vated carbon is placed into a mildly basic sulfite solution, no reaction occurs. When the solution is made mildly acidic, the reaction begins with the expected rate. Similar behavior is seen as the solution is changed back to basic and again to acidic. Studies are planned to examine the behavior of other activated carbons. The catalytic activity may be dependent on the method of activation for the different carbons.

We have done comparisons of this reaction with the rates of the other atmospherically important  $SO_2$  oxidation reactions.<sup>9</sup> As it has been recently shown<sup>10</sup> that carbonaceous particles are a significant portion of the ambient particulate burden, the carbon-catalyzed reaction can be a major contributor to the formation of aerosol sulfates.

Acknowledgment. This work was supported by the Biomedical and Environmental Research Division of the U.S. Department of Energy under contract No. W-7405-ENG-48 and by the National Science Foundation.

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# Photooxidation of Sulfur Dioxide in Low-Temperature Matrices

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The mechanism of photooxidation of sulfur dioxide has been investigated at low temperatures. Monomeric sulfur dioxide was found to be photochemically inactive, and no evidence was found for the existence of  $[SO_4]^*$  in an oxygen matrix. In contrast, the dimeric species,  $(SO_2)_2$ , was found to be readily photooxidized to sulfur trioxide in an oxygen matrix at 12 K.

## Introduction

A number of mechanisms have been proposed to explain the oxidation of atmospheric sulfur dioxide to sulfuric acid and sulfates. These may be classified into two types of process: (a) homogeneous gas-phase oxidation; (b) heterogeneous oxidation on droplets or particles.

Although the type-a mechanism is generally photochemically initiated, the *direct* oxidation of excited sulfur dioxide molecules is thought to be of relatively minor importance compared with reactions involving radical intermediates (e.g.,  $\dot{O}H$ ,  $RO_2$ , etc.) produced by other photolytic processes.<sup>1</sup>

However as part of a continuing study on photochemical reactions of monomer and dimer species at low temperatures,<sup>2</sup> we have investigated the direct photolysis of sulfur dioxide (S<sup>16</sup>O<sup>16</sup>O; S<sup>16</sup>O<sup>18</sup>O; S<sup>18</sup>O<sup>18</sup>O) in oxygen, argon, and nitrogen matrices at 12 K. Distinctive and distinguishing photooxidation behavior for sulfur dioxide was found during concentration studies in an oxygen matrix. This may indicate the importance of molecular donor-acceptor complexes in the observed photochemistry as has been previously suggested from gas-phase experiments.<sup>3</sup>

#### **Experimental Section**

Sulfur dioxide (S<sup>16</sup>O<sup>16</sup>O) was purchased from Liquid Carbonic with 99.98% stated purity. Isotopically labeled sulfur dioxide (70% atom purity S<sup>18</sup>O<sup>18</sup>O) was purchased from Prochem. Isotopically labeled oxygen <sup>18</sup>O<sup>18</sup>O (99% atom purity) was purchased from Prochem. The matrix gases were obtained from Liquid Carbonic: argon (99.9999% stated purity); nitrogen (99.9995% stated purity); oxygen (99.999% stated purity). All of the gases were used without further purification. Gaseous mixtures of known sulfur dioxide-matrix gas ratio (MR) were made up in 2-L bulb by standard manometric techniques at room temperature.

Low-temperature matrices of the above mixtures were prepared by the pulsed deposition method<sup>4,5</sup> and held at 12 K by a closed-cycle helium refrigerator (Air Products, Displex CSA 202B).

The effect of photolysis by a 1000-W super-high-pressure mercury arc (Ushio 1005D) and a 20-W zinc vapor lamp (Osram) was monitored with an infrared spectrometer (Perkin-Elmer Model 281). Calibration of the spectrometer was carried out by using ammonia, carbon dioxide, and water vapor.

### **Results and Discussion**

The present report may be divided into two photochemical regions of interest:

(a)  $\lambda < 219$  nm. Photodissociation into sulfur monoxide and an oxygen atom is energetically possible in this region,  $(D_0[OS-O] = 545 \pm 1 \text{ kJ mol}^{-1})^6$  via reaction 1.

$$\operatorname{SO}_2(\tilde{X}^1A_1) + h\nu \xrightarrow{(\lambda < 219 \text{ nm})} \operatorname{SO}(\tilde{X}^3\Sigma^-) + O(^3P)$$
 (1)

(b)  $\lambda > 219 \text{ nm}$ . Electronically excited states of SO<sub>2</sub> are produced in two main spectral ranges at wavelengths greater than 219 nm (eq 2-4).

$$\operatorname{SO}_2(\tilde{X}^1A_1) + h\nu \xrightarrow{340 < \lambda < 390 \text{ nm}} \operatorname{SO}_2(\tilde{a}^3B_1)$$
 (2)

$$SO_2(\tilde{X}^1A_1) + h\nu \xrightarrow{260 < \lambda < 330 \text{ nm}} SO_2(\tilde{B}^1B_1)$$
 (3)

$$\rightarrow \mathrm{SO}_2(\tilde{\mathrm{A}}^1\mathrm{A}_2) \tag{4}$$

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**Figure 1.**  $\nu_3$  stretch region of S<sup>16</sup>O<sup>16</sup>O–Ar (MR = 1:3000): (a) after deposition, showing SO<sub>2</sub> in two sites in argon, i.e., hcp (metastable) and ccp (stable); (b) after annealing to 20 K; loss of hcp site (1352.2 cm<sup>-1</sup>) accompanied by dimer production; (c) further annealing to 27 K.

The long-lived  $SO_2(\tilde{B}^1B_1)$  state has been thought to be relatively unreactive,<sup>1b</sup> but a recent study with isobutane shows that it is quite reactive.<sup>1d</sup> It is also physically quenched by other gases to form the triplet state,  $SO_2(\tilde{a}^3B_1)$ .<sup>7</sup> The formation of sulfur trioxide from this latter state has been suggested<sup>1.8,9</sup> to proceed via reactions 5 and 6. The above heats of reaction were calculated with

$$\mathrm{SO}_2(\tilde{a}^3\mathrm{B}_1) + \mathrm{SO}_2 \rightarrow \mathrm{SO}_3 + \mathrm{SO}(\tilde{X}^3\Sigma^-)$$
 (5)

 $\Delta H^{\circ} = -98.2 \text{ kJ mol}^{-1}$ 

$$\mathrm{SO}_2(\tilde{a}^3\mathrm{B}_1) + \mathrm{O}_2 \rightarrow \mathrm{SO}_3 + \mathrm{O}(^3\mathrm{P})$$
 (6)

$$\Delta H^{\circ} = -129.7 \text{ kJ mol}^{-1}$$

the electronic energy of  $SO_2(\tilde{a}^3B_1)$  taken to be 308.4 kJ mol<sup>-1</sup> above the ground state  $SO_2(\tilde{X}^1A_1)$ .<sup>10</sup>  $SO_3$  with  $O_3$  may also be formed by a much slower reaction of  $O_2$  and  $SO_4$  which was originally formed from the  $SO_2(^3B_1) + O_2$  reaction.<sup>1a</sup>

In the atmosphere, reaction with oxygen is thought to be the most significant chemical quenching process for the SO<sub>2</sub>( $\tilde{a}^{3}B_{1}$ ) state (although the importance of the reactions with H<sub>2</sub>O and NO is not well established). Studies of the quantum yield for photooxidation of SO<sub>2</sub> in the presence of excess oxygen have shown that the reaction is inefficient ( $\Phi_{SO_3} < 3 \times 10^{-4}$ ), presumably because of the spin-forbidden nature of the process.<sup>11</sup> Furthermore it should be noted that ozone is an expected product following reaction 6 but has not yet been observed in any gas-phase study.

In the present report, we will show that sulfur trioxide is formed only when dimers (and possibly higher aggregates) of sulfur dioxide are photolysed in oxygen matrices.

I. Photolysis of  $SO_2$  in Inert Matrices. (a) Argon Matrix. Infrared spectra, which, from earlier studies, are indicative of monomeric sulfur dioxide species, were taken at MR =  $1:3000.^{12,13}$  Two types of site were apparent and correspond to regions of cubic close packing (stable site) and hexagonal close packing (metastable site). Figure 1 shows the effect of annealing to 20 K with subsequent recooling to 12 K: loss of the hcp species accompanied by production of dimer species, etc., as observed initially by Hastie et al.<sup>14</sup> These same dimeric/aggregate forms were also produced by deposition of matrices with matrix ratios lower than 1:1500.

The matrix isolated and dimeric species were photolyzed with the 1000-W Hg arc in separate experiments under the following conditions: 4-h photolysis at  $230 < \lambda < 410$  nm

TABLE I:	<b>Observed IR</b>	Absorption	Frequencies	of SO,
in Matrices	(12 K)	-	-	-

		frequencies, cm <sup>-1</sup>			
species	mode	Ar (1:1000)	N <sub>2</sub> (1:1000)	O <sub>2</sub> (1:500)	
SO <sub>2</sub>	ν <sub>1</sub>	$1153.2^a$ $1148.5^b$	1153.8	1153.0	
	$\nu_2$	519.3 <sup>a</sup> 517.7 <sup>b</sup>	521.0	521.0	
	<i>v</i> <sub>3</sub>	$1356.0^a \\ 1352.2^b$	1352.5	1351.7	
$(\mathbf{SO}_2)_2$	$\nu_1^c$	d	d	1155.0	
	$\nu_2^c$	d	d	523.0	
	$\nu_3^c$	1349.5	1350.0	1347.8	
		1346.0	1347.5	1345.6	
		1342.3	1341.2	1342.5	

<sup>*a*</sup> Stable crystal site (cubic close packing). <sup>*b*</sup> Metastable crystal site (hexagonal close packing). <sup>*c*</sup> Corresponding vibrational mode of monomer SO<sub>2</sub>. <sup>*d*</sup> Not available.

(Corning 7-54 filter); or 4-h photolysis with the unfiltered Hg arc.

No change from the initial spectra was observed under either condition with both forms of sulfur dioxide.

(b) Nitrogen Matrix. The same photolysis and annealing experiments, as above, were performed on  $SO_2-N_2$ matrices (of initial MR = 1:3000). Again no effect of photolysis was observed on either monomeric or dimeric species. (The observed infrared frequencies for the  $SO_2$ species in argon and nitrogen matrices are presented in Table I.)

The above results indicate that the autoxidation reaction (eq 5) is not observable in an inert matrix. This may be due to the importance of "back"-reaction 7, as suggested

$$SO + SO_3 \rightarrow 2SO_2 \text{ or } (SO_2)_2$$
 (7)

$$\Delta H^{\circ} = -208.7 \text{ kJ mol}^{-1}$$

by Calvert et al.<sup>15</sup> (accentuated by the matrix "cageeffect"), and also to photoinduced recombination in the solid. Furthermore a dimer photolysis of the type shown in eq 8 does not appear to occur.

$$0 - s = 0 - \frac{h\nu}{Ar \text{ or } N_2} (S0)_2 + 0_2$$
 (8)

II. Concentration Dependence of  $SO_3$  Formation in Reactive Oxygen Matrices. The infrared spectra of the simple sulfur oxide species, i.e., SO, S<sub>2</sub>O, and SO<sub>3</sub>, have all been studied previously in low-temperature matrices. Sulfur monoxide (SO) absorbs at 1136.7 cm<sup>-1</sup> in argon, and disulfur monoxide (S<sub>2</sub>O) gives an IR spectrum consisting of three bands at 1156.2, 672.2, and 382.0 cm<sup>-1</sup> in the same matrix environment.<sup>17</sup> The strong doubly degenerate  $\nu_3(e')$ mode of sulfur trioxide (SO<sub>3</sub>) has been observed at 1404 and 1373 cm<sup>-1</sup> in a xenon matrix at 77 K (MR = 1:1500).<sup>18</sup> Under more concentrated conditions in an oxygen matrix, the SO<sub>3</sub> absorption features are observed at 1399 and 1385 cm<sup>-1,19</sup>

The present experiments provide no spectral evidence for the formation of SO or  $S_2O$  on photolysis of  $SO_2-O_2$ matrices (although this may be due to weak absorption by SO or  $S_2O$  coupled with obscuration by the parent  $SO_2$ absorption features). However concentration dependent production of sulfur trioxide was readily observable as was the formation of specifically labeled products when isotopic oxygen labeled  $SO_2$  and  $O_2$  mixtures were photolyzed.

(a)  $S^{16}O^{16}O^{-16}O^{16}O$  (MR = 1:4000). None of the sulfur oxides listed above (including SO<sub>3</sub>) was observed after 5-h photolysis of the matrix with the unfiltered mercury arc. A small but observable decrease in the doublet  $\nu_3$  ab-

sorption of monomeric SO<sub>2</sub> was apparent. (This "matrix splitting" effect is presumably due to the  $\alpha$  and  $\beta$  phases of solid oxygen.<sup>20</sup> A substantial amount of ozone was also produced, as recognized by its strong absorption at 1038.5 cm<sup>-1,21,22</sup> Ozone may be formed on photolysis of oxygen with  $\lambda < 242.4$  nm<sup>23</sup> via reactions 9 and 10. This was

$$O_2(\tilde{X}^3\Sigma_g) + h\nu \xrightarrow{175 < \lambda < 242 \text{ nm}} O(^3P) + O(^3P) \quad (9)$$

$$O_2(\tilde{X}^3\Sigma_g) + O(^3P) \rightarrow O_3(\tilde{X}^1A_1)$$
(10)

shown to be the mechanism by which ozone was produced in the matrix experiments as a second possible mechanism involving  $SO_2$  intermediacy was ruled out by the isotopic studies described below. In fact the photolysis of oxygen and ozone matrices shows several interesting features, which will be the subject of a separate report.

(b)  $S^{16}O^{16}O^{-16}O^{16}O(MR = 1:1000)$ . The same amount of total monomeric SO<sub>2</sub> was deposited as discussed in experiment IIa, and under these conditions a small amount of dimeric sulfur dioxide,  $(SO_2)_2$ , at 1346.0 cm<sup>-1</sup> was observable. Five-hour photolysis by the unfiltered mercury arc caused formation of ozone, indicated by absorption at 1038.5 cm<sup>-1</sup>, and also the appearance of a doublet at 1389.3 and 1385.8 cm<sup>-1</sup>. From the earlier studies discussed above,<sup>18,19</sup> we ascribe the observation of the doublet feature to the formation of sulfur trioxide. Photolysis of a similar matrix with a zinc lamp for 30 min ( $\lambda = 213.7$  nm) produced a deep yellow deposit on the window, which may be due to the formation of sulfur or large quantities of disulfur monoxide (from reaction 1). Good-quality infrared spectra could not be obtained because of light scattering, but no sulfur trioxide appeared to be formed under these short-wavelength photolysis conditions.

(c)  $S^{16}O^{16}O^{-16}O^{16}O$  (*MR* = 1:100). A large amount of dimer  $(SO_2)_2$  molecule species was obtained in this experiment by careful annealing of the matrix at 25 K for 1 min. After 5-h photolysis with the unfiltered mercury arc, (i) the  $v_3(e')$  doublet of SO<sub>3</sub> was observed at 1389.0 and 1386.0 cm<sup>-1</sup>, (ii) ozone was produced although in much smaller quantity than in the MR = 1:4000 and 1:1000 $(SO_2-O_2)$  experiments, (iii) a considerable decrease in the dimer infrared feature of SO<sub>2</sub> at 1346.0 cm<sup>-1</sup> was observed, indicating the efficient destruction of the  $(SO_2)_2$  species, (iv) little decrease in the intensity of the matrix-split,  $\nu_3$ doublet of the monomeric  $SO_2$  was apparent, and (v) the appearance of a broad absorption at  $\sim 1120 \text{ cm}^{-1}$  was also observed and is presumably due to the formation of sulfate ions  $(SO_4^{2-})$  from the reaction of  $SO_3$  and water<sup>24</sup> (present because of air leakage into the cryostat). These results are summarized in Figure 2.

(d)  $S^{16}O_2^{-16}O_2$  (MR = 1:40). No matrix-isolated SO<sub>2</sub> molecular species exist under these conditions, and dimer/aggregate forms predominate. The infrared bands are broad, and large perturbations between the SO<sub>2</sub> molecules exist. No ozone was produced after 5-h photolysis with the unfiltered mercury arc, but the  $\nu_3(e')$  doublet of sulfur trioxide was observed at 1390.0 and 1386.0 cm<sup>-1</sup> with the appearance of a new band at 1402.5 cm<sup>-1</sup>, which may represent a higher aggregate SO<sub>3</sub> species.

It is clear from the above results that a concentrationdependent mechanism for the formation of sulfur trioxide and ozone is operative: monomeric  $SO_2$  appears to be photochemically unreactive in a matrix, whereas photolysis of its dimeric form leads to the production of  $SO_3$  in solid oxygen.

The proposed mechanism can be represented in a general way by reaction 11, where n is an integer.

$$(\mathrm{SO}_2)_2 + (\mathrm{O}_2)_n \xrightarrow{n\nu} 2\mathrm{SO}_3 + (n-1)\mathrm{O}_2 \qquad (11)$$

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**Figure 2.** S<sup>16</sup>O<sup>16</sup>O<sup>-16</sup>O (MR = 1:100): (a and b)  $\nu_3$  stretch region of SO<sub>2</sub>; (c and d)  $\nu_3$  stretch region of O<sub>3</sub>; (a) after SO<sub>2</sub> deposition shows the  $\alpha$  and  $\beta$  sites of O<sub>2</sub> (1351.7 and 1350.8 cm<sup>-1</sup>); dimeric species indicated by the complex feature at 1347.8 cm<sup>-1</sup>; (b) after 4-h unfiltered Hg arc photolysis of sample a; production of SO<sub>3</sub> indicated by the infrared  $\nu_3(e')$  absorptions at 1389.0 and 1386.0 cm<sup>-1</sup>; notable decrease in dimer feature is indicated; (c) after SO<sub>2</sub> deposition; no O<sub>3</sub> present in sample a; (d) after 4-h unfiltered Hg arc photolysis of sample a; production of <sup>16</sup>O<sup>16</sup>O<sup>16</sup>O<sup>16</sup>O<sup>16</sup>O indicated by the 1038.5-cm<sup>-1</sup> absorption.

III. Mechanism of Photooxidation. Certain details of the process that should be established at this juncture may be listed as follows: (i) What is the nature of the excited species that participates in the reaction  $((SO_2)_2^* \text{ or } (O_2)_n^*)$ ? (ii) Does the formation of ozone in oxygen matrices involve the participation of sulfur dioxide? (iii) What is the role of  $(O_2)_2$  in the photooxidation?

Nature of the Excited Species. An experiment to test the following process was performed:

(

$$(\mathrm{SO}_2)_2 + h\nu \to (\mathrm{SO}_2)_2^* \tag{12}$$

$$(SO_2)_2^* + (O_2)_2 \rightarrow (SO_2)_2 + (O_2)_2^*$$
 (13)

$$(SO_2)_2 + (O_2)_2^* \rightarrow 2SO_3 + O_2$$
 (14)

(a) Photolysis of  $S^{16}O_2^{-16}O_2$  (MR = 1:100) at 632.8 nm. A 1:100 mixture of  $SO_2$ - $O_2$  was annealed at 27 K for 1 min and recooled (to sharpen the dimeric infrared features). The matrix was then irradiated with a He/Ne laser (Spectra Physics, 0.5 mW) for 16 h by using a plane mirror to reflect the beam back through the solid. Singlet oxygen would then be directly formed<sup>25,26</sup> via reaction 15. How-

$$(O_2)_2[({}^{3}\Sigma_g^{-})_2] + h\nu \xrightarrow{\lambda = 632.8 \text{ nm}} (O_2)_2[({}^{1}\Delta_g)_2]$$
 (15)

ever no sulfur trioxide was observed under these conditions: therefore, energy transfer to oxygen species should be of negligible effect.

Formation of Ozone. Its Potential Involvement in the Oxidation of Sulfur Dioxide. The following experiments were performed to establish the role of ozone in the  $(SO_2)_2$  dimer oxidation process.

(b) Photolysis of Pure <sup>16</sup>O<sup>16</sup>O and <sup>18</sup>O<sup>18</sup>O Matrices. Pure oxygen matrices were deposited at 12 K in the normal manner and photolyzed for 5 h with the unfiltered mercury arc. The photolysis of <sup>16</sup>O<sup>16</sup>O produced <sup>16</sup>O<sup>16</sup>O<sup>16</sup>O as recognized by its strong  $\nu_3$  absorption at 1038.5 cm<sup>-1</sup>. Similarly, <sup>18</sup>O<sup>18</sup>O was formed on <sup>18</sup>O<sup>18</sup>O photolysis under the

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Figure 3.  $S^{16}O^{16}O^{-16}O^{18}O$  (MR = 1:150): (a) after deposition of  $SO_2$ at 12 K; v<sub>3</sub> region of SO<sub>2</sub> indicated; (b) after 2.5-h photolysis with an unfiltered Hg arc and the production of isotopically labeled S16O18O and S<sup>18</sup>O<sup>18</sup>O; (c) after 5.0-h photolysis a feature at 1347.0 cm<sup>-1</sup> becomes apparent and due to SO<sub>3</sub> species with at least two <sup>18</sup>O atoms; (d) after 21.0-h photolysis almost complete scrambling to S<sup>18</sup>O<sup>18</sup>O has occurred.

same conditions ( $\nu_3$  absorption at 981.0 cm<sup>-1</sup>).<sup>21,22</sup> (c) Photolysis of  $S^{16}O^{16}O^{-18}O^{18}O$  (MR = 1:150). Fivehour photolysis of the matrix with the unfiltered mercury arc produced an absorption at 981.0 cm<sup>-1</sup>, i.e., at the same frequency as observed in the <sup>18</sup>O<sup>18</sup>O photolysis. It should  $tively.^{21}$ 

Furthermore, the sulfur trioxide that was produced contained at least two <sup>18</sup>O atoms (S<sup>16</sup>O<sup>18</sup>O<sup>18</sup>O and/or S<sup>18</sup>O<sup>18</sup>O<sup>18</sup>O), as recognized by the strong absorptions observed at 1347.0 and 1344.5 cm<sup>-1</sup>. Neither  $S^{16}O^{16}O^{16}O$  nor S<sup>16</sup>O<sup>16</sup>O<sup>18</sup>O was produced by photolysis.<sup>27,28</sup> Also after a period of 21-h photolysis, virtually complete scrambling of the S<sup>16</sup>O<sup>16</sup>O to S<sup>18</sup>O<sup>18</sup>O had occurred. The pertinent spectra from the above experiment are shown in Figure 3. It is clear that  $SO_2$  is not involved in the formation of ozone in a matrix (no <sup>16</sup>O<sup>18</sup>O<sup>18</sup>O, etc., was formed). However, the potential involvement of the produced  $O_3$  in the observed chemistry should be considered. Its effect is negligible on monomeric  $SO_2$  (experiment IIa) as no  $SO_3$ was observed when most ozone is apparently produced. Hence we suggest that reactions such as those in eq 16 and 17 do not occur in a matrix.

$$O_3 + h\nu \xrightarrow{\lambda < 1180 \text{ nm}} O(^3\text{P}) + O_2(^3\Sigma_g) \qquad (15a)$$

$$\xrightarrow{\Lambda < 310 \text{ nm}} O(^1\text{D}) + O_2(^1\Delta_g)$$
(15b)

$$SO_2 + O(^{3}P) + [M] \rightarrow SO_3 + [M]$$
 (16)

$$SO_2 + O(^1D) + [M] \rightarrow SO_3 + [M]$$
 (17)

At higher  $SO_2$  concentrations when less ozone is apparently observed a physical energy transfer process may be occurring to enhance reaction 18.

. . . . .

$$2O_3 \rightarrow 3O_2 \tag{18}$$

Also, as shown in experiments IIIb and IIIc, the photooxidation of  $(SO_2)_2^*$  dimer must proceed via the intermediacy of ground-state molecular oxygen rather than atomic oxygen as no S16O16O18O was produced on



Figure 4.  $S^{18}O^{18}O_{-}O_2$  (MR = 1:15000): 70% <sup>18</sup>O-atom purity;  $\nu_3$ region spectrum shows S16O16O at 1350.5 cm-1; 4-h photolysis with an unfiltered mercury arc has no apparent effect on these monomeric species.

 $(S^{16}O^{16}O)_2$  photolysis in  ${}^{18}O^{18}O$ .

Possible Role of  $(O_2)_2$  in the Photooxidation. Previous isotopic-exchange experiments of  $SO_2$  molecules in gas and solution phases were stated to be suggestive of dimeric  $(SO_2)_2$  with the following planar structure:<sup>29</sup>



A further experiment was performed to show that the above structure was the active photochemical species and that the photochemical reactivity of monomeric  $SO_2$  was negligible in an oxygen matrix.

(d) Photolysis of  $\bar{S}^{18}O^{18}O^{-16}O^{16}O$  (MR = 1:15000). The S<sup>18</sup>O<sup>18</sup>O sample used was stated to have 70% atom purity, as mentioned above. Hence, substantial amounts of  $S^{16}O^{18}O$  and  $S^{16}O^{16}O$  were present in the matrix, as shown in Figure 4. However, after 4-h photolysis with the unfiltered mercury arc, no change in the absorbance of any spectral feature of the sulfur dioxides was apparent. Also no sulfur trioxide was formed and no absorptions which could be ascribed to  $SO_4$  were observed. These observations indicate that  $[SO_4]^*$  is not an important intermediate in the photooxidation scheme as has been suggested.<sup>31</sup>

Experiment IIIc ( $S^{16}O^{16}O^{-18}O^{18}O$ , MR = 1:150) provides further insight into the mechanism of dimer photo-oxidation. Neither  $S^{16}O^{16}O^{18}O$  nor  $S^{16}O^{16}O^{16}O$  was produced on mercury-arc photolysis. If the reaction involved one  $O_2$  per  $(SO_2)_2$ , then the formation of  $S^{16}O^{16}O^{16}O$  could be expected:

However, if one  $(O_2)_2$  per  $(SO_2)_2$  is involved, then the observations may be rationalized by the following parallel plane structure:



An alternative mechanism for  $SO_3$  formation by the reaction of SO with  $O_2$  can be ruled out as  $(SO_2)_2$  does not produce SO,  $(SO)_2$ , etc., as shown in reaction 8.

One final point for discussion is raised by experiments IIIc (Figure 3) and IIId. Isotopic oxygen exchange does not occur on photolysis of monomeric  $SO_2$ . However, Figure 3 clearly shows the formation of  $S^{16}O^{18}O$  and S<sup>18</sup>O<sup>18</sup>O from  $(S^{16}O^{16}O)_2$  in an <sup>18</sup>O<sup>18</sup>O matrix. Apparently photolysis of S<sup>16</sup>O<sup>18</sup>O<sup>18</sup>O contributes to the observed scrambling effect, resulting in <sup>18</sup>O-atom-labeled sulfur dioxides. This is consistent with flash-photolysis experiments performed by Norrish.<sup>32</sup> S<sup>18</sup>O<sup>18</sup>O<sup>18</sup>O may then be formed by secondary photolysis of the isotopically scrambled  $(SO_2)_2$  dimers, such as  $(S^{18}O^{16}O \cdots S^{16}O^{16}O)$ .

## Conclusions

The photooxidation of sulfur dioxide in an oxygen matrix appears to proceed through the intermediacy of a dimeric form. Monomeric  $SO_2$  is photochemically inactive in both inert gas and oxygen matrices. We have no evidence for the formation of  $SO_4$  under our conditions. Relatively few dimer species might be expected to exist in the gas phase which would account for the low efficiency of the reaction. It may turn out that the  $(SO_2)_2^*$  species involved in the scheme may undergo singlet-triplet crossing as an excimer, which then reacts. The fact that there is an appreciable activation energy for quenching of  $SO_2(\tilde{a}^3B_1)$  by  $SO_2(\tilde{X}^1A_1)^{33}$  may be the reason for the relative photochemical stability of the  $(SO_2)_2$  dimers in Ar matrices. However, we have no direct evidence for the exact nature of the excited species or for the number of photons involved in the process.

Acknowledgment. We thank Dr. P. A. Bopp and Professor M. Wolfsberg for giving us the results of their calculations on the infrared frequencies of isotopically labeled  $SO_3$ . This research has been supported by NSF grant CHE-79-25451 and DOE (Office of Basic Energy Sciences) contract DE-AT-03-76-ER-20217.

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