allow t_{pulse} to vary. If saturation is absent, E_{abs}/F is practically constant. For example, in the classic experiments of Kolodner, Winterfeld, and Yablonovitch³⁴ on SF₆, at low pressures (where IR absorption is mostly collisionless) and high intensities (produced by using focused beams), $E_{\rm abs}/F$ was indeed nearly constant over a 100-fold variation in t_{pulse} . By contrast, in the present experiments, E_{abs}/F depends strongly on both t_{pulse} and P.

Our results are compiled in Table II. P and t_{pulse} vary by factors of more than 10. F varies by over 50-fold, and E_{abs}/F by more than 4-fold. However, as shown in Figure 8, when E_{abs}/F is plotted vs. $(F/t_{pulse}P)^{1/2}$, the experimental points nearly converge to a single curve. It should be stressed that this treatment is empirical and that other variables can be found which are equally effective at producing near-convergence. For instance, when E_{abs}/F is plotted vs. $[(F/t_{pulse})^{1/2}(1 + 0.075P)]/P$, convergence to a single, although different, approximate relationship is equally as good. The variables in the latter relationship are approximately consistent with theoretical expressions obtained²² for an absorption mechanism whose assumptions are compatible with those leading to ea 1.

Conversion of SO₂ to SO₃ Facilitated by in Situ UV Photolysis of H_2CO and SO₂ in an O₂ Matrix at 12 K

Martina Green and Edward K. C. Lee*

Department of Chemistry, University of California, Irvine, California 92717 (Received: April 15, 1986; In Final Form: July 21, 1986)

The photooxidation product distributions observed in photolyses of H₂CO and H₂CO·SO₂ molecular complexes in O₂ matrices at $\lambda = 270-420$ nm are compared. Photodissociation of H₂CO produces RO₂ species, i.e., HO₂ and HC(O)OO radicals, which then efficiently oxidize SO₂ to SO₃ (and H₂SO₄). This process occurs with an efficiency of $\sim 0.7 \pm 0.3$ per H₂CO·SO₂ molecular complex photodissociated. Various photooxidation mechanisms are considered. Implications of the low-temperature/matrix photooxidation results on atmospheric photooxidation of SO₂ by RO₂ species are discussed.

Introduction

Recent studies on in situ UV photooxidation of H₂S in solid O_2 at 12–15 K have shown that SO_2 , SO_3 , H_2SO_4 , H_2O , HO_2 , and O_3 are formed as oxidation products.^{1,2} Although our understanding of the H₂S UV photooxidation mechanism is far from being complete, it is likely that HO₂ radicals play an important role in the oxidation process. In order to gain further insight to the photooxidation mechanism involving HO_2 , we have carried out a study of UV photolysis of the H₂CO·SO₂ molecular complex in solid O₂ using light of $\lambda = 270-420$ nm. This molecular complex was chosen for our study, because in situ UV photolysis of SO₂ in solid O₂ at $\lambda = 270-420$ nm gives no product, whereas that of H₂CO gives HO₂ and HC(O)OO radicals which could then react with SO_2 in the photolysis cage. Previous matrix photo-oxidation studies of the H_2CO/O_2 ,^{3,4} H_2S/O_2 ,^{1,2} and SO_2/O_2 systems⁵ made in our laboratory provide requisite background information useful to our present work. The most important finding of the present work is that the oxidation of SO_2 to SO_3 (and H_2SO_4) is promoted by reactive radicals such as HO_2 and HC(O)OO (formylperoxyl) which are formed upon photodecomposition of H_2CO in solid O_2 . Since the homogeneous atmospheric oxidation of SO₂ to SO₃ is currently thought to occur via reactions 1-3, and similar processes can also occur in aerosols

$$HO + SO_2 + M \rightarrow [HOSO_2] + M$$
(1)

$$[HOSO_2] + O_2 \rightarrow [HOSO_2 \cdot O_2]$$
(2)

$$[HOSO_2 O_2] \rightarrow SO_3 + HO_2 \tag{3}$$

and liquids, it is interesting to compare our results with gas-phase

kinetic data regarding reactions 1-3.6-8 Furthermore, our results will be compared to the recent matrix isolation study of Hashimoto et al. in which the HOSO₂ radical was prepared in the gas phase by reaction 1 and its IR absorption spectrum in an argon matrix was characterized.9

Experimental Section

Monomeric H₂CO was prepared by thermal decomposition of solid formaldehyde polymer (Aldrich) at ~ 100 °C on a vacuum line. SO₂ (Matheson, 99.5% minimum stated purity) was used after a few freeze-pump-thaw cycles. O₂ (Liquid Carbonic, 99.999% stated purity) and CO (Matheson, 99.99% stated purity) were used without further purification. Deionized distilled water was used after degasing at -90° C. Gaseous mixtures of known matrix/reactant ratios (M/R) were made up in either 0.5- or 1-L bulbs by standard manometric techniques at room temperature.

Low-temperature matrices of the mixtures of interest were prepared by pulse deposition onto a CsI window held at 12 K by a close-cycle helium refrigerator (Air Products, Displex Model 202B). The effect of photolysis by a high-pressure mercury compact arc lamp (Osram HBO-500 W/2) equipped with a 10-cm water filter was monitored with a Fourier transform IR spectrometer (Nicolet Model 7199). Spectra were taken at a spectral resolution of ~ 0.37 cm⁻¹. Typically, light which passed through a set of Schott WG 295 and Corning CS 7-54 filters with a transmission envelope of 270-420 nm (a 10% transmission at 295 and 400 nm) was used for photolysis. Direct photooxidation of SO₂ which occurs at $\lambda < 240$ nm was effected by unfiltered (white) light from the mercury arc, but was avoided with the use of the above filter set. Two other filter sets were used for determining

⁽¹⁾ Tso, T.-L.; Lee, E. K. C. J. Phys. Chem. 1984, 88, 2776, 2781.

⁽²⁾ Woodbridge, E. L.; Lee, E. K. C. J. Phys. Chem., submitted for publication.

^{(3) (}a) Diem, M.; Lee, E. K. C. J. Phys. Chem. **1982**, 86, 4507. (b) Diem, M.; Tso, T.-L.; Lee, E. K. C. J. Chem. Phys. **1982**, 76, 6453. (c) Tso, T.-L.;

<sup>M., Iso, I.-L., Lee, E. K. C. J. Chem. Phys. 1982, 91, 339.
(4) (a) Tso, T.-L.; Lee, E. K. C. J. Phys. Chem. 1982, 91, 339.
(4) (a) Tso, T.-L.; Lee, E. K. C. J. Phys. Chem. 1985, 89, 1618.
(5) Sodeau, J. R.; Lee, E. K. C. J. Phys. Chem. 1980, 84, 3358.</sup>

⁽⁶⁾ Howard, C. J., et al., private communication, unpublished work.

⁽⁷⁾ See for a recent review: Calvert, J. G.; Stockwell, W. R. In SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations; Calvert, J. G., Ed.; Butterworth: Boston, 1984; pp 1-62. (8) Margitan, J. J. J. Phys. Chem. **1984**, 88, 3314.

⁽⁹⁾ Hashimoto, S.; Inoue, G.; Akimoto, H. Chem. Phys. Lett. 1984, 107, 198



Figure 1. FTIR spectra in the SO₃ (ν_3) and O₃ (ν_3) absorption regions following photolysis of (a) the SO₂:O₂ = 20:1000 sample showing negligible product formation due to photolysis with filtered light for 3 h; (b) the sample in (a) showing the formation of SO₃ species and O₃ due to photolysis with white light for 0.5 h; (c) the result of a warm-up to 32 K after (b); (d) SO₃ (ν_3) region showing the broad absorption features of the SO₃ (ν_3)·H₂O molecular complex made from white light photolysis of the H₂O:SO₂:O₂ = 1:20:1000 matrix sample; (e) the SO₃ (ν_3)·H₂O·CO molecular complex made from white light photolysis of the H₂O:CO: SO₂:O₂ = 1:5:20:1000 matrix sample.

the photolysis threshold of the SO_2/O_2 system: a Corning CS 7-54 filter either combined with a Schott WG 280 filter (10% transmissions at 280 nm and cutoff at 240 nm) or the former combined with a WG 305 filter (10% transmission at 305 nm and cutoff at 270 nm).

In order to pinpoint the products formed upon photolysis of the $H_2CO\cdot SO_2$ complex in a $H_2CO:SO_2:O_2$ matrix, we have carried out blank photolysis experiments with an $H_2CO:O_2 = 1:500$ matrix as well as $SO_2:O_2 = 1:50$ and 1:4000 matrices. Photolysis time dependence as well as SO_2 -concentration dependence studies were carried out. For the latter, $H_2CO:SO_2:O_2$ ratios were varied as follows: (a) 0.5:2.5:1000; (b) 1:5:1000; (c) 1:10:1000; (d) 1:20:1000. These matrix samples were prepared by depositing simulaneously the $H_2CO:O_2$ mixture contained in one flask and the $SO_2:O_2$ mixture contained in another flask. Most of the photolysis FTIR spectra will be presented as difference spectra (the absorbance spectrum of the photolyzed sample minus the absorbance spectrum of the preceding or prephotolysis sample).

Results

Photolysis of the $H_2CO:O_2 = 1:500$ Sample. A 3-h filtered light photolysis ($\lambda = 270-420$ nm) gave O_3 , HO_2 , H_2O , H_2O_2 , CO, CO_2 , HC(O)OO, HC(O)OOH, and HC(O)OH as products, in agreement with the earlier experiments.^{3,4} A subsequent 0.5-h white light photolysis ($\lambda \ge 220$ nm) gave significantly greater amounts of O_3 , H_2O , CO, and CO_2 but insignificant additional amounts of other products.

Photolysis of the $SO_2:O_2 = 1:4000$ Sample. Negligible amount of product was observed upon filtered light photolysis ($\lambda \ge 270$ nm) as shown in Figure 1a. This is consistent with an earlier observation concerning the photolysis of a dilute SO_2/O_2 matrix sample. But very minute amounts of O_3 and SO_3 were observed upon white light photolysis ($\lambda \ge 220$ nm) as reported in previous studies.⁵

Photolysis of the SO₂: $O_2 = 1:50$ Sample. A 3-h filtered light photolysis ($\lambda = 270-420$ nm) gave insignificant amounts of O₃ and SO₃, as observed with a dilute SO₂/O₂ matrix sample.



Figure 2. FTIR spectra of two matrix samples in the C-H stretching and the C=O stretching regions of H₂CO before photolysis. Different scale factors for absorbance are used in order to show the full absorption features. (a) H₂CO:O₂ = 1:500; the 1735.8-cm⁻¹ satellite is (H₂CO)₂.^{4a} (b) H₂CO:SO₂:O₂ = 1:20:1000; the 2893-, 2824-, 1729-, 1726-, and 1715-cm⁻¹ satellites are absorptions due to H₂CO in the H₂CO·SO₂ molecular complex. The untruncated height of the 1740-cm⁻¹ peak for the monomer in (b) is approximately equal to that in (a).

However, a 0.5-h white light photolysis ($\lambda \ge 220$ nm) gave significant amounts of O₃ and SO₃ species as shown in Figure 1b. A subsequent warm-up of the photolyzed sample (see Figure 1c) to 32 K broadened the 1385-cm⁻¹ peak of SO₃(M) as well as the 1400-cm⁻¹ peak of SO₃·SO_x (x = 2 or 3). Figure 1 shows the S=O antisymmetric stretching ($\nu_3 = 1385$ cm⁻¹) region of SO₃ and the O–O antisymmetric stretching ($\nu_3 = 1038.0$ cm⁻¹) of O₃ for this sample.

Photolysis of the $H_2O:SO_2:O_2$ and the $H_2O:CO:SO_2:O_2$ Samples. In order to identify the broad absorption features near 1386 and 1400 cm⁻¹ which appear in the photolyzed $H_2CO:SO_2:O_2$ samples (to be shown in Figure 3), we have carried out white light photolyses of SO_2/O_2 samples doped with H_2O and CO. White light photolysis of these samples should show some absorption features of molecular complexes such as SO_3 · H_2O , SO_3 · H_2O ·CO, SO_3 · SO_x , and SO_3 · SO_x · H_2O (x = 2 or 3). The spectra are shown in Figure 1, d and e.

Photolysis of the $H_2CO:SO_2:O_2$ Samples. The FTIR spectra of the C-H and C=O stretching regions before photolysis of the $H_2CO:O_2 = 1:500$ and the $H_2CO:SO_2:O_2 = 1:20:1000$ samples are shown in Figure 2. The extra satellite peaks appearing to the higher frequency side of ν_5 (2874 cm⁻¹) and ν_1 (2810 cm⁻¹) of H₂CO and those appearing to the lower frequency side of ν_2 (M) of H₂CO at 1740 cm⁻¹ and ν_2 (D) of (H₂CO)₂ at 1736 cm⁻¹ are absorption features of the H_2CO -SO₂ molecular complex. The absorption oscillator strengths for the vibrational fundamentals of $H_2CO(M)$, $(H_2CO)_2$, and $H_2CO \cdot SO_2$ in solid O_2 are not known. However, if we assume that they are approximately equal, we could estimate the relative amounts of the H₂CO species present in solid O₂ from the relative areas observed under each absorption peak. The peak integration data obtained on this basis are summarized in the upper part of Table I. The full heights of the 1740-cm⁻¹ peaks shown in Figure 2 are nearly equal for both samples a and b, while the peak height of the 1736-cm⁻¹ peak for sample b is 3-4 times smaller compared to sample a. This is indicative of a substantial reduction of the formation of the dimer, $(H_2CO)_2$, upon addition of SO₂ (20 times more SO₂ than H₂CO) to a $H_2CO:O_2 = 1:500$ mixture. As expected for statistical distribution of the solutes in a matrix and as shown in Table I, an increase in the proportion of H₂CO·SO₂ complex is observed upon further addition of SO_2 to a H_2CO/O_2 mixture. Table I shows also that photochemical decompositions of H₂CO (M) and H₂C- $O \cdot SO_2$ (C) by filtered light proceeds with an approximately equal

Green and Lee

	sample						
	1	2	3	4	5	6	
$H_2CO:SO_2 (O_2 = 1000)$	2:0	0.5:2.5	1:5	1:10	1:20	1:20	
gas mix., Torr L	142	300	300	400	284	284	
H ₂ CO spr., Torr L	0.2	0.1	0.1	0.2	0.2	0.2	
	Area ((v ₂) before Photoly	vsis (arb unit); t	= 0			
$H_{2}CO(M)$	27.8	9.1	9.8	10.4	4.5	4.6	
$[\hat{H}_{3}CO]_{2}$ (D)	3.1	0.3	0.6	0.8	0.3	0.4	
$H_2CO(SO_2)$ (C)	0	1.5	3.3	12.7	18.6	23.2	
$(\dot{M} + D + \dot{C})$	30.9	10.9	13.7	23.9	23.4	28.2	
$\dot{C}/(M + D)$	0	0.16	0.32	1.13	3.89	4.64	
time, h	3.1	3.3	3.4	2.7	2.9	3.0	
	Area	a Change after Ph	otolysis (arb uni	it)			
$H_2CO(M), \nu_2$	-19.7	-3.9	-5.0	-3.1	-2.9	-3.3	
$[H_2CO]_2$ (D), ν_2	-2.2	-0.23	-0.3,	-0.2_{8}	-0.1_{8}	-0.24	
$(M + D) \nu_{2}$	-21.9	-4.1	-5.3	-3.4	-3.1	-3.6	
$H_2CO \cdot SO_2(C), \nu_2$	0	-1.1	-2.6	-4.2	-4.7	-5.0	
$(\dot{M} + D + C), \nu_2$	-21.9	-5.2	-7.9	-7.6	-7.8	-8.6	
CO, <i>v</i> ₀	8.6	1.8	3.1	5.1	3.4	3.3	
CO_2, ν_2	7.4	1.4	6.2	4.3	3.3	3.3	
$HC(O)OO, \nu(C=O)$	1.5	0.4	0.4	0.6	0.1	0.1	
$HC(O)OH, \nu(C=O)$	0.4	0.1	0.1	0.1	0.02	0.03	
$H_{2}O, \nu_{2}$	8.1	7.3	6.9	2.6	6.9	4.8	
HO_2, ν_2	5.8	0.9	1.1	1.4	0.3	0.2	
$H_{2}O_{2}, \tilde{\nu}_{6}$	5.4	1.2	1.4	1.6	0.4	0.2	
O_3, ν_3	3.1	0.8	1.0	1.1	0.4	0.4	
$SO_{3}(M), \nu_{3}$	0	0.4	1.2	3.5	4.9	5.0	
$SO_3 \cdot X, \nu_3$	0	1.0	2.8	7.3	12	12	
$SO_3(M) + SO_3 X, \nu_3$	0	1.4	4.0	11	17	17	
	H ₂ CO:SO ₂ (O ₂ = 1000) gas mix., Torr L H ₂ CO spr., Torr L H ₂ CO gas mix., Torr L H ₂ CO (M) [H ₂ CO] ₂ (D) H ₂ CO:SO ₂ (C) (M + D + C) C/(M + D) time, h H ₂ CO (M), ν_2 [H ₂ CO] ₂ (D), ν_2 (M + D) ν_2 H ₂ CO:SO ₂ (C), ν_2 (M + D + C), ν_2 CO, ν_0 CO ₂ , ν_2 HC(O)OO, ν (C=O) HC(O)OO, ν (C=O) HC(O)OH, ν (C=O) H ₂ O, ν_2 HO ₂ , ν_2 HO ₂ , ν_2 HO ₂ , ν_2 HO ₂ , ν_3 SO ₃ (M), ν_3 SO ₃ (M) + SO ₃ ·X, ν_3	$ \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 $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

TABLE II: Some IR Integrated Absorption Coefficients (α) of Gaseous Molecules (Adapted from Pugh and Rao^a)

molecule	vibrl fundam	$\nu, {\rm cm}^{-1}$	α , ^b cm ⁻² atm at 300 K
СО	1-0	2143	~220
CO,	ν_2	667	194
O ₃	ν_3	1042	~330
SO_2	ν_3	1362	~780
$H_2\tilde{O}$	ν_2	1595	~280
H_2O_2	ν_6	1266	~ 388°
H ₂ CO	ν_2	1746	237
SO_3	v3	~1390	$\sim 1200^{d}$
HC(0)00	C=0	~1791 (in O ₂)	$\sim 240^{e}$
HCOOH	C=0	$\sim 1760 (in O_2)$	$\sim 240^{e}$

^{*a*} A compilation by: Pugh, L. A.; Rao, K. N. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic: New York, 1976; Vol. II, p 165. ^{*b*} An average value of recent measurements, if more than one measurement is reported. Often, the reported values vary by more than 10%. ^{*c*} Valero, F. P. J.; Goorvitch, D.; Bonomo, F. S.; Boese, R. W. *Appl. Opt.* **1981**, 20, 409. ^{*d*} Calvert, J. G., private communication. α of SO₃ (v_3) estimated to be ~1.5 times α of SO₂ (v_3) as in ref 1. ^{*e*} Assumed to be similar to α (C=O) of H₂CO.



Figure 3. FTIR spectra in the SO₃ (ν_3) , H₂O₂ (ν_6) , and O₃ (ν_3) regions after filtered light photolysis of the H₂CO:SO₂:O₂ samples with varying amounts of SO₂.

TABLE III: Summary of Estimated Photolysis Yields (mol/mol)

		sample (H ₂ CO:	SO ₂ ; O ₂	= 1000)	
	1	2	3	4	5	6
	(2:0)	(0.5:2.5)	(1:5)	(1:10)	(1:20)	(1:20)
$-\Delta(M)/(M)_0^a$	0.73	0.43	0.51	0.30	0.64	0.72
$-\Delta(D)/(D)_0^a$	0.71	0.7,	0.53	0.35	0.60	0.60
$-\Delta(C)/(C)_0^a$		0.73	0.79	0.33	0.25	0.22
$\Delta(CO)/\Delta F^b$	0.42	0.37	0.42	0.72	0.47	0.42
$\Delta(\text{CO}_2)/\Delta \text{F}^b$	0.41	0.33	е	0.69	0.52	0.47
$\Delta(\text{HC}(0)\text{OO})\Delta F^{b}$	0.07	0.08	0.05	0.08	0.01	0.01
$\Delta(\text{HCOOH})/\Delta F^{b}$	0.02	0.02	0.01	0.01	0.00	0.00
$\Delta(H_2O)/\Delta F^b$	0.31	е	0.74	0.29	0.75	0.47
$\Delta(\mathrm{HO}_2)/\Delta \mathrm{F}^{b,c}$	0.32	0.21	0.17	0.23	0.05	0.03
$\Delta(H_2O_2)/\Delta F^b$	0.15	0.14	0.11	0.13	0.03	0.01
$\Delta(O_3)/\Delta F^b$	0.10	0.11	0.09	0.10	0.04	0.03
$\Delta(S(VI))/\Delta C^d$		0.25	0.30	0.51	0.71	0.67

^{*a*} Fraction consumed by photolysis calculated from the data in Table I. ^{*b*} Ratio of the product formed per the "formaldehyde", F, consumed, i.e., (F = M + D + C), adjusted for the IR absorptivity (α) in Table II. ^{*c*} α of HO₂ (ν_2) was assumed to be 0.5 of the α of H₂O₂, (ν_6). ^{*d*} Ratio of the "S(VI)" product formed (SO₃ + SO₃·X) per H₂CO·SO₂ complex consumed, adjusted for the IR absorptivity (α) in Table II. ^{*e*} Unreliable measurement.

efficiency, within the accuracy of the peak area measurements of $\sim 10\%$.

The product distribution of SO₃ species, H_2O_2 , and O_3 obtained after 3-h photolysis with filtered light is shown in Figure 3. Although some amounts of H_2O were observed in the 1600-cm⁻¹ region, sharp absorption features^{1,2} of neither H_2O -SO₃ (1397 cm⁻¹) nor H_2SO_4 (1452; 1219 cm⁻¹) were observed in any samples. The observed peak areas are summarized for these samples in Table I. The gas-phase integrated absorption coefficients for the vibrational fundamentals which are listed in Table II were used in conjunction with peak areas of the observed IR absorptions in the matrix/photolysis samples to estimate the mole ratios of the parent reactants consumed (see Table I) and the photooxidation products formed (see Table II). The optical density of the ν_2 peak of $H_2CO(M)$ is quite high (often greater than 1), particularly for sample 1 and this can reduce the photometric accuracy substantially by strong deviation from the Beer-Lambert law.

Therefore, in such cases, we have used the optical density of the weaker absorption peak (ν_3) to estimate the correct ν_3 intensity. Since ν_1 absorption features are not useful in distinguishing the absorptions by $H_2CO(M)$, $(H_2CO)_2$, and $H_2CO\cdot SO_2$ from one another, ν_2 absorptions were used for quantitative measurements. The peaks of $SO_2(\nu_3)$ were so strongly distorted due to high concentration that no attempt was made to use them for photometric estimates.

Discussion

A. White Light Photolysis of SO_2 . In the absence of H_2CO , photooxidation of SO_2 to SO_3 in a concentrated matrix does not take place with long-wavelength UV light (270-420 nm), as is shown in Figure 1a. However, the photooxidation is effected readily with short-wavelength UV light (≥220 nm) as shown in Figure 1b,d,e. The present observations confirm an earlier study of the UV wavelength dependence and the SO₂ concentration dependence of photooxidation of SO₂ to SO₃ in an O₂ matrix.⁵ In a concentrated matrix (SO₂:O₂ = 1:50), certainly a significant amount of the SO₂ dimer is present, and therefore, there are two SO_3 species observed after photolysis: monomeric SO_3 (M) which is characterized by ν_3 fundamental at 1386 cm⁻¹ and SO₃·SO_x complex (an undetermined mixture of $(SO_3)_2$ and $SO_3 \cdot SO_2$) which is characterized by a broad feature of the ν_3 fundamental of SO₃ at ~1400 cm⁻¹ (see Figure 1). Both of these features of SO₃ (ν_3) fundamentals are broadened further upon a brief warm-up of the photolyzed matrix leading to aggregation of the photolytic SO₃ as shown in Figure 1c. Similar broad features of SO₃ (ν_3) fundamentals are also seen upon photolysis of matrix samples containing SO₂, H₂O, and CO in solid O₂. A similar broadening of the O₃ peak (ν_3 at 1038 cm⁻¹) is also observed as shown in Figure 1. An addition of 0.1% of H_2O to an SO_2/O_2 matrix sample has little effect on further broadening of SO₃ (ν_3) absorption peaks (see Figure 1d vs. 1b), but an addition of 0.5% CO together with 0.1% H₂O definitely broadens them (see Figure 1e vs. 1b). As will be discussed later, the SO₃ (ν_3) absorption features in the photolysis sample of a H₂O:CO:SO₂:O₂ = 1:5:20:1000 matrix are very similar to the ν_3 features of SO₃ (M) and SO₃·X found in the photolysis sample of a $H_2CO:SO_2:O_2 = 1:20:1000$ matrix (see Figure 3d).

B. H₂CO·SO₂ Molecular Complex. In solid O₂, the vibrational frequency shifts (Δv_i) observed for the H₂CO-SO₂ complex relative to the monomer H_2CO (M) are somewhat greater than those observed for the dimer, (H₂CO)₂, in solid O₂:⁴ $\Delta \nu_1 = +16$, $\Delta \nu_2 = -7/-10/-21$, and $\Delta \nu_3 = +21$ cm⁻¹ for H₂COSO₂ vs. $\Delta \nu_1 = +9$, $\Delta \nu_2 = -4$, and $\Delta \nu_3 = +14$ cm⁻¹ for (H₂CO)₂. The complex shift observed for H_2CO -HOH in solid Ar at 11 K are $\Delta \nu_1 = +19/+17$, $\Delta \nu_2 = -5$, and $\Delta \nu_5 = +19/+14$ cm^{-1.10} From IR studies in inert matrices,^{10,11} Nelander has suggested that H_2CO -HOH has a hydrogen-bonded structure while $(H_2CO)_2$ has a structure in which the two C=O groups are nearly antiparallel ($\sim 140^{\circ}$) and the two molecular planes are roughly orthogonal. The dipole moments of H₂CO and SO₂ are both large, i.e., 2.33 and 1.63 D, respectively. Therefore, dipole-dipole interaction between these molecules can contribute substantially to the equilibrium geometry of the molecular complex. However, SO₂ could interact as a Lewis acid with H₂CO as in the case of the H₂CO·H₂O complex and the H₂CO·H₂S complex for which $\Delta \nu_1$ (C–H) = +12 cm⁻¹ has been observed.¹⁰ Since the C-H stretching frequencies (ν_1 and ν_5) show large positive values of $\Delta \nu_i$ (+16 and +21 cm⁻¹, respectively), an O-S bonding or an antiparallel dipole (sandwich type) structure may be quite reasonable for the $H_2CO \cdot SO_2$ complex.

It should also be noted that the intensity of the 1715-cm⁻¹ peak is considerably weaker than that of 1729/1726-cm⁻¹ peaks in the samples containing SO_2 (samples 2-4 vs. samples 5 and 6). Furthermore, the 1715-cm⁻¹ peak is much more slowly photolyzed than the 1729/1726-cm⁻¹ peaks. Thus, it is suggested that the 1715-cm⁻¹ feature observed at high values of SO₂:H₂CO ratio may

be due to a ternary complex, $H_2CO-2SO_2$, and this is photodecomposed with a considerably lower efficiency than the binary complex, H₂CO·SO₂,

C. Filtered Light Photolysis of H_2CO . The ultraviolet absorption band of H₂CO which occurs at 250-350 nm is about 15-20 times weaker than the UV absorption band of SO_2 which occurs at 240-330 nm. The compact Hg arc lamp used in these studies has broad emission bands (near the UV absorption bands) at 334, 313, 302, 296, 288, and 280 nm in order of decreasing intensity. The filter set used has a transmission envelope at 270-420 nm. Furthermore, it is known from previous matrix/ photolysis studies that the photooxidation threshold wavelength of H₂CO in solid O₂ is \sim 330 nm^{4a} while SO₂ in solid O₂ is photochemically inert in this wavelength range.⁵ Therefore, direct photodecomposition can occur only for H₂CO species in an O₂ matrix sample containing H_2CO and SO_2 , despite the fact that most of the photolytic light is absorbed by SO_2 species. For this reason, we will consider the initial decomposition of H₂CO to H and HCO as the first step in the photooxidation mechanism

$$H_2CO + h\nu(\lambda \le 330 \text{ nm}) \rightarrow H + HCO$$
 (4)

Subsequent reactions of H and HCO with O₂ gives CO, HO₂, and HC(0)00

$$H + O_2 (+M) \rightarrow HO_2 (+M)$$
 (5)

$$HCO + O_2 \rightarrow HO_2 + CO$$
 (6)

It has been established^{4a} that a substantial fraction of the HC(O)OO formed in reaction 7 undergoes secondary photolysis to give HO₂, CO₂, and O₃.

The fractional amounts of the parent molecules consumed by photolysis in each matrix sample are tabulated in the first three rows of Table III as $\Delta(M)/(M)_0$ for monomeric H₂CO, $\Delta(D)/(M)_0$ (D)₀ for dimeric H₂CO, and $\Delta(C)/(C)$ for the H₂CO complexed to SO₂. Because the absorption peak of the H₂CO (M) is measured with a poor photometric accuracy due to high optical densities in some samples, the fraction consumed can be estimated with an accuracy no better than ± 0.2 . It is reasonable to say that about 1/2 of M and D species have been consumed by a 3-h photolysis in all samples whereas only about 1/4 of C species have been consumed in samples 4, 5, and 6 containing a high ratio of SO_2/H_2CO . The lower photochemical activity of the $H_2CO \cdot SO_2$ complex as compared to that of the monomeric and dimeric H₂CO could be due to the greater ability of the SO₂ partner (in the complex) in deactivating (or quenching) the photoexcited H₂CO by some nonradiative processes that compete with photodissociation process 4.

The efficiency of the photooxidation of SO_2 to SO_3 was evaluated by two methods: (i) fractional molar yield of the species containing no sulfur atom relative to the consumption of the total H_2CO species, $\Delta F = \Delta(M) + \Delta(D) + \Delta(C)$; (ii) fractional molar yield of the species containing sulfur atom relative only to the consumption of the H_2CO ·SO₂ species, $\Delta(C)$. The former provides quantitative information about the H2CO photooxidation product distribution and the latter only about the SO₂ oxidation product distribution. The data shown in the lower part of Table III show clearly that in samples 5 and 6 the oxidizing agents for SO_2 such as HC(O)OO, HO_2 , H_2O_2 , and O_3 are greatly reduced whereas the oxidized sulfur species, S(VI), are substantially increased. Again it should be noted that the reliability of these values is no better than $\pm 50\%$.

D. $SO_3 \cdot X$ Complex. In the photolysis cage which originally hosted an H₂CO·SO₂ complex, the H₂CO photooxidation process (which has effected the conversion of SO_2 to SO_3) should give a set of three reaction products, i.e., SO_3 , H_2O , and CO. These products should aggregate among themselves to form molecular complexes having various geometric structures (or a H₂SO₄·CO complex). However, if the original matrix cage contained H_2CO and two SO₂ molecules, one should expect to find SO₂, SO₃, H₂O, and CO which can then aggregate to form more complex struc-

⁽¹⁰⁾ Nelander, B. J. Chem. Phys. 1980, 72, 77.

 ⁽¹¹⁾ Nelander, B. J. Chem. Phys. 1980, 73, 1034.
 (12) Gleason, J.; Howard, C. J. Paper presented at the American Geophysical Union Meeting, San Francisco, Nov. 1985.

tures (or a $H_2SO_4 \cdot SO_2 \cdot CO$ complex). The broad absorption feature near ~ 1400 cm⁻¹ as shown in Figure 3d is similar to the broad absorption feature of $SO_3 \cdot SO_2$, $(SO_3)_2$, $SO_3 \cdot H_2O$, or $SO_3 \cdot SO_x \cdot H_2O$ near 1400 cm⁻¹ as shown in Figure 1. In a previous study of in situ matrix photolyses of the H_2S/O_2 system,^{1,2} a sharper absorption feature of $H_2O \cdot SO_3(\nu_3)$ at 1397 cm⁻¹ has been observed. Therefore, the broad feature at ~ 1400 cm⁻¹ is most likely a ternary complex of $SO_3(\nu_3)$ such as $SO_3 \cdot SO_x \cdot H_2O$ or $SO_3 \cdot H_2O \cdot CO$ rather than a binary complex. It should also be noted that the broadness of the 1386-cm⁻¹ peak may be correlated with high ratios of SO_2/O_2 and this may indicate the presence of $SO_3(\nu_3) \cdot CO$.

There is also a weak, extremely broad absorption feature extending from 1420 to 1460 cm⁻¹. In view of a sharp feature of the S=O stretching of H_2SO_4 (M) observed at 1452 cm⁻¹ in the previous in situ photolysis of the H_2S/O_2 system,^{1,2} this broad feature may be assigned to an aggregated H_2SO_4 species such as H_2SO_4 ·CO, H_2SO_4 ·SO₂·CO, or H_2SO_4 ·H₂O·CO. Positive identification of the broad absorption features at 1400 and 1420–1460 cm⁻¹ is nearly impossible. Therefore, we shall simply designate them as "SO₃(ν_3)·X", and their yields are evaluated by integrating the area between 1394 and 1460 cm⁻¹ and listed in Table I. The partitioning of the S(VI) species into three components, SO₃, SO₃·H₂O, and H₂SO₄ species, is only approximate, i.e., 1:1:1, SO₃ and H₂SO₄ being somewhat smaller than SO₃·H₂O. The sum of the yields of "SO₃(M)" and "SO₃·X" is tabulated in Table III as "S(VI)", the fully oxidized form of sulfur compounds.

E. Conversion of SO_2 to SO_3/H_2SO_4 . In Table III, the fractional photooxidation yields for six samples are summarized, but the major changes associated with the addition of SO_2 (which forms $H_2CO\cdot SO_2$) can be seen easily by comparing the most concentrated samples 5 or 6 with sample 1 containing no SO_2 . The other samples show gradual changes from sample 1 containing no SO_2 .

No obvious changes in the product yields of CO, CO₂, and H₂O species are seen within the accuracy of our measurements. The O₃ yield is reduced by a factor of 2–3, whereas the yields of HO₂, H₂O₂, and HC(O)OO are reduced by an order of magnitude. A check of mass balance as represented by these data for samples 1, 5, and 6 can be made for hydrogen, carbon, and sulfur atoms: 0.7, 0.8, 0.5 for H atom; 1.1, 1.1, 1.0 for C atom; 0, 0.7, 0.7 for S atom. These values fall within the overall \pm 50% uncertainty mentioned earlier in our FTIR photometric measurement combined with our estimate of the integrated absorption coefficients of various species in solid O₂. We shall regard the observed mass balance to be satisfactory. Now, we can consider the photo-oxidation mechanism involving SO₂.

There are four obvious oxidizing agents capable of converting SO_2 to SO_3 (or H_2SO_4), i.e., HC(O)OO, HO_2 , H_2O_2 , and O_2 , whose yields are known. Although the OH radical should be added to the list, we shall ignore it for the time being since the concentration of OH was probably too low to be monitored in our FTIR experiments. In the absence of SO_2 (sample 1), the fractional yields of HC(O)OO, HO₂, H_2O_2 , and O_3 were 0.07, 0.32, 0.15 and 0.10, the sum being 0.64. Recall that a lower yield of HC(O)OO (0.07) compared to the HO₂ yield (0.32) is probably indicative of secondary photochemical decomposition of the former to give HO₂, CO₂ and O₃. In samples 5 and 6, the fractional yield of S(VI) is ~0.7. In the H_2CO/O_2 system,^{3c,4a} it has been established that H_2O_2 and O_3 are formed in secondary processes involving HO, and HC(O)OO. Since the reduction in the sum of the H_2O_2 and O_3 yields are only 0.19 (see Table III), it is unlikely that these species are responsible for the entire amount of S(VI) observed. Therefore, it is suggested that almost all of HO₂ and HC(O)OO (prior to their conversion to H_2O_2 and O_3) are consumed in converting SO_2 to SO_3 (or H_2SO_4), with HO_2 being the major oxidizer of SO₂

$$HO_2 + SO_2 \rightarrow OH + SO_3$$
 (8)

$$C(O)OO + SO_2 \rightarrow H + CO_2 + SO_3$$
(9)

The presence of SO₂ in the photolysis cage of the $H_2CO \cdot SO_2$ complex probably preempts the formation of H_2O_2 and O_3 via

Η

TABLE IV: Reaction Enthalpies (at 0 K) and Gas-Phase Rate Constants (at 300 K)^{a}

ΔH° ,	
kcal/mol	k, cm ³ s ⁻¹
-50	5.5×10^{-32}
-59	$<1 \times 10^{-19}$
-15	$\leq 1 \times 10^{-18}$
+43	
-24	
-24	
-80	
-26	1.5×10^{-13}
~ 0	
-68	7×10^{-11}
-43	6.8×10^{-14}
-32^{b}	
$+2^{b}$	$4 \times 10^{-13 a,c}$
	$\begin{array}{r} \Delta H^{\circ}, \\ \text{kcal/mol} \\ \hline -50 \\ -59 \\ -15 \\ +43 \\ -24 \\ -24 \\ -24 \\ -80 \\ \hline -26 \\ \sim 0 \\ -68 \\ -43 \\ -32^{b} \\ +2^{b} \end{array}$

^aGas-phase bimolecular reaction rate constants were taken from: DeMore, W. B. et al. *Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling*; Evaluation No. 7; JPL Publications 85-37, NASA, July 1, 1985. For termolecular reactions, the highpressure limiting values or rates in units of cm⁶ s⁻¹ are listed. ^bReference 8. ^cReference 12.

TABLE V: Various Mechanisms and Product Sets in the Cage from the Photooxidation of the $\rm H_2CO{\cdot}SO_2$ Complex

mechanism	key oxidizer of SO ₂	product sets ^{a,b}		
I: c, j	HO ₂	H ₂ O, CO, SO ₃		
II: c, h, i, a	HO ₂	2HO ₂ , CO ₂ , SO ₃		
III: b, l, m	OH	2HO ₂ , CO ₂ , SO ₃		
IV: g	HC(0)00	2HO ₂ , CO ₂ , SO ₃		

^{*a*}CO is a decarbonation product from H_2CO photolysis (see ref 4). ^{*b*}Some of HO_2 will self-react to give H_2O_2 via reaction 10.

reactions of HO_2 and HC(O)OO; reactions 8 and 9 dominate over reactions 10 and 11

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{10}$$

$$HC(O)OO + HO_2 \rightarrow HC(O)OH + O_3$$
(11)

Reaction enthalpies and gas-phase rate constants of various pertinent free-radical reactions are listed in Table IV. For convenience, reactions in Table IV are labeled uniformly with alphabetical letters. Only reactions d and m are endothermic. In the absence of SO₂, HO₂ is consumed by reaction b to give OH and CO₂, and reaction j consumes the OH formed and HO₂ to give the final product set, H₂O and CO₂. If photooxidation of H₂CO is incomplete, the product sets which maintain the cage stoichiometry are HO₂ + HC(O)OO, (HO₂)₂ + CO, H₂O₂ + CO, HC(O)OOH or HC(O)OH + O₃. Since all these products except CO are substantially reduced in the presence of SO₂ (see Table III), four possible mechanisms of SO₂-to-SO₃ conversion involving OH, HO₂, and HC(O)OO radicals are summarized in Table V. Note that only exothermic reaction steps from Table IV, except reaction m which is slightly endothermic, have been used.

We shall first consider mechanisms I and II. Mechanism I consumes HO₂, whereas mechanism II regenerates HO₂ via reactions i + a, although HO₂ was initially consumed via reaction c. Mechanism I gives CO, whereas mechanism II gives CO₂. Since the addition of SO₂ reduces the HO₂ yield, mechanism I is favored over mechanism II. Mechanism IV which involves HC(O)OO via reaction g gives the same product set as mechanism II, and hence again it should be of minor importance. Mechanism III involves OH radical as the oxidizer of SO₂ via reaction l, but the net reaction is the same as mechanism II; HO₂ is regenerated, contrary to the observed result. Therefore, mechanism III can also be ruled out as a major SO₂ oxidation mechanism. Note also that mechanisms II-IV do not produce H₂O as a product. Since no OH absorption has been detected in our FTIR spectra after photolysis, it is difficult to justify mechanism III any further. The

facile reaction of OH with the other HO₂ as in reaction j or with HC(O)OO may deplete the OH concentration so rapidly that no OH can be detected in our experiments. Therefore, mechanism I is most consistent with our observations. However, mechanism IV involving HC(O)OO radical should account for some SO₂-to-SO₃ conversion with CO₂ as a product.

The results summarized in Table III show that $\Delta(CO)/\Delta F$ and $\Delta(CO_2)/\Delta F$ remain constant within experimental error, although mechanism I should increase the value of $\Delta(CO)/\Delta F$ and decrease the value of $\Delta(CO_2)/\Delta F$ when H₂CO·SO₂ species are photooxidized. This discrepancy can be rationalized if we include mechanism IV and/or if we recognize that the observed product yields in samples 5 and 6 represent contributions from not just $H_2CO \cdot SO_2$ but from two sources, i.e., ~40% from monomeric/dimeric H₂CO and $\sim 60\%$ from H₂CO·SO₂ complex. Since the reaction of HO_2 with SO_2 is known to be very slow in the gas phase, $k_c \le 1 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ (see Table IV), we need to justify our use of reaction c as the primary oxidation route (in mechanism I) for converting SO_2 to SO_3 in solid O_2 at 12 K. It can be speculated that the nascent HO₂ generated from photolysis of the H_2CO that is complexed to SO_2 in solid O_2 could be more reactive than thermalyzed HO₂. It is also possible that the SO_2 -to- SO_3 conversion process is aided by secondary photolysis of either HO₂ or HC(O)OO in our experiments. If this is the case, the efficiency of the secondary photolysis must be very high to justify the observed value of $\Delta S(VI)/\Delta C \simeq 0.7$. The UV absorption threshold wavelength of HO_2 is below 270 nm in the gas phase at room temperature.¹³ However, our photolysis occurs at wavelength above 270 nm, and therefore the extent of the secondary photolysis of HO_2 to give HO and O should be negligible. Unfortunately, we know nothing about the UV absorption of HC(O)OO. Although at present we cannot clarify these uncertainties, we conclude that mechanism I together with a minor contribution from mechanism IV may explain an efficient conversion of SO_2 to SO_3 by RO_2 in the photolysis of H_2CO in solid O_2 .

F. Implication to Atmospheric Conversion of SO_2 to S(VI). Hashimoto et al. did not observe SO_3 nor H_2SO_4 in their matrix

(13) (a) Paukert, T. T.; Johnston, H. S. J. Chem. Phys. 1972, 56, 2824.
(b) For solution, see: Hochnedel, C. J.; Ghormely, J. A.; Ogren, P. J. J. Chem. Phys. 1972, 56, 4426.

isolation study of the gas-phase reaction involving OH, SO₂, and O₂ in Ar.⁹ According to homogeneous gas kinetic rate constants listed in Table IV, reaction c which involves a reaction of HO₂ with SO₂ is at least 5 orders of magnitude slower than reactions 1 and m and involving HO + SO₂. Therefore it appears odd that reaction c is the key reaction in mechanism I. Recent experimental results support an SO₂ oxidation mechanism (via homogeneous gas-phase reactions 1–3 plus 12) which involves HO, HO₂, and

$$HO_2 + NO \rightarrow HO + NO_2$$
 (12)

NO radicals, and gives a net reaction

$$SO_2 + NO + O_2 \rightarrow SO_3 + NO_2$$
 (13)

It is interesting to find that this HO_x cycle in the gas phase is somewhat similar to the HO_x cycle in solid O_2 (mechanisms II-IV).

The reaction scheme involved in our O₂ matrix/photolysis system could also be operative in oxygenated liquids containing dissolved SO₂ and H₂CO or other small molecules which can potentially provide HO_x species upon photolysis. Since SO_2 and H_2CO (or other polar molecules) may form molecular complexes, light absorption characteristics such as absorption threshold and absorption coefficient can be significantly modified by chargetransfer phenomena. In addition, such complex formation can significantly modify photolysis characteristics, and "cage effects" can enhance the photooxidation efficiency of SO₂. Such effects may provide an important pathway for SO₂ photooxidation (or nonphotochemical oxidation) in droplets present in clouds, polluted urban atmosphere, etc. We have not yet simulated any such experiments, but the present study provides a firm base for future experiments to investigate the role that molecular complexes play in homogeneous and heterogeneous processes.

Acknowledgment. We thank J. G. Calvert, C. J. Howard, J. R. Sodeau, K. C. Clemitshaw, and A. Beeby for helpful discussions. This research has been supported by the National Science Foundation grant ATM-83-16572.

Registry No. H₂CO, 50-00-0; O₂, 7782-44-7; SO₂, 7446-09-5; H₂O, 7732-18-5; CO, 630-08-0; SO₃, 7446-11-9; HO₂, 3170-83-0; HC(O)OO, 56240-83-6; H₂SO₄, 7664-93-9; O₃, 10028-15-6.

Solvent Dynamics and Twisted Intramolecular Charge Transfer in Bis(4-aminophenyl) Sulfone

Shyh-Gang Su and John D. Simon*[†]

Department of Chemistry, University of California—San Diego, La Jolla, California 92093 (Received: May 21, 1986; In Final Form: July 14, 1986)

Picosecond time-resolved fluorescence spectroscopy is used to probe the formation kinetics of the twisted intramolecular charge-transfer state of bis(4-aminophenyl) sulfone in acetonitrile and alcohol solvents. Emission kinetics were measured at 20-nm intervals from 400 to 560 nm, covering the entire visible region of the emission spectrum. Wavelength-independent rise times were observed in methanol and acetonitrile. In all the longer chain alcohol solvents examined (ethanol to hexanol), wavelength-dependent rise times were observed; longer rise times were observed with decreasing emission energy. In addition, for wavelengths higher in energy than the maximum of the TICT emission maximum, λ_{max}^{TICT} , multiple decay components were observed in all solvents. Only the red edge of the emission ($\lambda > \lambda_{max}^{TICT}$) revealed rises and decays that could be described by single exponentials. The observed kinetics are interpreted in terms of solvent restructuring to stabilize the charge-separated state. Excellent agreement between the fitted rise times of the emission at 500, 540, and 560 nm and the solvent longitudinal relaxation time, τ_L , is observed.

Introduction

Since the observation of dual fluorescence for dimethylaminobenzonitrile (DMABN) in polar solvents, numerous investigations into the details of this phenomenon have appeared.¹⁻¹¹ Solvent studies as well as recent picosecond experiments conclude that the Stokes-shifted emission arises from a twisted intramo-

⁺ Presidential Young Investigator 1985-1990.

⁽¹⁾ Rettig, W.; Wermuth, G.; Lippert, E. Ber. Bunser-Ges. Phys. Chem. 1979, 83, 692.

⁽²⁾ Rettig, W.; Lippert, E. J. Mol. Struct. 1980, 61, 17.