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THE PHOTOLYSIS OF SULPHUR DIOXIDE IN THE PRESENCE OF FOREIGN GASES

XI: PHOTOLYSIS OF SO_2 AT 313.0 nm IN THE PRESENCE OF BOTH ACETYLENE AND OXYGEN

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Summary

SO_2 was photoexcited at 25 °C and 313.0 nm in the presence of acetylene and oxygen. The quantum yield of the sole gas phase product, CO, was determined at several [acetylene]/[SO_2] ratios for a wide range of O_2 pressures both in the presence and absence of 600 Torr of CO_2. The quantum yield $\Phi\{CO\}$ of CO increased at constant [acetylene]/[SO_2] ratios with the addition of O_2 up to pressures of about 1 Torr of O_2. With further increases in O_2 pressure, $\Phi\{CO\}$ is quickly quenched. The addition of 600 Torr of CO_2 appears to have little effect upon either the enhancement or quenching of $\Phi\{CO\}$. Both of the two non-emitting triplet states as well as the emitting triplet state of SO_2 previously proposed to be important in the photochemistry of SO_2 are necessary to interpret the results of this study. A relatively complete mechanism is proposed, all of the pertinent rate coefficients are derived and tabulated and from these values $\Phi\{CO\}$ values are computed which agree well with the observed values.

Introduction

The photolysis of sulfur dioxide in the atmosphere is one of the pathways for its oxidation to give H_2SO_4, $(NH_4)_2SO_4$ and organic sulfur compounds. Although SO_2 is a structurally simple molecule, its photophysical and photochemical processes are not clearly established. The absorption band of SO_2 which is centered at about 290 nm and which extends from 240 to 330 nm is of primary importance in the atmospheric chemistry of SO_2. As radiation above 218 nm is of insufficient energy to rupture the S—O bond, any photochemically induced reactions of SO_2 in the atmosphere must be the result of interactions with bound excited states of the molecule. Two emitting states of SO_2, a singlet $SO_2(^1B_1)$ and a triplet $SO_2(^3B_1)$, have been observed upon excitation into this region. The simplest interpretation of this fact is that the initial absorption is the $SO_2(^1B_1) \leftarrow SO_2(\tilde{X}, {}^1A_1)$ transition and that $SO_2(^3B_1)$ is produced by intersystem crossing.

Excited SO_2 has been shown to be chemically reactive upon excitation into the 240 - 330 nm absorption band [1 - 9]. Quenching reactions of $SO_2(^1B_1)$ and $SO_2(^3B_1)$ have been studied using a variety of quenching gases and reaction conditions [8 - 13]. Past work in this laboratory [8, 9, 13 - 17, 23, 24] and elsewhere [1 - 4, 7, 18 - 22] with photoexcited SO_2 has not been consistent with a mechanism including only these two excited states. The fluorescence quantum yields do not obey Stern–Volmer quenching and there is evidence that $SO_2(^1B_1)$ is not the state formed initially upon absorption [13]. Participation of a non-emitting singlet state, SO_2^*, and one or two non-emitting triplet states, SO_2^{**} and $SO_2^{\ddagger}$, have been included in the various mechanisms to explain the data [8, 9, 13 - 17, 23, 24].

Cehelnik *et al.* [14] were the first to characterize the SO_2^{**} state as an excited triplet state of SO_2 which is produced by collisional quenching of another excited state and not by a first order process. It has since been well characterized by others [8, 9, 15 - 17, 23, 24]. Fatta *et al.* [17] found that two triplet states of SO_2, SO_2^{**} and $SO_2^{\ddagger}$, must be invoked to explain the SO_2-sensitized phosphorescence of biacetyl and that neither of these states had the properties of the emitting triplet $SO_2(^3B_1)$. Kelly *et al.* [8] found evidence for this same $SO_2^{\ddagger}$ state but in a different manner. They found that the addition of small amounts of NO to mixtures of SO_2 and acetylene increased the quantum yield of the photolysis product CO. This observation was explained by the presence of a second non-emitting excited triplet state, $SO_2^{\ddagger}$.

In several previous papers from this laboratory the photolysis of SO_2 at wavelengths above 300 nm in the presence of acetylene was studied in the absence and presence of various gases [8, 24, 25]. In those systems the reaction products were CO and solid particles composed of the trimer of $C_3H_4S_2O_3$ [25]. The quantum yield $\Phi\{CO\}$ was found to increase with the ratio $[C_2H_2]/[SO_2]$ to an upper limiting value of 0.052 [8]. From quenching studies with various added gases it was determined that the emitting triplet, $SO_2(^3B_1)$, as well as two non-emitting triplet states, SO_2^{**} and $SO_2^{\ddagger}$, were necessary to interpret the photochemistry of SO_2 in the presence of acetylene.

Previous studies of the irradiation of SO_2 in the presence of various hydrocarbons and O_2 by near-ultraviolet radiation have been reported [3, 26]. Reaction products were found to contain an aerosol and/or a liquid oil. In several studies O_2 was found to be less efficient than SO_2 at quenching $^3SO_2$ [10, 26, 27].

The present study involves the photolysis of SO_2 at 313.0 nm in the presence of acetylene, O_2 and at times about 600 Torr of CO_2. It is believed that the quantum yield of CO will serve as a measure of the participation of the various reactive states of SO_2 and that the addition of O_2 and CO_2 will permit the further characterization of these states as well as simulate atmospheric conditions.

Experimental

Photolysis was carried out in an opaque cylindrical cell of dimensions 50 cm × 5.0 cm o.d. which had quartz windows bonded to both ends. A 6 mm o.d. perforated tube passed down the length of the cell to ensure thorough mixing when the gases were introduced through it. The radiation source was a Hanovia 140 W medium pressure U-shaped type SH mercury arc. The radiation was collimated by a quartz lens and passed through a Corning 7-54 (type 9863) glass filter and an Ealing 313.0 nm interference filter before entering the cell through the quartz window. A General Electric 935 photodiode was placed at the opposite end of the cell to measure light intensity.

All work was carried out in a high vacuum line using Teflon stopcocks with Viton O-rings. Pressures from 20 to 750 Torr were measured on 0 - 50 Torr or 0 - 800 Torr Wallace and Tiernan absolute pressure gauges. A silicone oil manometer was employed for most pressure measurements below 20 Torr. Pressures of less than 0.8 Torr were achieved by expansion.

All gases were supplied by Matheson Gas Products. Sulfur dioxide (anhydrous) was distilled once from —95 °C to —130 °C. The middle fraction was collected and placed in a darkened storage bulb. Acetylene and carbon dioxide (dry) were distilled from —130 °C to —196 °C. In each case the middle fraction was retained. The oxygen was used as received after passing it through a trap at —196 °C. Gas chromatographic analysis of all gases showed no detectable CO. The azomethane used as an actinometer was prepared according to the procedure given by Renaud and Leitch [28]. It was then purified by distillation from —90 °C to —130 °C and stored in an opaque storage bulb. All of the condensable gases were degassed at —196 °C immediately before use.

After irradiation the carbon monoxide was analyzed by one of several methods using gas chromatography. In the first method, which was applicable only for experiments where there was little or no O_2 present, the reaction mixture was allowed to expand into two spiral traps maintained at —196 °C and then the non-condensable carbon monoxide and O_2 were pumped by means of a Toepler pump into a gas chromatograph injection loop. In the second method, which could be used regardless of O_2 pressure, the reaction mixture was allowed to expand directly from the reaction cell into the injection loop. Once in the injection loop the sample was injected into a 3 ft by 3/16 in o.d. copper column packed with Linde 13X molecular sieves maintained at 25 °C with a flow rate of 30 cm^3 min^{-1} of helium which provided separation of CO from other injected gases but primarily from O_2.

In the experiments where it was possible to collect the CO by means of the Toepler pump the gases passed directly from the molecular sieve column to a Gow Mac model 40 - 05D gas chromatograph using a thermistor detector maintained at 0 °C. In the experiments where the above procedure could not be used, owing to the inability to collect large amounts of O_2 in a small injection loop and then to separate out a small amount of CO, a second procedure was used which provided much greater sensitivity for CO detection but which was less reliable owing to greater complexity. In this method CO was passed over a heated nickel catalyst by the method of Williams *et al.* [29] and converted to methane which could be detected with great sensitivity by a Varian Model 1200 flame ionization gas chromatograph. The O_2 had to be removed first from the molecular sieve column effluent as it would poison the catalyst. This was accomplished by monitoring the column effluent by the thermistor detector mentioned above, and once the O_2 was eluted the column was switched to the catalytic convertor/flame ionization detector for CO detection. Both methods were carefully calibrated for CO detection.

Azomethane was used as the actinometer in this study. The quantum yield of azomethane for N_2 production is unity at 313.0 nm. The N_2 produced in the azomethane photolysis was determined in the same manner as described above using the Gow Mac thermistor gas chromatograph with the same column and detectors. The gas chromatograph was calibrated for N_2 using standard samples. The General Electric 935 photodiode was used to match absorbances of SO_2 and azomethane. The amount of carbon monoxide produced in each experiment was determined and converted to quantum yields by knowledge of the N_2 yield obtained from azomethane photolysis at equal absorbances.

Results

Photolysis of SO_2 in the presence of acetylene, O_2 and occasionally about 600 Torr of CO_2 was performed at 25 °C with radiation of 313.0 nm. An SO_2 pressure of 2.7 Torr reduced the intensity of radiation reaching the photodiode by approximately 50%. Photolysis times for similar mixtures of reactants were varied over a wide period of time. Also from previous more extensive work in this laboratory on this same chemical system [8] it has been shown that CO production as a function of time is linear and shows no detectable induction period as well as no fall-off at longer photolysis times. Mixtures of reactants allowed to stand for several hours gave no products, indicating that the CO was a primary product and that there was not a significant amount of light scattering from the aerosol under the experimental conditions employed.

In the first series of experiments with the absorbed intensity $I_a = 3.3 \pm 0.1$ mTorr min^{-1}, $[SO_2]$ and [acetylene] were held constant at pressures of 2.83 ± 0.07 Torr and 2.84 ± 0.19 Torr respectively, while the O_2 pressure was varied from 0.0307 to 244 Torr. The values of $\Phi\{CO\}$ increased to a maximum as the O_2 pressure was increased to 1 - 2 Torr and then decreased with further increases in the pressure of O_2 (Fig. 1).

In another series of experiments, again with $I_a = 3.3 \pm 0.1$ mTorr min^{-1}, $[SO_2]$ and [acetylene] were held constant at pressures of 2.81 ± 0.09 Torr and 0.0865 ± 0.0026 Torr respectively, while the O_2 pressure was varied from 0.0176 to 117 Torr. The value of $\Phi\{CO\}$ again was found to increase slightly with increasing O_2 pressure to a maximum at approximately 0.3 Torr O_2 and then to decrease with the addition of larger pressures of O_2 (Fig. 2).

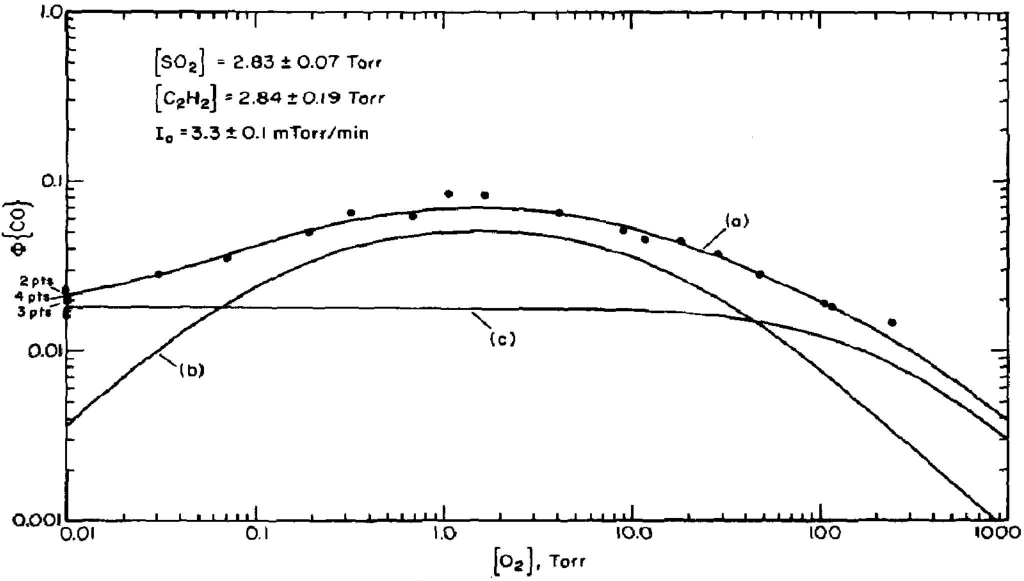

Fig. 1. Log–log plot of Φ{CO} *vs.* O_2 pressure. The curves are theoretically computed from the rate coefficients listed in Table 1: curve (a), total Φ{CO}; curve (b), $\Phi^{**}_{O_2}$ {CO}; curve (c), Φ^3 {CO}.

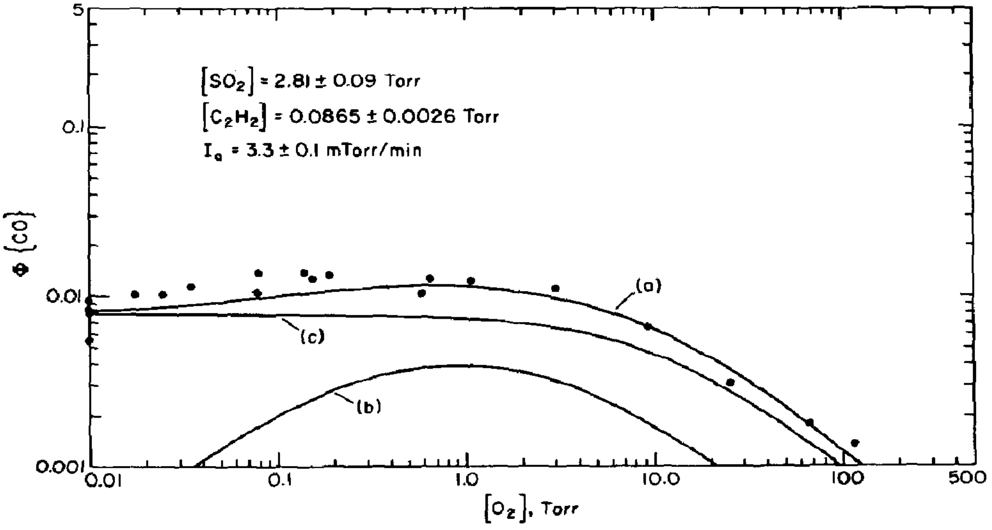

Fig. 2. Log–log plot of Φ{CO} *vs.* O_2 pressure. The curves are theoretically computed from the rate coefficients listed in Table 1: curve (a), total Φ{CO}; curve (b), $\Phi^{**}_{O_2}$ {CO}; curve (c), Φ^3 {CO}.

In a third series of experiments, also with $I_a = 3.3 \pm 0.2$ mTorr min^{-1}, a constant pressure of 601 ± 7.0 Torr CO_2 was included with 2.85 ± 0.15 Torr SO_2 and 2.82 ± 0.12 Torr acetylene. To these mixtures O_2 was added to pressures varying from 0.0894 to 101 Torr. As the O_2 pressure was increased, Φ{CO} increased to a maximum at slightly greater than 1 Torr O_2 pressure. At higher O_2 pressures, Φ{CO} quickly decreased (Fig. 3).

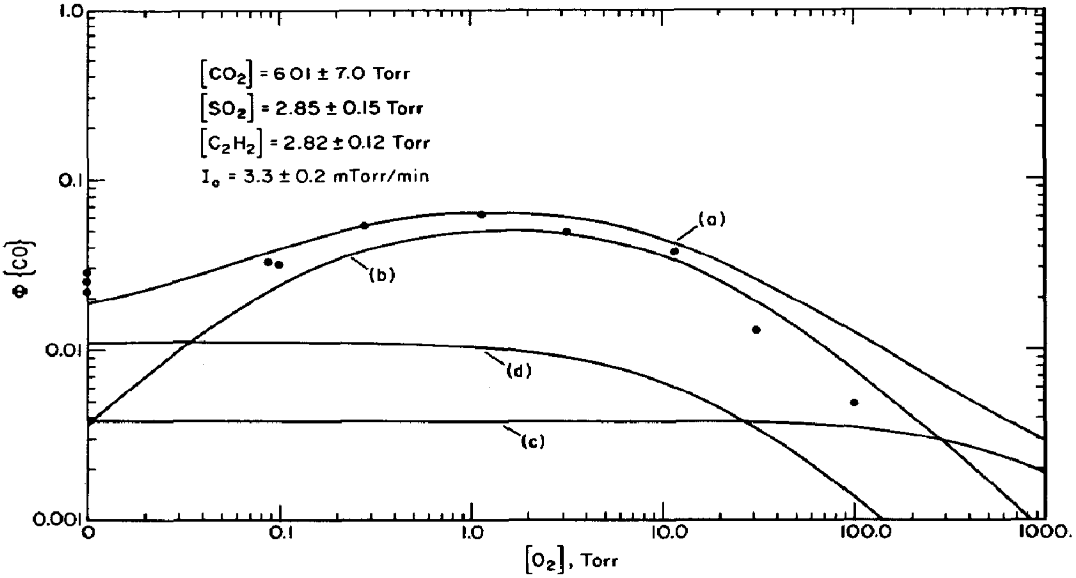

Fig. 3. Log–log plot of $\Phi\{CO\}$ *vs.* O_2 pressure in the presence of ~600 Torr CO_2. The curves are theoretically computed from the rate coefficients listed in Table 1: curve (a), total $\Phi\{CO\}$; curve (b), $\Phi_{O_2}^{**}\{CO\}$; curve (c), $\Phi^3\{CO\}$; curve (d), $\Phi_M^{**}\{CO\}$.

Discussion

The major conclusions to be drawn from this study are as follows.

(1) SO_2 photoexcited at 313.0 nm reacts with C_2H_2 to produce CO. The addition of O_2 up to 1 Torr pressure to this reaction mixture enhances $\Phi\{CO\}$ under all conditions studied. A further increase in O_2 pressure reduces $\Phi\{CO\}$.

(2) The shorter lived singlet state formed upon absorption (SO_2^*), the chemically reactive triplet states of SO_2 ($^3SO_2$ and SO_2^{**}) and a third non-reactive triplet state $SO_2^{\ddagger}$, all previously proposed by various workers in this laboratory, are adequate and sufficient to explain our results as shown below.

The mechanism we have used to fit our results is one in which the major steps have been obtained from previous studies. A few new steps have been added to explain the uniqueness of the system when O_2 is present. $SO_2(^3B_1)$ is abbreviated as $^3SO_2$, the fluorescing state as $^1SO_2$, the state formed by absorption as SO_2^*, the non-emitting triplet state which is important at high pressure as SO_2^{**}, and a third triplet state introduced by Fatta *et al.* [17] as $SO_2^{\ddagger}$. The entire mechanism proposed to explain this study is

$$SO_2 + h\nu \xrightarrow{313\text{ nm}} SO_2^* \qquad \text{rate} = \beta I_a \qquad (1a)$$

$$\xrightarrow{313\text{ nm}} {}^3SO_2 \qquad \text{rate} = \alpha I_a \qquad (1b)$$

$$SO_2^* \rightarrow {}^1SO_2 \qquad (2a)$$

$$\rightarrow SO_2 \qquad (2b)$$

$$SO_2^* + C_2H_2 \rightarrow SO_2^{**} + C_2H_2 \tag{3a}$$
$$\rightarrow \text{removal of } SO_2^* \tag{3b}$$
$$SO_2^* + O_2 \rightarrow SO_2^{**} + O_2 \tag{3a$'$}$$
$$\rightarrow \text{removal of } SO_2^* \tag{3b$'$}$$
$$SO_2^* + CO_2 \rightarrow SO_2^{**} + CO_2 \tag{3a$''$}$$
$$\rightarrow \text{removal of } SO_2^* \tag{3b$''$}$$
$$^1SO_2 \rightarrow SO_2 + (h\nu_f) \tag{4}$$
$$^1SO_2 + SO_2 \rightarrow \text{removal of } ^1SO_2 \tag{5a}$$
$$^1SO_2 + CO_2 \rightarrow \text{removal of } ^1SO_2 \tag{5b}$$
$$^1SO_2 + O_2 \rightarrow \text{removal of } ^1SO_2 \tag{5c}$$
$$^1SO_2 + C_2H_2 \rightarrow \text{removal of } ^1SO_2 \tag{5d}$$
$$^3SO_2 \rightarrow SO_2 + (h\nu_p) \tag{6}$$
$$^3SO_2 + C_2H_2 \rightarrow CO \tag{7a}$$
$$\rightarrow \text{removal of } ^3SO_2 \tag{7b}$$
$$^3SO_2 + SO_2 \rightarrow \text{removal of } ^3SO_2 \tag{8a}$$
$$^3SO_2 + CO_2 \rightarrow \text{removal of } ^3SO_2 \tag{8b}$$
$$^3SO_2 + O_2 \rightarrow \text{removal of } ^3SO_2 \tag{8c}$$
$$SO_2^{**} + C_2H_2 \rightarrow CO \tag{9}$$
$$SO_2^{**} + O_2 \rightarrow \text{removal of } SO_2^{**} \tag{10}$$
$$SO_2^{**} \rightarrow \text{removal of } SO_2^{**} \tag{11}$$
$$SO_2 + h\nu \rightarrow SO_2^{\ddagger} \qquad \text{rate} = \gamma I_a \tag{12}$$
$$SO_2^{\ddagger} + O_2 \rightarrow SO_2^{**} + O_2 \tag{13}$$
$$SO_2^{\ddagger} \rightarrow SO_2 \tag{14}$$

The SO_2^* state is produced at a constant fraction β of the absorbed radiation I_a. It unimolecularly forms either $^1SO_2$ (discussed below) or ground state SO_2. The SO_2^* state also can be collisionally deactivated to produce ground state SO_2 as well as SO_2^{**} and possibly $SO_2^{\ddagger}$, but does not react to produce products. Cehelnik *et al.* [14] were the first to find that SO_2^{**} must come from this collisional quenching and not from a first order process as this state is present only at high pressures where it is not quenched by SO_2, CO_2 or H_2O. The SO_2^{**} state is quenched by both acetylene and O_2. The quenching by acetylene produces CO. It is not possible to evaluate whether SO_2^{**} is physically quenched by acetylene, so this reaction is omitted for simplicity.

$^3SO_2$ is produced at a constant fraction α of the absorbed radiation intensity I_a. This is not to imply that $^3SO_2$ must be produced directly on absorption but rather that whatever process of intersystem crossing leads to it must be constant and thus pressure independent. $^3SO_2$ might be produced from SO_2^* but this would necessitate a constant fraction of production by first order as well as collisional quenchings of SO_2^* by acetylene, CO_2 and O_2 because the Stern–Volmer quenching curve for $^3SO_2$ is linear [13]. It is unlikely that these removal processes would give $^3SO_2$ the same fraction of the time. A more likely possibility is that the $^3SO_2$ comes from the $^1A_2$ state which is formed in absorption and is collisionally deactivated at the pressures where this study was performed. The $^3SO_2$ state is then collisionally quenched by any gas present in the system and the reaction with acetylene to produce CO occurs a fraction of the time. Under our conditions first order removal steps are unimportant.

The longer lived state formed by absorption of radiation has been presumed to be $^1B_1$, but because of its non-linear Stern–Volmer quenching plot the state which fluoresces must be kinetically distinct and formed by a first order process from SO_2^*. We designate this state $^1SO_2$ [13]. From the viewpoint of photochemical kinetics it is immaterial whether $^1SO_2$ is spectroscopically distinct from SO_2^* or merely the result of a perturbation with the ground electronic state, as proposed by Brus and McDonald [20], because it behaves as a distinct entity.

Evidence for the $SO_2^\ddagger$ state has been proposed by Fatta *et al.* [17] and supported recently by Kelly *et al.* [8]. This state is incorporated here to explain the increase in $\Phi\{CO\}$ when approximately 1 Torr O_2 is added in both the absence and presence of 600 Torr CO_2 to the reaction mixture. A state is necessary which is quenched by 1 Torr O_2 but is not quenched by CO_2. This quenching process must lead to additional CO production. The simplest explanation of this observation is that the quenching of $SO_2^\ddagger$ by O_2 produces SO_2^{**}. For simplicity it is assumed that $SO_2^\ddagger$ is produced at a constant fraction γ of I_a, but there is no direct evidence that this is a true constant or that the state is produced directly on absorption. The $SO_2^\ddagger$ state is not chemically reactive and only serves to populate the reactive triplet SO_2^{**} when O_2 is present.

By a detailed analysis of the steady state expressions it is seen that

$$\Phi\{CO\} = \frac{\alpha k_{7a}[C_2H_2]}{k_7[C_2H_2] + k_8[X]} + \frac{\beta k_9[C_2H_2]k_{3a}[M]}{(k_2 + k_3[M])(k_9[C_2H_2] + k_{10}[O_2] + k_{11})} + \\ + \frac{\gamma k_9[C_2H_2]k_{13}[O_2]}{(k_{13}[O_2] + k_{14})(k_9[C_2H_2] + k_{10}[O_2] + k_{11})} \qquad \text{(I)}$$

In the first term [X] is $[SO_2]$, $[CO_2]$ or $[O_2]$ as shown in reactions (8a) - (8c). In the second term [M] is any gas which causes the internal conversion of $SO_2^\ddagger$ to SO_2^{**} as shown in reactions (3a), (3a′) and (3a″). The first term on the right-hand side of the above expression is the contribution from the emitting triplet $SO_2(^3B_1)$, which will be referred to as $\Phi^3\{CO\}$. The second term is the contribution from SO_2^{**} and will be referred to as $\Phi_M^{**}\{CO\}$. The third term is also a contribution from SO_2^{**} but comes from $SO_2^\ddagger$ and, in order to differentiate it, it will be referred to as $\Phi_{O_2}^{**}\{CO\}$. It must be remembered that $SO_2^\ddagger$ is not chemically reactive so that there are only two reactive states,

$^3SO_2$ and SO_2^{**}, and that one of these states, SO_2^{**}, has two precursor states. Thus

$$\Phi\{CO\} = \Phi^3\{CO\} + \Phi_M^{**}\{CO\} + \Phi_{O_2}^{**}\{CO\} \tag{II}$$

$$\Phi^3\{CO\}^{-1} = \frac{k_7}{\alpha k_{7a}}\left(1 + \frac{k_8[X]}{k_7[C_2H_2]}\right) \tag{III}$$

$$\Phi_M^{**}\{CO\}^{-1} = \frac{k_3}{\beta k_{3a}}\left(1 + \frac{k_2}{k_3[M]}\right)\left(1 + \frac{k_{10}[O_2]}{k_9[C_2H_2]} + \frac{k_{11}}{k_9[C_2H_2]}\right) \tag{IV}$$

$$\Phi_{O_2}^{**}\{CO\}^{-1} = \frac{1}{\gamma}\left(1 + \frac{k_{14}}{k_{13}[O_2]}\right)\left(1 + \frac{k_{10}[O_2]}{k_9[C_2H_2]} + \frac{k_{11}}{k_9[C_2H_2]}\right) \tag{V}$$

At low [M] the first term in eqn. (I), $\Phi^3\{CO\}$, determines $\Phi\{CO\}$, and thus as a first approximation $\Phi\{CO\}^{-1}$ should vary linearly with low O_2 pressures. When this assumption is made an approximate value can be obtained for k_{8c}/k_{7a} from the slope of the plot and this value can be used along with several rate coefficient ratios from the similar study of Kelly *et al.* [8] (which are listed in Table 1) to calculate the contributions of the other excited states at higher values of [M]. The rate coefficients are then refined by successive approximations. The results of this are the following.

TABLE 1

Summary of rate coefficient data

Ratio	Value	Units	M	Reference
α	0.10	None	–	Demerjian and Calvert [7]
γ	0.092	None	–	This work
	0.064	None	–	This work
	0.0193	None	–	Kelly *et al.* [8]
$\beta = 1 - \alpha - \gamma$	0.81	None	–	This work
k_2/k_3	73.1	Torr	C_2H_2	Kelly *et al.* [8]
k_2/k_3''	56.0	Torr	CO_2	Kelly *et al.* [8]
k_3/k_{3a}	28.5	None	C_2H_2	Kelly *et al.* [8]
k_3''/k_{3a}''	45.2	None	CO_2	Kelly *et al.* [8]
k_{7a}/k_7	0.189	None	C_2H_2	Kelly *et al.* [8]
k_7/k_{8a}	23	None	C_2H_2	Kelly *et al.* [8]
k_{8b}/k_{8a}	0.42	None	CO_2	Kelly *et al.* [8]
k_{8c}/k_{8a}	0.34	None	O_2	This work
	0.34	None	O_2	This work
	0.25	None	O_2	Sidebottom *et al.* [12]
	0.37	None	O_2	Mettee [11]
	0.42	None	O_2	Stockburger *et al.* [13]
k_{11}/k_9	1.38	Torr	C_2H_2	Kelly *et al.* [8]
k_{11}/k_{10}	4.6	Torr	O_2	This work
	2.45	Torr	O_2	This work
k_{14}/k_{13}	0.160	Torr	O_2	This work
	0.25	Torr	O_2	This work

For experiments performed at 0.0865 ± 0.0026 Torr acetylene and 2.81 ± 0.09 Torr SO_2 with $[O_2]$ varied, a plot of $(\Phi\{CO\} - \Phi_M^{**}\{CO\} - \Phi_{O_2}^{**}\{CO\})^{-1}$ *versus* $[O_2]$ is linear. From the slope we obtain $k_{8c}/\alpha k_{7a} = 0.78$ (Fig. 4). The value for α has been determined in numerous studies in Calvert's laboratory [7] and elsewhere [5]. The best value at 313.0 nm is 0.10 [7]. Thus $k_{8c}/k_{7a} = 0.078$. By the use of several rate coefficient ratios obtained by Kelly *et al.* [8], which are listed in Table 1, it is seen that $k_{8c}/k_{8a} = 0.34$. From the ratio of slope to intercept we also obtain a value for $k_{8c}/(k_7[C_2H_2] + k_{8a}[SO_2]) = 0.071$, which is independent of α. From Kelly *et al.* [8] we know $k_7/k_{8a} = 23$ and thus find, independently, that $k_{8c}/k_{8a} = 0.34$. This illustrates the agreement of this study with that of Kelly *et al.* [8]. These values can be compared with values of 0.25 obtained by Sidebottom *et al.* [12], 0.37 obtained by Mettee [11] and 0.42 obtained by Stockburger *et al.* [13] and seen to be in excellent agreement.

For experiments performed at 2.84 ± 0.19 Torr acetylene and 2.83 ± 0.07 Torr SO_2 with various pressures of added O_2, enhancement of $\Phi\{CO\}$ is seen (Fig. 1). This enhancement has been attributed to $SO_2^\ddagger$ being quenched by O_2 to SO_2^{**} which is chemically reactive with acetylene to give CO. From eqn. (II) we know that

$$\Phi_{O_2}^{**}\{CO\} = \Phi\{CO\} - \Phi^3\{CO\} - \Phi_M^{**}\{CO\} \qquad \text{(VI)}$$

For values of $[O_2] \leqslant 2$ Torr we assume that $k_9[C_2H_2] + k_{11} > k_{10}[O_2]$ and that $\Phi_M^{**}\{CO\}$ is small. From Kelley *et al.* [8] we know that $k_{11}/k_9 = 1.38$ Torr for acetylene. A plot of $(\Phi\{CO\} - \Phi^3\{CO\} - \Phi_M^{**}\{CO\})^{-1}$ *versus* $[O_2]^{-1}$ (Fig. 5)

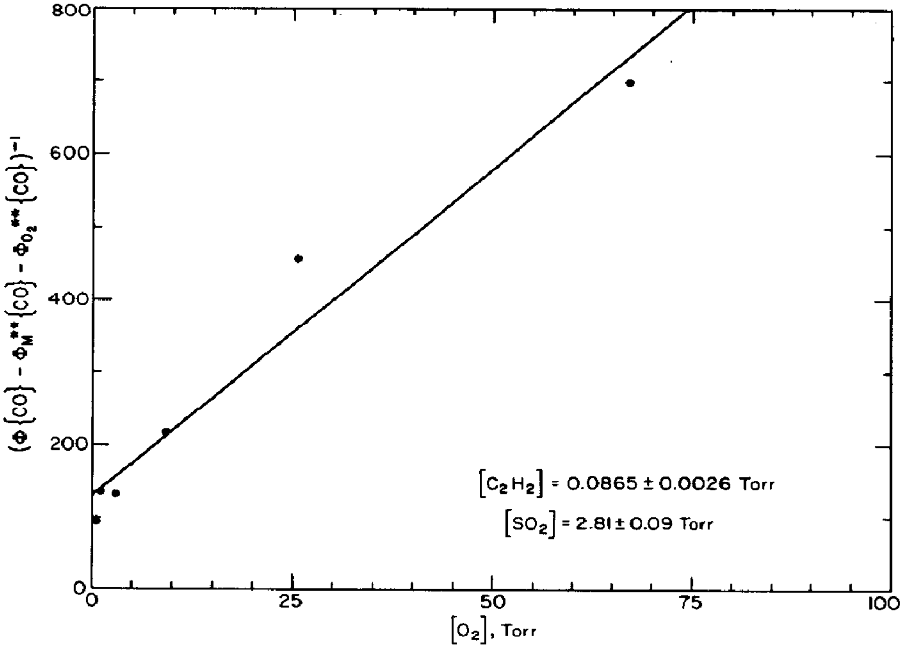

Fig. 4. Plot of $(\Phi\{CO\} - \Phi_M^{**}\{CO\} - \Phi_{O_2}^{**}\{CO\})^{-1}$ *vs.* O_2 pressure in the irradiation of SO_2–C_2H_2 mixtures at low C_2H_2 pressure.

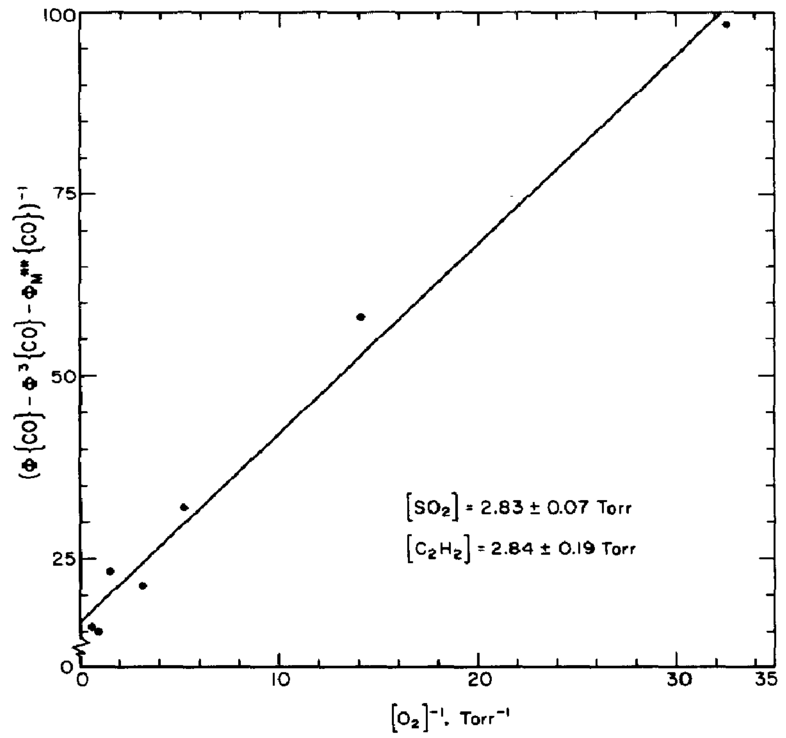

Fig. 5. Plot of $(\Phi\{CO\} - \Phi^3\{CO\} - \Phi_M^{**}\{CO\})^{-1}$ *vs.* the reciprocal O_2 pressure for O_2 pressures less than 2 Torr in the irradiation of SO_2–C_2H_2 mixtures.

is linear. Utilization of eqn. (V) and Fig. 5 gives values of $\gamma = 0.092$ and $k_{14}/k_{13} = 0.160$ Torr.

A similar series of experiments was performed with the addition of 601 ± 7.0 Torr CO_2. In these experiments 2.82 ± 0.12 Torr acetylene and 2.85 ± 0.15 Torr SO_2 were present. Enhancement of $\Phi\{CO\}$ was seen with addition of O_2 pressures up to 1 Torr (Fig. 3), and this was again attributed to $SO_2^{\ddagger}$ being quenched by O_2 to SO_2^{**}. Although the data are sparse, a plot of $(\Phi\{CO\} - \Phi^3\{CO\} - \Phi_M^{**}\{CO\})^{-1}$ *versus* $[O_2]^{-1}$ (Fig. 6) is linear, and by utilization of eqn. (V) and Fig. 6 gives approximate values of $\gamma = 0.064$ and $k_{14}/k_{13} = 0.25$ Torr. These results generally agree with the above, but will not be used in the computations as they represent fewer and more irreproducible experiments.

The value for γ found here differs significantly from the value of 0.0193 given by Kelly *et al.* [8]. There are several possible reasons for this. It is possible that γ is not a true constant and/or that $SO_2^{\ddagger}$ is not formed directly upon absorption but by various modes of intersystem crossings or internal conversions and may be dependent upon [M]. Also the data of Kelly *et al.* [8] were measured in the presence of much higher pressures of C_2H_2 and exhibited some scatter.

For experiments run at 2.84 ± 0.19 Torr acetylene and 2.83 ± 0.07 Torr SO_2, but with values of $[O_2] > 1$ Torr, $\Phi\{CO\}$ is seen to decrease with increasing O_2 pressure (Fig. 1). At higher O_2 pressures the O_2 must be competing

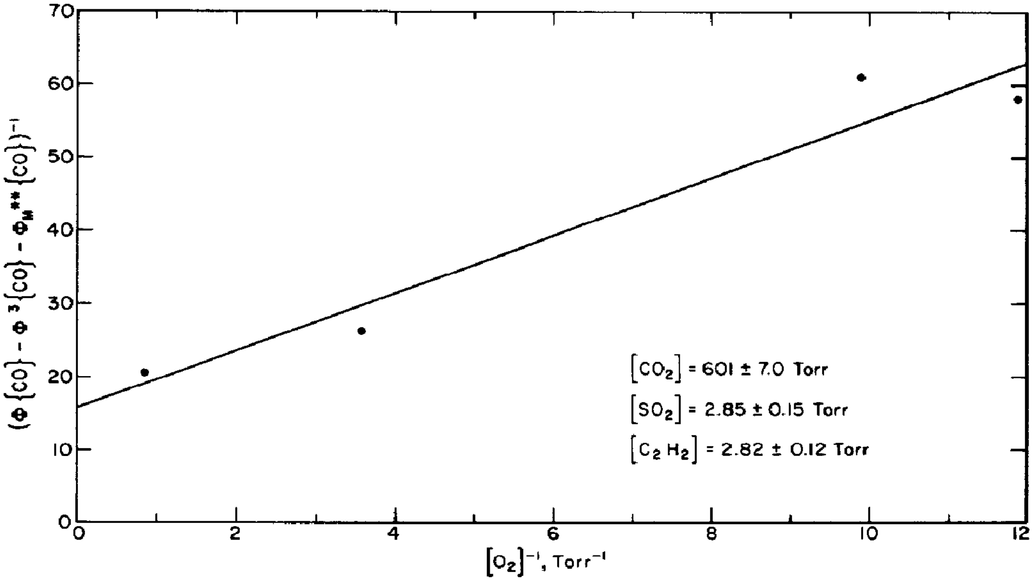

Fig. 6. Plot of $(\Phi\{CO\} - \Phi^3\{CO\} - \Phi_M^{**}\{CO\})^{-1}$ *vs.* the reciprocal O_2 pressure for O_2 pressures less than 1 Torr in the irradiation of SO_2–C_2H_2 mixtures in the presence of ~600 Torr CO_2.

successfully with acetylene for the SO_2^{**} as well as the $^3SO_2$ to give lower quantum yields. In this region

$$\begin{aligned}\Phi\{CO\} - \Phi^3\{CO\} &= \Phi_{O_2}^{**}\{CO\} + \Phi_M^{**}\{CO\}\\ &= \frac{\beta k_{3a} k_9 [C_2H_2]\,[M]}{(k_2 + k_3[M])(k_9[C_2H_2] + k_{10}[O_2] + k_{11})} +\\ &\quad + \frac{\gamma k_9 k_{13} [C_2H_2]\,[O_2]}{(k_9[C_2H_2] + k_{10}[O_2] + k_{11})(k_{13}[O_2] + k_{14})} \qquad \text{(VII)}\end{aligned}$$

As $k_2 > k_3[M]$ and $k_{13}[O_2] > k_{14}$ eqn. (VII) rearranges to

$$(\Phi\{CO\} - \Phi^3\{CO\})^{-1} =$$
$$\left(1 + \frac{k_{10}[O_2]}{k_9[C_2H_2]} + \frac{k_{11}}{k_9[C_2H_2]}\right) \frac{k_2}{\gamma k_2 + \beta k_{3a}[M]} \qquad \text{(VIII)}$$

A plot of $(\Phi\{CO\} - \Phi^3\{CO\})^{-1}$ *versus* $[O_2]$ is linear (Fig. 7). As the ratio of slop to intercept $(k_{10}/k_9[C_2H_2])/(1 + k_{11}/k_9[C_2H_2]) = 0.072$ and the value of $k_{11}/k_9 = 1.38$ [8], it is possible to evaluate k_{11}/k_{10} as 4.6 Torr.

Again, a similar series of experiments were performed with the addition of 601 ± 7.0 Torr CO_2 to 2.82 ± 0.12 Torr of acetylene and 2.85 ± 0.15 Torr of SO_2. The value of $\Phi\{CO\}$ again is seen to decrease with increasing O_2 pressures greater than 1 Torr (Fig. 3). This result is interpreted in the same manner as when no CO_2 is present. As $k_3[M] > k_2$ and $k_{13}[O_2] > k_{14}$, eqn. (VII) rearranges to

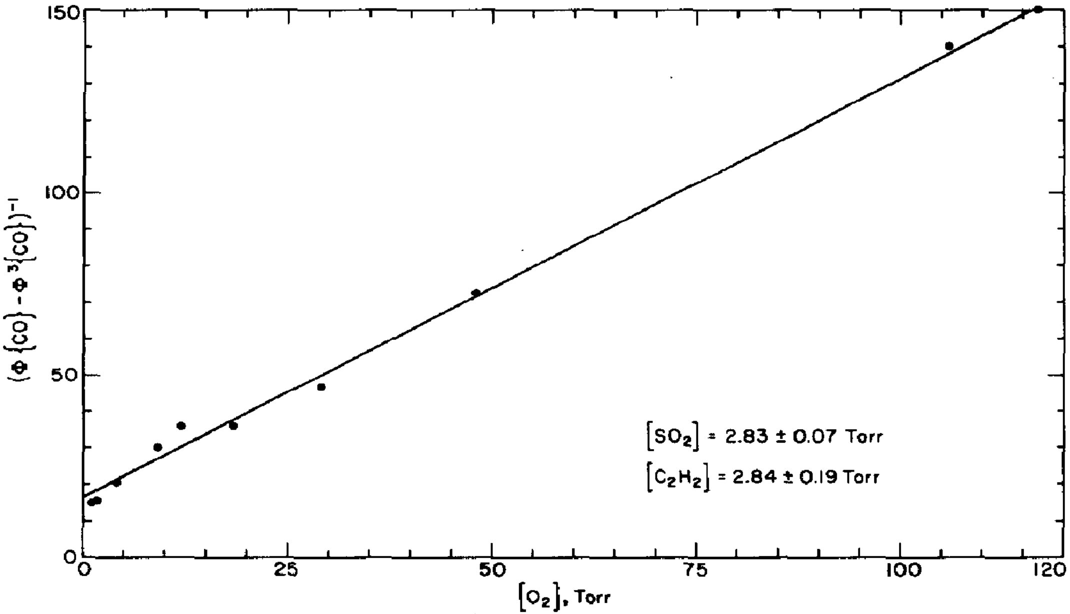

Fig. 7. Plot of $(\Phi\{CO\} - \Phi^3\{CO\})^{-1}$ *vs.* O_2 pressure for O_2 pressures greater than 1 Torr in the irradiation of SO_2–C_2H_2 mixtures.

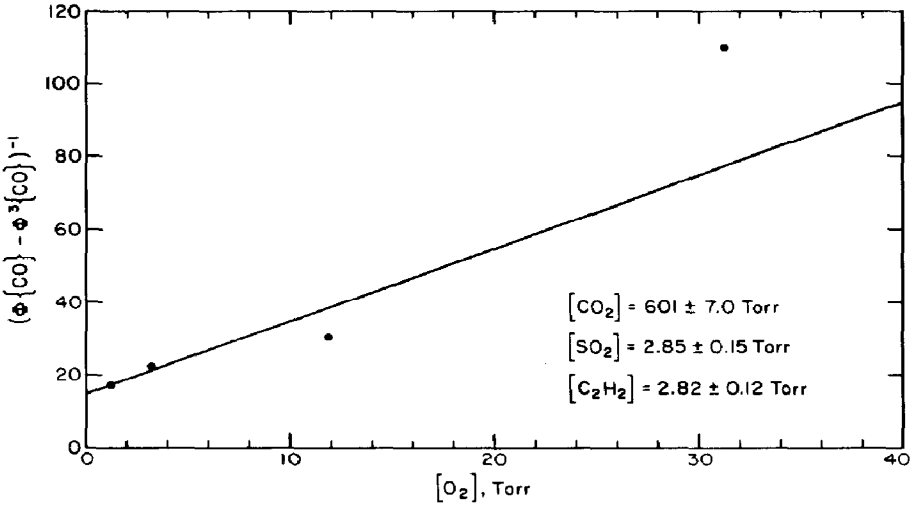

Fig. 8. Plot of $(\Phi\{CO\} - \Phi^3\{CO\})^{-1}$ *vs.* O_2 pressures for O_2 pressures greater than 1 Torr in the irradiation of SO_2–C_2H_2 mixtures in the presence of ~600 Torr of CO_2.

$$(\Phi\{CO\} - \Phi^3\{CO\})^{-1} = \left(1 + \frac{k_{10}[O_2]}{k_9[C_3H_2]} + \frac{k_{11}}{k_9[C_2H_2]}\right) \frac{k_3}{\beta k_{3a} + \gamma k_3} \quad \text{(IX)}$$

Although there are little data, a plot of $(\Phi\{CO\} - \Phi^3\{CO\})^{-1}$ *versus* $[O_2]$ is drawn as linear (Fig. 8). The ratio of slope to intercept, as above, equals 0.134 and, as the value of $k_{11}/k_9 = 1.38$ [8], it is possible to evaluate $k_{11}/k_9 =$ 2.45 Torr. This is in general agreement with the above result in the absence of CO_2. The major reason for the discrepancy is the small number of hard-to-reproduce data points.

The rate coefficient ratios obtained in this study as well as some from Kelly *et al.* [8], which are all tabulated in Table 1, were substituted into eqn. (I) and theoretical values of $\Phi\{CO\}$ were computed. These theoretical computed curves as well as the computed contributions from the individual excited states are shown in Figs. 1 - 3. The fit appears to be satisfactory as the general trend is predicted and the shape is reproduced in all cases.

Conclusion

The SO_2–C_2H_2–O_2 system is complex in that it involves contributions from several excited states of SO_2. The proposed mechanism is an attempt to fit the data obtained in this study to the basic mechanism for SO_2 photochemical reactions, which have been worked out in this laboratory and elsewhere, in the most tractable manner. The mechanism does represent a good approximation of reality, as the rate coefficient ratios obtained from this study have been used to compute the expected quantum yields as well as the contributions from the individual excited states of SO_2 and are seen to reproduce the experimental results satisfactorily (Figs. 1 - 3). In most cases rate constant ratios agree well with those of other workers. Most importantly, this study demonstrates that the emitting states of photoexcited SO_2 are not always sufficient to explain the data. The $SO_2^{\ddagger}$ state is shown to be of importance in the explanation of the excess chemical yield of CO as it may be physically quenched by O_2 to form chemically active SO_2^{**}. The SO_2^{**} state is also again shown to be important to explain CO production at high total pressures.

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