THE PHOTOLYSIS OF SULFUR DIOXIDE IN THE PRESENCE OF FOREIGN GASES
XII: PHOTOLYSIS OF SO_2 AT 313.0 nm IN THE PRESENCE OF BOTH ALLENE AND OXYGEN

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Summary

SO_2 was photolyzed at 25 °C and 313.0 nm in the presence of allene and oxygen. The quantum yields of the gas phase products CO and C_2H_4 were determined over a wide range of allene and oxygen pressures as well as in the presence and absence of 600 Torr of CO_2. The quantum yield $\Phi\{CO\}$ of CO increased at constant [allene]/[SO_2] ratios with the addition of O_2 up to pressures of 1 - 30 Torr depending upon the [allene]/[SO_2] ratio. With further increases in O_2 pressure, $\Phi\{CO\}$ was quenched. The quantum yield $\Phi\{C_2H_4\}$ of C_2H_4 exhibited similar behavior. The addition of 600 Torr of CO_2 appeared to have little effect upon either the enhancement or quenching of $\Phi\{CO\}$. The addition of increasing amounts of CO_2 to a constant [allene]/[SO_2]/[O_2] ratio decreased $\Phi\{C_2H_4\}$ to a limiting value of approximately 4×10^{-3} at 600 Torr of CO_2. Both the singlet and triplet emitting states as well as two non-emitting states 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 the pertinent rate coefficients are tabulated, and from these values $\Phi\{CO\}$ and $\Phi\{C_2H_4\}$ values are computed and compared with the observed values. The proposed mechanism is found to underestimate total $\Phi\{C_2H_4\}$ at low allene and high O_2 pressures. There must be an additional source of C_2H_4 which is not included in the mechanism.

Introduction

SO_2 has been shown to be chemically reactive upon excitation into its 240 - 330 nm absorption band [1 - 16]. As radiation above 218 nm is of insufficient energy to rupture the S—O bond, any photochemically induced reactions of SO_2 must be the result of interactions with bound excited states

of the molecule. Two of the 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. Past work in this laboratory [7 - 17] and elsewhere [1 - 3, 5, 18 - 22] with photo-excited SO_2 has not been consistent with a mechanism including only these two excited states. Participation of a non-emitting singlet state, designated as SO_2^*, and one or two non-emitting triplet states, designated as SO_2^{**} and $SO_2^†$, have been included in the various mechanisms to explain the data.

In previous papers from this laboratory [7 - 9, 15], the study of the photolysis of SO_2 at 313.0 nm in the presence of allene and acetylene in the absence and presence of various gases including O_2 has been reported. The products of these photolyses were CO, C_2H_4 and an aerosol for allene, and CO and an aerosol for acetylene. From quenching studies with various added gases it was determined that all of the five above-mentioned excited states of SO_2 were necessary to interpret the photochemistry of the SO_2-allene system and that all but $SO_2(^1B_1)$ were necessary to interpret the results of the SO_2-acetylene system.

The present study, which is the last in the series of twelve papers, involves the photolysis of SO_2 at 313.0 nm in the presence of allene, O_2 and at times about 600 Torr of CO_2. It is believed that the quantum yields of CO and C_2H_4 will serve as a measure of the participation of the various reactive states of SO_2 and that the additions of O_2 and CO_2 will allow the testing of previously reported mechanism and rate constant ratios. Several new rate constant ratios which are unique to this system are reported.

Experimental

The apparatus used in this study was identical to that used in our two previous studies of the SO_2-allene and SO_2-acetylene systems [8, 9]. The gas handling and purification procedures were exactly as described for SO_2, allene, O_2 and CO_2. The photolysis cell, radiation source, UV filter system and gas chromatographic analysis system, as well as the procedure for matching the SO_2 absorbance to that of azomethane, is described there.

Results

Photolysis of SO_2 in the presence of allene, O_2 and at times approximately 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%. CO and C_2H_4 analyses were performed for identical experiments with different photolysis times. In these experiments product growth as a function of time was linear and showed no detectable induction period as well as no fall off at longer photolysis times. Mixtures of reactants allowed to stand overnight gave no products. This indicates that the CO and C_2H_4 were initial products and that there was not a significant

amount of light scattering from the aerosol under the experimental conditions employed.

It should be noted that because of experimental difficulties it was not practical to measure both $\Phi\{CO\}$ and $\Phi\{C_2H_4\}$ from the same experiment and thus all experiments were performed twice, once to measure $\Phi\{CO\}$ and once to measure $\Phi\{C_2H_4\}$.

In the first series of experiments with an absorbed intensity I_a in the range of 4.8 - 5.4 mTorr min^{-1}, $[SO_2]$ and [allene] were held constant at pressures of 2.83 ± 0.09 Torr and 0.0862 ± 0.0008 Torr respectively, while the O_2 pressure was varied from 0.0107 to 73 Torr. $\Phi\{CO\}$ increased to a maximum value as the O_2 pressure was increased to about 1 Torr and then decreased with further increases in the pressure of O_2 (Fig. 1). Similarly, with I_a = 3.17 ± 0.11 mTorr min^{-1}, $[SO_2]$ = 2.86 ± 0.13 Torr and [allene] = 0.0865 ± 0.0010 Torr, the O_2 pressure was varied from 0.0172 to 201 Torr.
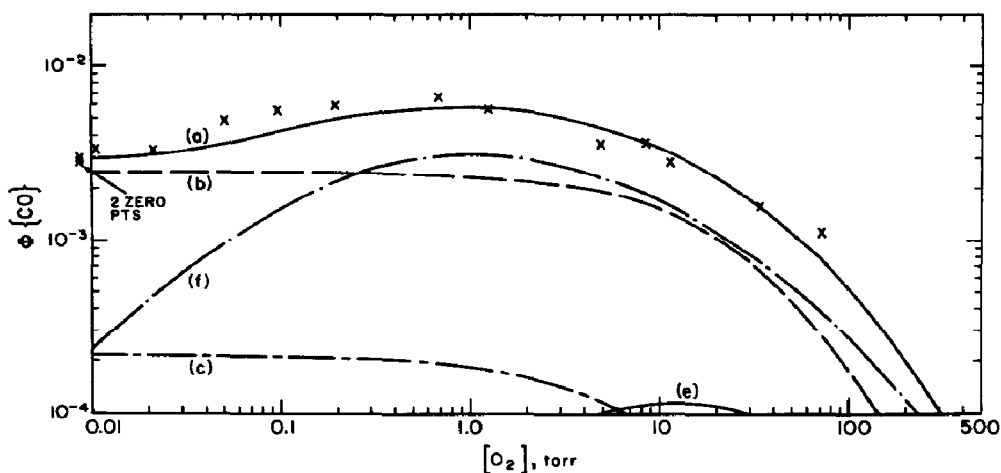

Fig. 1. Log–log plot of $\Phi\{CO\}$ vs. $[O_2]$ for the photolysis of SO_2–allene mixtures in the presence of O_2: [allene] = 0.0862 ± 0.0008 Torr; $[SO_2]$ = 2.83 ± 0.09 Torr; I_a = 4.8 - 5.4 mTorr min^{-1}. The curves are theoretically computed from the rate coefficients listed in Table 1. Curve a, total $\Phi\{CO\}$; curve b, $\Phi^3\{CO\}$; curve c, $\Phi^1\{CO\}$; curve d, $\Phi_{C_3H_4}{}^{**}\{CO\}$; curve e, $\Phi_{O_2}{}^{**}\{CO\}$; curve f, $\Phi_{O_2}{}^{\dagger}\{CO\}$.

$\Phi\{C_2H_4\}$ increased slightly to a maximum value as the O_2 pressure was increased to 0.5 - 1.0 Torr, and then decreased with further increases in the pressure of O_2 (Fig. 2).

In the second series of experiments with I_a ranging from 5.85 to 9.51 mTorr min^{-1}, $[SO_2]$ and [allene] were held constant at pressures of 2.82 ± 0.09 Torr and 2.84 ± 0.07 Torr respectively, while the O_2 pressure was varied from 0.0106 to 217 Torr. $\Phi\{CO\}$ increased to a maximum value as the O_2 pressure was increased to 1 - 3 Torr and then decreased with further increases in the pressure of O_2 (Fig. 3). Similarly, with I_a = 3.67 ± 0.63 mTorr min^{-1}, $[SO_2]$ = 2.78 ± 0.05 Torr and [allene] = 2.80 ± 0.18 Torr, the O_2 pressure was varied from 0.0403 to 282 Torr. $\Phi\{C_2H_4\}$ increased slightly to a maxi-

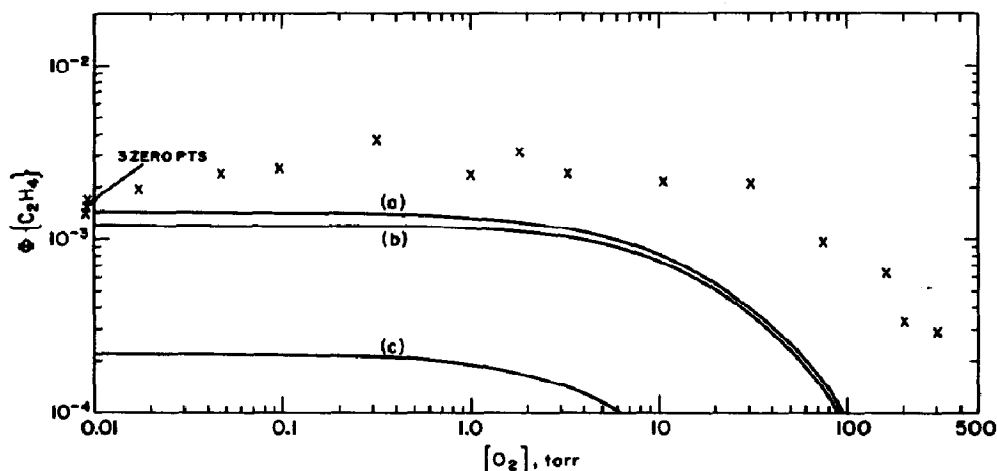Fig. 2. Log–log plot of $\Phi\{C_2H_4\}$ vs. $[O_2]$ for the photolysis of SO_2–allene mixtures in the presence of O_2: [allene] = 0.0865 ± 0.0010 Torr; $[SO_2]$ = 2.86 ± 0.13 Torr; I_a = 3.17 ± 0.11 mTorr min^{-1}. The curves are theoretically computed from rate coefficients listed in Table 1. Curve a, total $\Phi\{C_2H_4\}$; curve b, $\Phi^3\{C_2H_4\}$; curve c, $\Phi^1\{C_2H_4\}$.
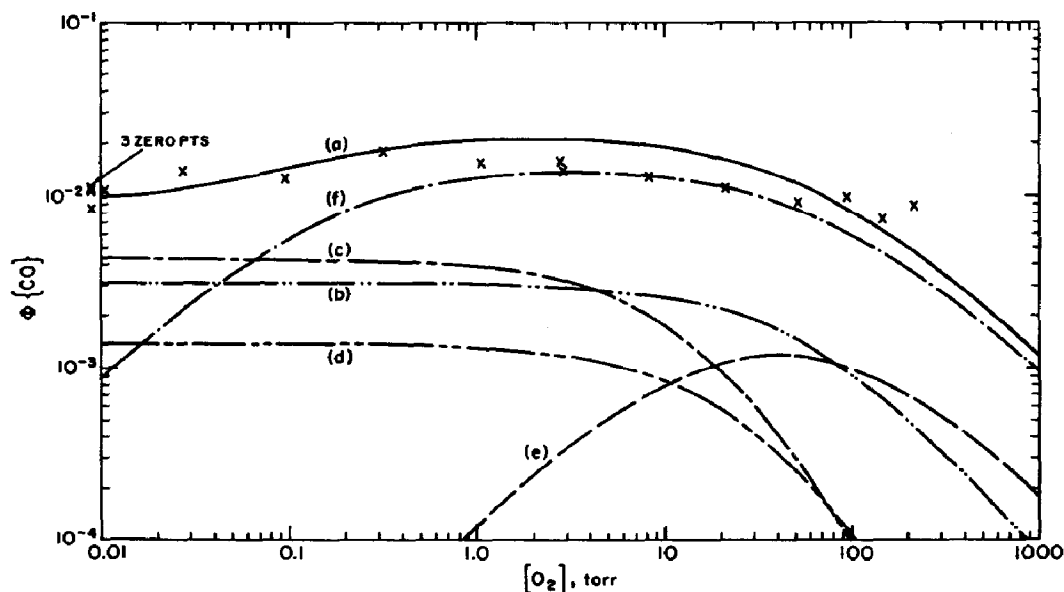

Fig. 3. As for Fig. 1 with [allene] = 2.84 ± 0.07 Torr, $[SO_2]$ = 2.82 ± 0.09 Torr and I_a = 5.85 - 9.51 mTorr min^{-1}.

mum value as the O_2 pressure was increased to about 1 Torr, and then decreased with further increases in the pressure of O_2 (Fig. 4).

In a third series of experiments with I_a ranging from 4.22 to 4.73 mTorr min^{-1}, $[SO_2]$ and [allene] were held constant at pressures of 2.83 ± 0.04 Torr and 100 ± 1 Torr respectively, while the O_2 pressure was varied from 0.0318 to 100 Torr. $\Phi\{CO\}$ increased to a maximum value as the O_2 pressure was increased to 10 - 30 Torr and then decreased slightly with further increases in
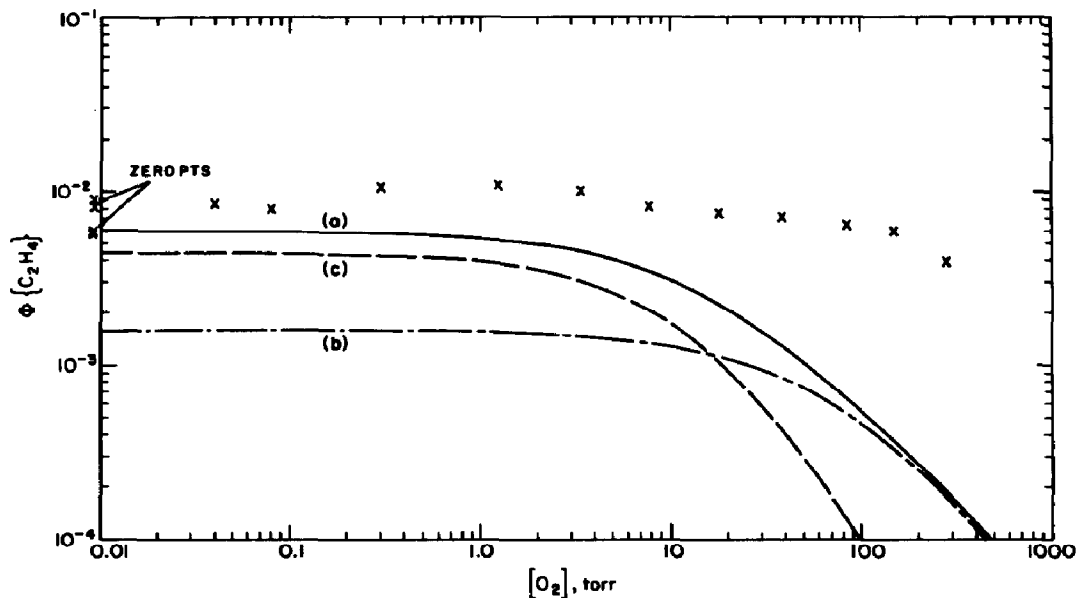
Fig. 4. As for Fig. 2 with [allene] = 2.80 ± 0.18 Torr, [SO₂] = 2.78 ± 0.05 Torr and I_a = 3.67 ± 0.63 mTorr min^{-1}.
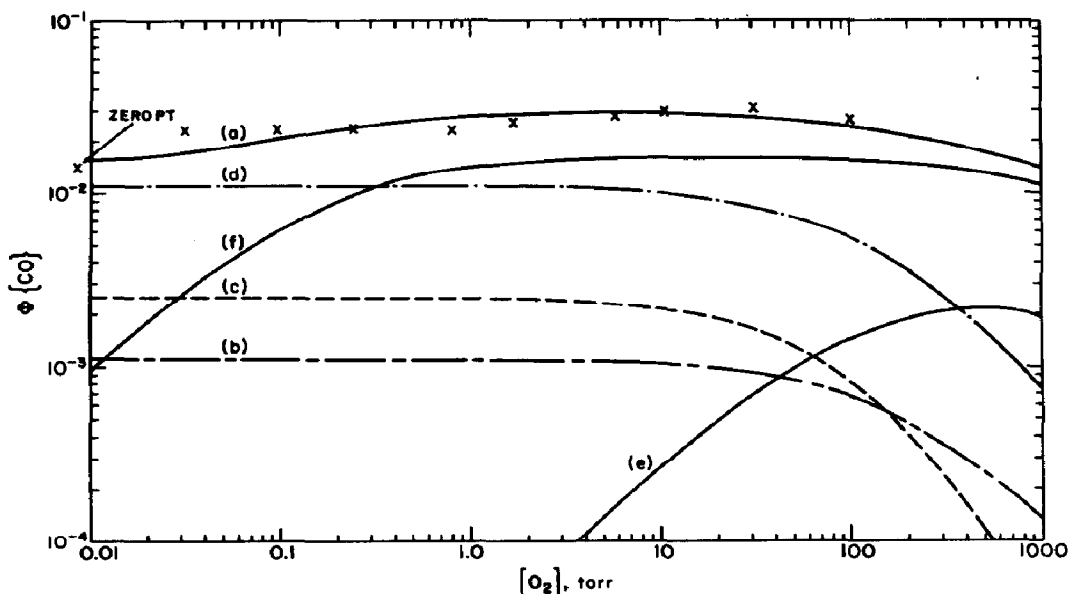
Fig. 5. As for Fig. 1 with [allene] ≈ 100 Torr, [SO₂] = 2.83 ± 0.04 Torr and I_a = 4.22 - 4.73 mTorr min^{-1}.

the pressure of O_2 (Fig. 5). Similarly, with I_a = 3.15 ± 0.11 mTorr min^{-1}, [SO₂] = 2.84 ± 0.10 Torr and [allene] = 100 ± 1 Torr, the O_2 pressure was varied from 0.0988 to 327 Torr. $\Phi\{C_2H_4\}$ increased very slightly to a maximum value as the O_2 pressure was increased to about 1 - 3 Torr, and then decreased with further increases in the pressure of O_2 (Fig. 6).
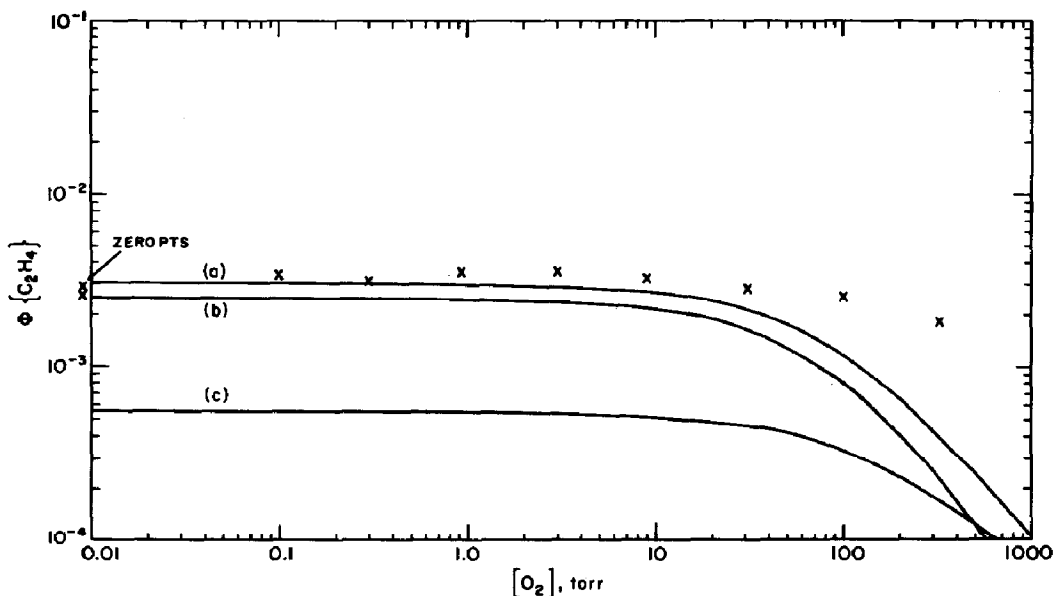
Fig. 6. As for Fig. 2 with [allene] $\approx$ 100 Torr, [SO_2] = 2.84 ± 0.10 Torr and I_a = 3.15 ± 0.11 mTorr min^{-1}.

In a fourth series of experiments with I_a ranging from 3.47 to 4.03 mTorr min^{-1}, about 600 Torr of CO_2 was added to mixtures of [SO_2] and [allene] which were held constant at pressures of 2.78 ± 0.08 and 2.84 ± 0.12 Torr respectively, while the O_2 pressure was varied from 0.00973 to 100 Torr. Φ {CO} increased to a maximum value as the O_2 pressure was increased from 1 to 10 Torr and then decreased slightly with further increases in the pressure of O_2 (Fig. 7).

In the last series of experiments with I_a = 3.70 ± 0.13 mTorr min^{-1}, 3.62 ± 0.42 Torr of O_2 was added to mixtures of SO_2 and allene the pressures of which were held constant at 2.82 ± 0.11 Torr and 2.83 ± 0.05 Torr respectively, while the CO_2 pressure was varied from 1.20 to 600 Torr. Φ {C_2H_4} decreased with increasing CO_2 pressures to a minimum value at 300 - 600 Torr of CO_2 (Fig. 8).

Discussion

The major conclusions that can be drawn from this study can be summarized as follows.

(1) SO_2 photoexcited at 313.0 nm reacts with C_3H_4 to produce CO and C_2H_4. The addition of O_2 pressures up to about 1 - 30 Torr, depending upon the [allene]/[SO_2] ratio, enhances both Φ {CO} and Φ {C_2H_4}. A further increase in O_2 pressure reduces both Φ {CO} and Φ {C_2H_4}. This result is similar to that found previously for Φ {CO} in the SO_2–acetylene system when O_2 was added [9]. In that system, no C_2H_4 was produced.
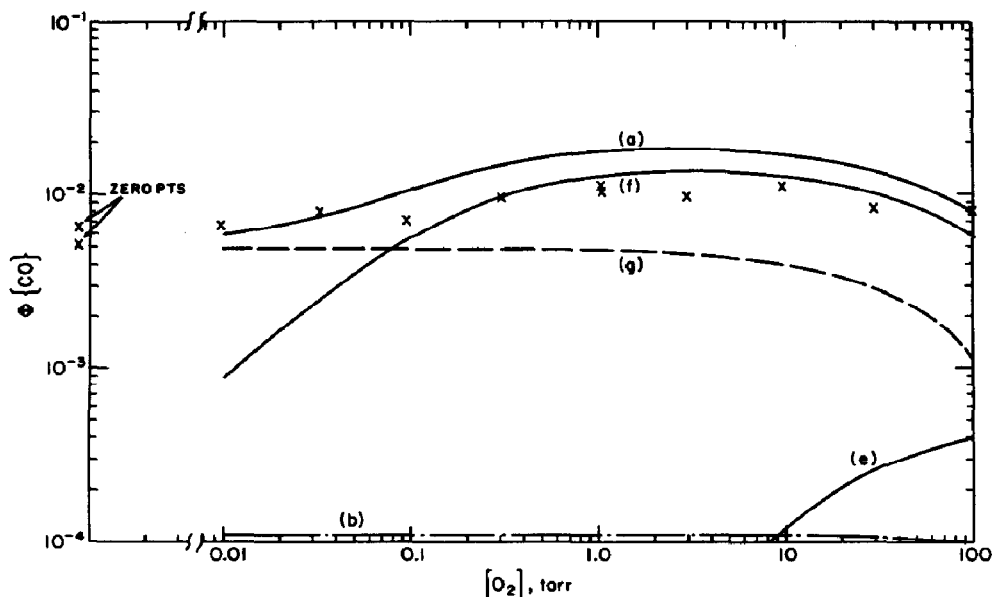
Fig. 7. Log–log plot of $\Phi\{CO\}$ vs. $[O_2]$ for the photolysis of SO_2–allene mixtures in the presence of about 600 Torr of CO_2 and varying amounts of O_2. The curves are theoretically computed from the rate coefficients listed in Table 1. Curve a, total $\Phi\{CO\}$; curve b, $\Phi^3\{CO\}$; curve e, $\Phi_{O_2}**\{CO\}$; curve f, $\Phi_{O_2}{}^\dagger\{CO\}$; curve g, $\Phi_{CO_2}**\{CO\}$.
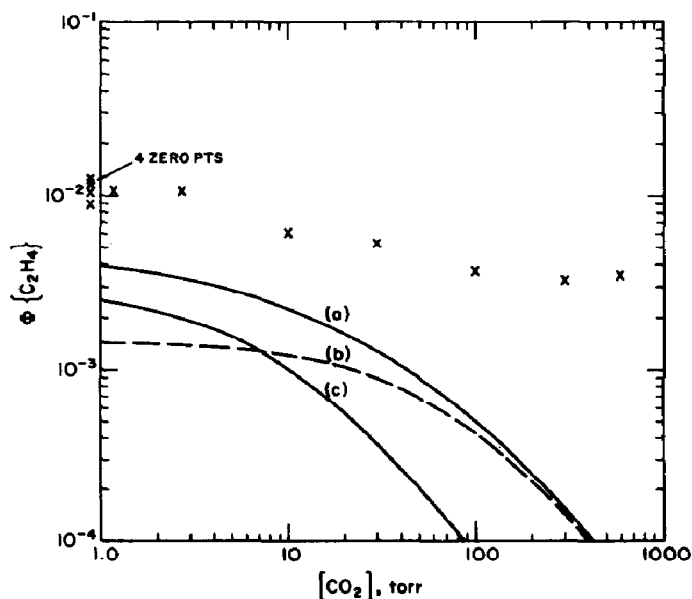
Fig. 8. Log–log plot of $\Phi\{C_2H_4\}$ vs. $[CO_2]$ for the photolysis of SO_2–allene mixtures in the presence of 3.62 ± 0.42 Torr of O_2 and varying amounts of CO_2. The curves are theoretically computed from the rate coefficients listed in Table 1. Curve a, total $\Phi\{C_2H_4\}$; curve b, $\Phi^3\{C_2H_4\}$; curve c, $\Phi^1\{C_2H_4\}$.

(2) When mixtures of approximately 3 Torr each of SO_2, allene and O_2 were photolyzed in the presence of about 600 Torr of CO_2, $\Phi\{C_2H_4\}$ was not

completely quenched (Fig. 8). In a previous study of the SO_2–allene system in the absence of O_2, it was found that about 600 Torr of CO_2 would efficiently quench $\Phi\{C_2H_4\}$ [8]. Thus the presence of even a few torr of O_2 is sufficient to give an additional contribution to $\Phi\{C_2H_4\}$.

The mechanism we have used to attempt to fit our results is one in which all the major steps have been obtained from previous studies. A few new steps have been added to explain the uniqueness of the allene–SO_2 system when O_2 is present. The singlet state formed on absorption is abbreviated as SO_2^*, the fluorescing state as $^1SO_2$, the emitting triplet state $SO_2(^3B_1)$ as $^3SO_2$, the non-emitting triplet state which is important at high pressures as SO_2^{**} and a third triplet state introduced by Fatta et $al.$ [14] as $SO_2^{\dagger}$. I symbolizes an intermediate postulated to form when $^3SO_2$ reacts with allene [8]. It can decompose unimolecularly to give CO or C_2H_4 or it can be quenched, possibly to give the aerosol found to be present in this system. The entire mechanism proposed to explain this study is

$$SO_2 + h\nu \xrightarrow{\text{313 nm}} {}^3SO_2 \qquad\qquad (\text{rate} = \alpha I_a)$$

$$\xrightarrow{\text{313 nm}} SO_2^* \qquad\qquad (\text{rate} = \beta I_a)$$

$$^3SO_2 \rightarrow SO_2 + h\nu_p \tag{1}$$

$$^3SO_2 + C_3H_4 \rightarrow I \tag{2a}$$

$$\rightarrow \text{removal of } {}^3SO_2 \tag{2b}$$

$$I \rightarrow 2CO + C_2H_4 \tag{3}$$

$$I + C_3H_4 \rightarrow \text{no CO or } C_2H_4 \tag{4a}$$

$$I + CO_2 \rightarrow \text{no CO or } C_2H_4 \tag{4b}$$

$$I + O_2 \rightarrow \text{no CO or } C_2H_4 \tag{4b'}$$

$$^3SO_2 + SO_2 \rightarrow \text{removal of } {}^3SO_2 \tag{5}$$

$$^3SO_2 + CO_2 \rightarrow \text{removal of } {}^3SO_2 \tag{6}$$

$$^3SO_2 + O_2 \rightarrow \text{removal of } {}^3SO_2 \tag{6'}$$

$$SO_2^* \rightarrow {}^1SO_2 \tag{7a}$$

$$\rightarrow SO_2 \tag{7b}$$

$$SO_2^* + C_3H_4 \rightarrow SO_2^{**} + C_2H_4 \tag{8a}$$

$$\rightarrow \text{removal of } SO_2^* \tag{8b}$$

$$SO_2^* + CO_2 \rightarrow SO_2^{**} + CO_2 \tag{9a}$$

$$\rightarrow \text{removal of } SO_2^* \tag{9b}$$

$$SO_2^* + O_2 \rightarrow SO_2^{**} + O_2 \tag{9a'}$$

$$\rightarrow \text{removal of } SO_2^* \tag{9b'}$$

$$^1SO_2 \rightarrow SO_2 + h\nu_f \qquad (10)$$

$$^1SO_2 + C_3H_4 \rightarrow CO + C_2H_4 \qquad (11a)$$

$$\rightarrow \text{removal of } ^1SO_2 \qquad (11b)$$

$$^1SO_2 + SO_2 \rightarrow \text{removal of } ^1SO_2 \qquad (12)$$

$$^1SO_2 + CO_2 \rightarrow \text{removal of } ^1SO_2 \qquad (13)$$

$$^1SO_2 + O_2 \rightarrow \text{removal of } ^1SO_2 \qquad (13')$$

$$SO_2** \rightarrow \text{removal of } SO_2** \qquad (14)$$

$$SO_2** + C_3H_4 \rightarrow CO \qquad (15a)$$

$$\rightarrow \text{removal of } SO_2** \qquad (15b)$$

$$SO_2** + O_2 \rightarrow \text{removal of } SO_2** \qquad (16')$$

$$SO_2 + h\nu \rightarrow SO_2^\dagger \qquad (\text{rate} = \gamma I_a)$$

$$SO_2^\dagger + O_2 \rightarrow SO_2** + O_2 \qquad (17)$$

$$SO_2^\dagger \rightarrow SO_2 \qquad (18)$$

For comparison purposes the above reaction numbers are the same as those from earlier studies of the SO_2–allene system [8, 17].

The SO_2* state is produced at a constant fraction β of the absorbed radiation I_a. Unimolecularly, it forms either $^1SO_2$ (discussed below) or ground state SO_2. The SO_2* state can also be deactivated to produce ground state SO_2 as well as SO_2** and possibly $SO_2^\dagger$, but it does not react to produce products. Cehelnik *et al.* [10] 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 pressure where it is not quenched by SO_2 or CO_2. The SO_2** state is quenched by allene and O_2. The quenching by allene produces CO but not C_2H_4 [8].

$^3SO_2$ 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 the process of intersystem crossing which leads to it must be constant and pressure independent [12]. $^3SO_2$ 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 allene, O_2 and CO_2 because the Stern–Volmer quenching curve for $^3SO_2$ is linear [12]. It is unlikely that these removal processes would give $^3SO_2$ the same fraction of the time. A likely possibility is that the $^3SO_2$ comes from the $^1A_2$ state which is formed on absorption and is collisionally deactivated at the pressures at which this study is performed. The $^3SO_2$ state may be collisionally quenched by any gas present in the system. First order removal steps are unimportant at the experimental pressures employed. The $^3SO_2$ state is postulated to react with allene to produce an excited intermediate I.

The proposed excited intermediate I is formed by reaction of $^3SO_2$ with allene. It may decompose unimolecularly to give CO and C_2H_4 in relative

proportions of 2:1 via reaction (3). Reaction (3) cannot, of course, proceed as written but represents two parallel paths of equal importance, one of which produces CO + C_2H_4 and the other which produces CO but not C_2H_4. I may also be quenched by allene, CO_2 and O_2 but not by SO_2 (at the pressures used).

The longer lived fluorescing state is 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 $^1SO_2$ [12]. From the viewpoint of photochemical kinetics it is immaterial whether this state is spectroscopically distinct 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. $^1SO_2$ may be collisionally quenched by any gas present in the system. First order removal of $^1SO_2$ is unimportant at the experimental pressures used. $^1SO_2$ reacts chemically with allene to form both CO and C_2H_4 in equal proportions.

Evidence for the $SO_2^\dagger$ state was first proposed by Fatta *et al.* [14]. In previous studies of the photolysis of SO_2–acetylene mixtures in the presence of NO [7] and O_2 [9] an enhancement of $\Phi\{CO\}$ with the addition of small amounts of NO or O_2 was found. This effect was explained with the incorporation of the $SO_2^\dagger$ state. This state is also incorporated in this study to explain the increase in $\Phi\{CO\}$ when up to approximately 1 - 30 Torr of O_2 is added to the reaction mixture in both the absence and presence of approximately 600 Torr of CO_2. This state must be quenched by about 1 Torr of O_2 but 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 $SO_2^\dagger$ by O_2 produces SO_2^{**}. For simplicity it is assumed that $SO_2^\dagger$ is produced at a constant fraction γ of I_a, but there is no direct evidence that γ is a true constant or that the state is produced directly on absorption. The $SO_2^\dagger$ state used here as well as in the SO_2–acetylene system [9] is assumed to be chemically unreactive 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

$$\Phi\{CO\} = \frac{2\alpha k_{2a}k_3[C_3H_4]}{(k_2[C_3H_4] + k_5[SO_2] + k_6[M])(k_3 + k_{4a}[C_3H_4] + k_{4b}[M])} +$$

$$+ \frac{\beta k_{7a}k_{11a}[C_3H_4]}{(k_7 + k_8[C_3H_4] + k_9[M])(k_{11}[C_3H_4] + k_{12}[SO_2] + k_{13}[M])} +$$

$$+ \frac{\beta k_{15a}[C_3H_4](k_{8a}[C_3H_4] + k_{9a}[M])}{(k_7 + k_8[C_3H_4] + k_9[M])(k_{14} + k_{15}[C_3H_4] + k_{16'}[O_2])} +$$

$$+ \frac{\gamma k_{15a}k_{17}[C_3H_4][O_2]}{(k_{14} + k_{15}[C_3H_4] + k_{16'}[O_2])(k_{17}[O_2] + k_{18})} \tag{I}$$

and similarly

$$\Phi\{C_2H_4\} = \frac{\alpha k_{2a}k_3[C_3H_4]}{(k_2[C_3H_4] + k_5[SO_2] + k_6[M])(k_3 + k_{4a}[C_3H_4] + k_{4b}[M])} +$$

$$+ \frac{\beta k_{7a}k_{11a}[C_3H_4]}{(k_7 + k_8[C_3H_4] + k_9[M])(k_{11}[C_3H_4] + k_{12}[SO_2] + k_{13}[M])} \quad (II)$$

where [M] in the above two equations represents $[CO_2]$ and/or $[O_2]$. The first term on the right-hand side in each of the two equations represents the contribution to the quantum yield from the emitting triplet state $SO_2(^3B_1)$ via the intermediate I and will be referred to as $\Phi^3\{CO\}$ or $\Phi^3\{C_2H_4\}$. The second term on the right-hand side in each equation is the contribution from the fluorescing singlet state $^1SO_2$ and will be referred to as $\Phi^1\{CO\}$ or $\Phi^1\{C_2H_4\}$. The penultimate term in the equation for $\Phi\{CO\}$ represents the contribution from SO_2^{**} (via [M] and $[C_3H_4]$ quenching SO_2^*) and will be referred to as $\Phi_M^{**}\{CO\}$, where M represents CO_2, O_2 and C_3H_4. The fourth term is also a contribution from SO_2^{**} but comes from $SO_2^\dagger$, and, in order to differentiate it, it will be referred to as $\Phi_{O_2}^\dagger\{CO\}$. It must be remembered that previous work indicated that $SO_2^\dagger$ is not chemically reactive so that there are only three reactive states, $^1SO_2$, $^3SO_2$ and SO_2^{**}, and that one of these states, SO_2^{**}, which comes from two precursor states, does not lead to C_2H_4 production. Thus

$$\Phi\{CO\} = \Phi^3\{CO\} + \Phi^1\{CO\} + \Phi_M^{**}\{CO\} + \Phi_{O_2}^\dagger\{CO\} \quad (III)$$

and

$$\Phi\{C_2H_4\} = \Phi^3\{C_2H_4\} + \Phi^1\{C_2H_4\} \quad (IV)$$

where

$$\Phi^3\{CO\}^{-1} = 2\Phi^3\{C_2H_4\}^{-1} = \frac{k_2}{2\alpha k_{2a}} \left(1 + \frac{k_5[SO_2]}{k_2[C_3H_4]} + \frac{k_6[M]}{k_2[C_3H_4]}\right) \times$$

$$\times \left(1 + \frac{k_{4a}[C_3H_4]}{k_3} + \frac{k_{4b}[M]}{k_3}\right) \quad (V)$$

$$\Phi^1\{CO\}^{-1} = \Phi^1\{C_2H_4\}^{-1} = \frac{k_7 k_{11}}{\beta k_{7a}k_{11a}} \left(1 + \frac{k_8[C_3H_4]}{k_7} + \frac{k_9[M]}{k_7}\right) \times$$

$$\times \left(1 + \frac{k_{12}[SO_2]}{k_{11}[C_3H_4]} + \frac{k_{13}[M]}{k_{11}[C_3H_4]}\right) \quad (VI)$$

$$\Phi_M^{**}\{CO\}^{-1} = \frac{k_8 k_{15}}{\beta k_{8a} k_{15a}} \left(1 + \frac{k_7}{k_8[C_3H_4]} + \frac{k_9[M]}{k_8[C_3H_4]}\right) \times$$

$$\times \left(1 + \frac{k_{14}}{k_{15}[C_3H_4]} + \frac{k_{16'}[O_2]}{k_{15}[C_3H_4]}\right) + \frac{k_9 k_{15}}{\beta k_{9a} k_{15a}} \times$$

$$\times \left(1 + \frac{k_8[C_3H_4]}{k_9[M]} + \frac{k_7}{k_9[M]}\right)\left(1 + \frac{k_{14}}{k_{15}[C_3H_4]} + \frac{k_{16'}[O_2]}{k_{15}[C_3H_4]}\right) \quad \text{(VII)}$$

$$\Phi_{O_2}^{\dagger}\{CO\}^{-1} = \frac{k_{15}}{\gamma k_{15a}} \left(1 + \frac{k_{18}}{k_{17}[O_2]}\right)\left(1 + \frac{k_{14}}{k_{15}[C_3H_4]} + \frac{k_{16'}[O_2]}{k_{15}[C_3H_4]}\right) \quad \text{(VIII)}$$

All rate constant ratios in eqn. (V), which determines the contribution from $^3SO_2$, are known from previous work in this laboratory except for $k_{4b'}/k_3$ which was approximated by computer fitting the $\Phi\{CO\}$ quenching data with O_2 at low allene pressure where the $\Phi^3\{CO\}$ contribution is most significant (Fig. 1). All rate constant ratios used in the calculation of $\Phi^1\{CO\}$ by eqn. (VI) were also known from previous work except for $k_{9'}/k_7$, which also occurs in the Φ_M^{**} expression, eqn. (VII). This value was also estimated by computer fitting of the $\Phi\{CO\}$ quenching data at higher allene pressures (Figs. 3 and 5). In the calculation of $\Phi_M^{**}\{CO\}$, $k_{9'}/k_7$ (mentioned above) and $k_{9'}/k_{9a'}$ were the only undetermined values. $k_{9'}/k_{9a'}$ was estimated at high allene and high O_2 pressures where the excess $\Phi\{CO\}$ could be attributed to SO_2^{**} formed in reaction (9a) (Fig. 7). In the calculation of $\Phi_{O_2}^{\dagger}\{CO\}$ by eqn. (VIII) $k_{15}/\gamma k_{15a}$ was estimated to be 0.016 from the enhancement of $\Phi\{CO\}$ under the conditions used. Allowing γ to be equal to 0.064 - 0.092, as determined with C_2H_2 in a previous paper [9], gives values of 4 - 5.75 for k_{15}/k_{15a} which is in excellent agreement with values of 4 - 5 suggested in earlier work [8, 17]. Other rate constant ratios used in the computer simulation may differ very slightly from previously reported values, but these changes are of no consequence and are due primarily to rounding off values of reciprocals of the ratios.

There is a discrepancy between the value of γ reported in this and in our last report [8] and that reported by Kelly *et al.* [7]. It is possible that γ is not a true constant and/or that $SO_2^{\dagger}$ is not formed directly on absorption but by various modes of intersystem crossings or internal conversions and may be dependent upon the nature of M. In the work by Kelly *et al.* [7] M was NO, while in this study M is O_2.

The rate coefficient ratios used in this study are presented in Table 1 and are compared with those reported by others. The values arrived at from this study were substituted into eqns. (V) - (VIII), and theoretical values of $\Phi\{CO\}$ and $\Phi\{C_2H_4\}$ as well as the various contributions from the individual excited states were computed. These theoretical computed curves are shown in Figs. 1 - 8. For the case of $\Phi\{CO\}$ the fit appears to be satisfactory as the

TABLE 1

Summary of rate coefficients data

Ratio	Value	Units	M	Reference
α	0.10	None	–	Demerjian and Calvert [6]
γ	0.064	None	–	Partymiller and Heicklen [9]
	0.092	None	–	Partymiller and Heicklen [9]
	0.0193	None	–	Kelly et al. [7]
$\beta = 1 - \alpha - \gamma$	0.835	None	–	This work
k_2/k_{2a}	60	None	C_3H_4	Partymiller et al. [8]
k_2/k_5	90	None	C_3H_4	Partymiller et al. [8]
	124	None	C_3H_4	Kelly and Heicklen [17]
k_6/k_5	0.55	None	CO_2	Partymiller et al. [8]
	0.55	None	CO_2	Stockburger et al. [12]
	0.42	None	CO_2	Kelly et al. [7]
	0.31	None	CO_2	Mettee [23]
	0.29	None	CO_2	Sidebottom et al. [24]
$k_{6'}/k_5$	0.36	None	O_2	This work
	0.34	None	O_2	Partymiller and Heicklen [9]
	0.42	None	O_2	Stockburger et al. [12]
	0.37	None	O_2	Mettee [23]
	0.25	None	O_2	Sidebottom et al. [24]
k_{4a}/k_3	0.02	$Torr^{-1}$	C_3H_4	Partymiller et al. [8]
	0.029	$Torr^{-1}$	C_3H_4	Kelly and Heicklen [17]
k_{4b}/k_3	0.02	$Torr^{-1}$	CO_2	Partymiller et al. [8]
	0.012	$Torr^{-1}$	CO_2	Kelly and Heicklen [17]
$k_{4b'}/k_3$	0.02	$Torr^{-1}$	O_2	This work
k_8/k_7	0.045	$Torr^{-1}$	C_3H_4	Partymiller et al. [8]
k_9/k_7	0.015	$Torr^{-1}$	CO_2	Partymiller et al. [8]
	0.0179	$Torr^{-1}$	CO_2	Kelly et al. [7]
	~ 0.025	$Torr^{-1}$	CO_2	Stockburger et al. [12]
$k_{9'}/k_7$	0.05	$Torr^{-1}$	O_2	This work
k_8/k_{8a}	15.7	None	C_3H_4	This work
	~ 15.7	None	C_3H_4	Partymiller et al. [8]
k_9/k_{9a}	35.5	None	CO_2	Partymiller et al. [8]
	45.2	None	CO_2	Kelly et al. [7]
$k_{9'}/k_{9a'}$	65	None	O_2	This work
$k_7 k_{11}/\beta k_{7a} k_{11a}$	68	None	C_3H_4	Partymiller et al. [8]
k_{11}/k_{12}	0.49	None	C_3H_4	Partymiller et al. [8]

TABLE 1 *(continued)*

Ratio	Value	Units	M	Reference
k_{13}/k_{12}	0.85	None	CO_2	Partymiller *et al.* [8]
	0.76	None	CO_2	Stockburger *et al.* [12]
	0.73	None	CO_2	Rao *et al.* [25]
	0.63	None	CO_2	Mettee [23]
$k_{13'}/k_{12}$	0.29	None	O_2	This work
	0.37	None	O_2	Stockburger *et al.* [12]
	0.31	None	O_2	Rao *et al.* [25]
	0.27	None	O_2	Mettee [23]
k_{15}/k_{15a}	4	None	C_3H_4	This work
	~ 5	None	C_3H_4	Partymiller *et al.* [8]
	4	None	C_3H_4	Kelly and Heicklen [17]
k_{15}/k_{14}	3.9	$Torr^{-1}$	C_3H_4	Partymiller *et al.* [8]
	6.3	$Torr^{-1}$	C_3H_4	Kelly and Heicklen [17]
$k_{16'}/k_{14}$	0.18	$Torr^{-1}$	O_2	This work
	0.22	$Torr^{-1}$	O_2	Partymiller and Heicklen [9]
	0.41	$Torr^{-1}$	O_2	Partymiller and Heicklen [9]
k_{17}/k_{18}	6.2	$Torr^{-1}$	O_2	Partymiller and Heicklen [9]
	4.0	$Torr^{-1}$	O_2	Partymiller and Heicklen [9]

general trend is predicted and the shapes of the quenching plots are reproduced In the presence of about 600 Torr of CO_2 (Fig. 7) the theoretical computed curve overestimates $\Phi\{CO\}$. This could be due to some quenching of the $SO_2^{\dagger}$ state taking place when large pressures of CO_2 are present.

In the case of $\Phi\{C_2H_4\}$ there appears to be an excess contribution to $\Phi\{C_2H_4\}$ which occurs in the presence of O_2 and which is not explained by our mechanism. Some explanations of this observation which are consistent with our mechanism are as follows. An energy transfer from excited triplet SO_2^{**} to O_2 might occur forming singlet O_2 which is known to react with olefins. A reaction mechanism might be

$$SO_2^{**} + O_2 \rightarrow SO_2 + O_2(^1\Delta_g)$$

$$O_2(^1\Delta_g) + C_3H_4 \rightarrow CO_2 + C_2H_4$$
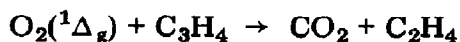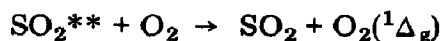
A second possibility is that a carbon-containing fragment C_2H_4SO from one of the reactions in the mechanism might react with O_2 to produce C_2H_4. This would seem to be a less likely possibility for two reasons. The excess C_2H_4 does not contain oxygen as would be expected from the reaction of O_2 and C_2H_4SO. The excess C_2H_4 is not as prevalent at high allene pressures where it

would be expected to be large if the reaction of C_2H_4SO with O_2 was important. A third possibility is that some SO_3 (or SO_4), which must be present in the system, reacts with allene to produce excess C_2H_4.

Conclusion

The $\Phi\{CO\}$ data obtained from this study are accommodated by the previous mechanisms proposed by this laboratory except at high CO_2 pressures where the $SO_2^\dagger$ state is overestimated. In the presence of O_2, however, there appears to be an excess of C_2H_4 which is not explained by this mechanism. Additional reactions must occur which are not contained in our mechanism. This study, along with those which have preceded it, demonstrates that the emitting states of photoexcited SO_2 are not sufficient to explain the data. Previously proposed non-emitting triplet states, designated SO_2^{**} and $SO_2^\dagger$, are shown to be of importance in the explanation of excess chemical yield of CO at high total pressures and in the presence of O_2 respectively. We feel that a combination of all of our studies leads to a consistent if not complete interpretation of the SO_2–allene and SO_2–acetylene systems.

Acknowledgments

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