *neither* enhance nor suppress the "SO3" and H2SO4 formation processes. This probably means that in an O₂ matrix the H₂O-catalyzed reaction of

$$H_2O + SO_3 \rightarrow H_2SO_4 \tag{1}$$

does not take place in the in situ UV photolysis of the H₂S:H₂O:O₂ samples, although it has been observed in the matrix co-deposition process of the SO₃/Ne and H_2O/Ne samples.⁴

c. Photooxidation Mechanism. Since the presence of H_2O in the photolysis cage that hosts H₂S does not affect the overall photooxidation product distribution, it is proposed that H₂O is essentially inert and also H₂O does not catalyze the conversion of $SO_3 H_2O$ to H_2SO_4 in an O_2 matrix. However, the presence of a second H_2S molecule in the photolysis cage does substantially reduce or entirely suppress the S(VI) photooxidation products by closing certain reaction channels. Also no new photoproduct is formed. We shall now consider plausible interfering steps following the initial photodissociation process¹

$$H_2S + h\nu \ (\lambda \le 300 \text{ nm}) \rightarrow H + HS$$
 (2)

The first possibility is the reaction of the hot photolytic H atom with the second H_2S molecule in the photolysis cage

$$H + H_2 S \rightarrow H_2 + HS$$
(3)

and a subsequent reaction of the HS formed in reaction 3 with the HS (or HSOO formed subsequent to reaction 2)

$$HS + HS \rightarrow HSSH$$
 (4)

$$HS + HSOO \rightarrow H_2S + SOO$$
 (5)

and

$$SOO \rightarrow \rightarrow SO_2$$
 (6)

Net reaction for the processes 2-6 is

$$(\mathrm{H}_2\mathrm{S})_2 + h\nu \; (\lambda \le 300 \; \mathrm{nm}) \rightarrow \mathrm{H}_2 + \mathrm{H}_2\mathrm{S} + \mathrm{SO}_2 \qquad (7)$$

This mechanism (reactions 2-6) can preempt the "SO₃" and H_2SO_4 formation. We are unable to observe H_2 because H_2 is IR inactive and also it diffuses out of an O₂ matrix at 12 K, even if it is formed. Therefore, we should find $SO_2 H_2S$ complex in the photolysis cage, and we could attribute the structureless broad absorption feature underlying the sharp $SO_2(v_3)$ ·H₂O absorption (at 1343.6/1342.5 cm⁻¹ in Figure 3c) to the $SO_2(\nu_3)$ ·H₂S absorption. A more pronounced broadening due to the H₂S complexes of $SO_2(v_3)$ and $SO_3(v_3)$ is seen in Figure 4d (vs. Figure 4c).

The second possibility involves the escape of the hot photolytic H atom from the photolysis cage as in reaction 8 and a subsequent

$$(H_2S)_2 + h\nu \rightarrow H + HS \cdot H_2S \tag{8}$$

oxidation of HS in the presence of the second H_2S molecule in an O_2 matrix. We can only speculate here that H_2S may act as a reducing agent of the precursors (such as HO₂, HS, and SO¹) of the S(VI) products or that when HO₂ dissociates by secondary photolysis the H atom may react with the second H₂S molecule as in reaction 3 and give an HS radical. Unfortunately, without further experiments we are unable to substantiate the necessary elementary steps for the HS oxidation or to give more information

than what had been presented previously.¹ However, we have interesting observations when unfiltered light is used for photolysis and a subsequent warmup is carried out.

Normally, unfiltered light photolysis ($\lambda > 220$ nm) at 13 K gives a slightly greater ratio of "SO₃": "SO₂", by $\sim 20\%$, than filtered light photolysis ($\lambda > 270$ nm) at 13 K. But the observed ratio of H₂O-complex to monomer for "SO₃" or "SO₂" is nearly the same regardless of photolysis wavelength. A matrix sample of $H_2S:H_2O:O_2 = 1:80:8000$ was photolyzed with unfiltered light $(\lambda > 220 \text{ nm})$ at 30 K, and it was found that SO₃(ν_3) and $SO_3(v_3) \cdot H_2O$ were present in about an equal amount but all of "SO₂" appeared as SO₂(ν_3)·H₂O. Again normally, when the photolyzed sample is treated by a brief warmup, $13 \rightarrow 30 \rightarrow 13$ K, monomeric SO_2 finds H_2O and all of $SO_2(M)$ is converted to $SO_2 \cdot H_2O$ complex. Therefore, we can conclude that (i) some "SO₂"s formed initially as $SO_2(M)$ finds H_2O formed in an adjacent matrix cage, but (ii) some "SO₃"s formed initially as $SO_3(M)$ have no H_2O in an adjacent matrix cage to complex with. This means that $SO_3(M)$ is formed when the first H atom from reaction 2 has migrated away (as HO_2)⁷ from the photolysis cage and subsequently the second H also migrates as HO_x species. The migration of HO_2 in an O_2 matrix can be facilitated readily by repeated photodissociation-combination cycles as observed previously.⁸ A similar migration mechanism also works for O_3 in an O_2 matrix, and it is supported by the observation that unfiltered light photolysis of the $H_2O:O_2 = 1:200$ sample gave H_2O_2 via $O(^{1}D)$ atom formation, which was mentioned in the Results. The present work does not provide a more comprehensive mechanism on the H_2S photooxidation in an O_2 matrix than that presented in an earlier paper.¹ However, it is useful to note some related recent works.^{9,10} Hashimoto et al.⁹ have observed the infrared absorption spectrum of HOSO₂ radicals trapped in an Ar matrix from the gas-phase reaction of

$$\mathbf{OH} + \mathbf{SO}_2 (+\mathbf{M}) \to \mathbf{HOSO}_2 (+\mathbf{M}) \tag{9}$$

but not H_2SO_4 . In the present experiment, we found no IR absorptions attributable to HOSO₂, and its absence in our system can be explained with the possibility that either reaction 9 is not a viable mechanism for the H_2S/O_2 system or HOSO₂ reacts further with O_2 in the matrix⁹ if formed via reaction 9. A very recent result¹⁰ from our laboratory shows that "SO₃" species (perhaps including " H_2SO_4 " species) are formed in the UV photolysis of the H₂CO:SO₂:O₂ matrix samples in which the HO₂ radicals (formed from the H_2CO photolysis)⁸ can react with SO_2 to form SO_3 (and H_2SO_4). It is interesting that, in the in situ photolysis of the $H_2CO:SO_2:O_2$ matrix (containing some H_2C - $O \cdot SO_2$ molecular complexes), "SO₃·H₂O" as well as "H₂SO₄" species are formed from the HO₂ reaction with SO_2^{10} but they are not formed from the OH reaction with SO₂ in the gas-phase reaction/matrix deposition experiment of Hashimoto et al.⁹ Therefore, it is unlikely that a direct reaction of OH or HO₂ radical with SO_2 in solid O_2 is responsible for the formation of H_2SO_4 found in the H_2S photolysis cage in solid O_2 . The observed lack of the effect of H_2O addition to the $H_2S:O_2$ matrix is not inconsistent with the preceding statement.

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Registry No. H₂S, 7783-06-4; O₂, 7782-44-7; H₂O, 7732-18-5; (H₂S)₂, 33410-62-7; SO₃, 7446-11-9; H₂SO₄, 7664-93-9; HO₂, 3170-83-0; SO₂, 7446-09-5.

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