

PHOTOLYSIS OF SO₂ IN THE PRESENCE OF FOREIGN GASES IV. WAVELENGTH AND TEMPERATURE EFFECTS WITH CO*

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SUMMARY

Studies of the photolysis of SO₂ in the presence of CO have been extended (from 3130 Å and 300 K) to 2537 and 3261 Å at 300 K, and to 415 and 520 K at 3130 Å. Experiments were also performed in the presence of either or both of NO and N₂. The quantum yield for CO₂ formation, $\Phi\{\text{CO}_2\}$, is independent of temperature and the absorbed intensity, but shows a mild wavelength dependence. At high SO₂ pressures, $\Phi\{\text{CO}_2\}$ is nearly independent of [SO₂] and directly proportional to [CO]. At lower SO₂ pressures, $\Phi\{\text{CO}_2\}$ increases with decreasing [SO₂]. $\Phi\{\text{CO}_2\}$ is markedly reduced by the addition of small amounts of NO, but is not zero. The addition of a large excess of N₂ gives only a slight reduction in $\Phi\{\text{CO}_2\}$.

Further experimental evidence is provided for the non-emitting singlet and triplet states. The results are fitted with a three electronic state model of two excited singlets (one emitting and one non-emitting) and the non-emitting triplet state. A set of rate constants is obtained which is consistent with all the spectroscopic data and satisfactorily fits almost all of the 216 data points at 300 K as well as those at elevated temperatures.

INTRODUCTION

The primary photophysical processes in SO₂ excited by absorption in the band centered at about 3000 Å have been elucidated through lifetime measurements of emission¹⁻⁶, fluorescence and phosphorescence yields during steady-state exposure⁷⁻¹³, and by biacetyl sensitization^{11, 14-17}. It was thought the initial absorp-

* Most of this work was abstracted from the Ph. D. thesis of E. Cehelnik.

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tion was to the emitting singlet state, $^1\text{SO}_2$. The excited singlet state could either fluoresce or pass to the emitting $^3\text{B}_1$ triplet state, $^3\text{SO}_2$. The removal of both $^1\text{SO}_2$ and $^3\text{SO}_2$ could be first order or could be a result of collisional quenching. However, at pressures above 1 Torr, only the collisional removal steps are significant.

In Part I of this series, Cehelnik *et al.*¹⁸ examined the photochemistry in the presence of CO and C_2F_4 . The chemistry was rather insensitive to either the SO_2 pressure or the pressure of added N_2 under some conditions. Also, experiments with triplet quenchers showed that both singlet and triplet states were responsible for the chemical reactions. Since these states were insensitive to pressure quenching, two new non-emitting excited states were postulated: SO_2^* , a singlet, and SO_2^{**} , a triplet.

Further support for the additional non-emitting states was given in Part II of this series¹⁹. Braslavsky and Heicklen¹⁹ examined the photolysis of SO_2 in the presence of thiophene and found that part of the reaction came from a triplet state (*i.e.* it could be inhibited by NO, a known triplet quencher). However, direct production of $^3\text{SO}_2$ by irradiation at 3660 Å gave no photochemical products.

Wampler *et al.*¹⁷ re-examined the CO_2 formation in the 3130 Å irradiated mixtures of SO_2 and CO. Their data were less extensive than those of Cehelnik *et al.*¹⁸. The two sets of data were consistent except that they differed by a constant scale factor of 30–40%. Presumably this difference reflects actinometry uncertainties in the two laboratories. Wampler *et al.* concurred with Cehelnik *et al.* that the new state, SO_2^* , was needed, but felt that their data could be interpreted without the SO_2^{**} state or without chemical reaction between SO_2^* and CO. The excess triplet yield, they felt, could be attributed to formation of $^3\text{SO}_2$ by collisional quenching of SO_2^* . We have computed the expected values of their data from their mechanism and rate constants. The fit with their experimental data is not very good. Of more consequence is the fact that their data contains only runs with CO in excess of SO_2 . The data of Cehelnik *et al.*¹⁸ contain many runs with excess SO_2 . For these runs the mechanism of Wampler *et al.*¹⁷ fails badly.

In order to see if there really is an excess $^3\text{SO}_2$ yield, Stockburger *et al.*²⁰ in Part III of this series examined the $^3\text{SO}_2$ phosphorescence in the presence of several quenching gases at pressures up to one atmosphere. Over the whole pressure range, phosphorescence quenching obeyed Stern–Volmer kinetics, and there was no evidence for an excess production of $^3\text{SO}_2$.

Additional evidence that the emitting triplet is not the photochemically active triplet comes from the relative quenching efficiencies of biacetyl and NO. Cehelnik *et al.*¹⁸ found NO to be 2.9 times more efficient than biacetyl in inhibiting CO_2 formation during the irradiation of SO_2 –CO mixtures. However, the $^3\text{SO}_2$ phosphorescence is quenched about twice as readily by biacetyl as by NO as measured from direct excitation of $^3\text{SO}_2$ ^{21, 22}. Thus there is a factor of 6 difference between the two sets of quenching data.

We feel that there is overwhelming evidence that the Wampler *et al.*¹⁷ mechanism is deficient and can be discarded. In this paper the studies of the SO₂-CO system, which were done at 3130 Å and room temperature in Part I of this series, have been extended to 3261 and 2537 Å and to 520 K at 3130 Å. Additional evidence for SO₂* and SO₂** is provided, and a complete reaction scheme is presented.

EXPERIMENTAL

The experimental apparatus and procedures were the same as used for the later runs in Part I of this series¹⁸, except for the modifications needed to change the temperature and wavelength. Complete details are given by Cehelnik²³.

For the studies at 2537 Å, a mercury-free vacuum line was used. A sulfuric acid manometer was used to measure pressures from 100 mTorr to 50 Torr, and a Wallace and Tiernan 0-800 Torr absolute pressure indicator was used to measure pressures from 50-800 Torr.

For the high temperature studies the quartz cell was placed in a cylindrical aluminium furnace block which was wrapped with nichrome wire and covered with asbestos. Quartz windows were placed on the ends of the furnace so light could enter and heat loss be kept to a minimum. The temperature was measured using an iron *versus* constantan thermocouple with a reference junction at 0°C. This was connected to a Leeds and Northrup potentiometer.

The absorption coefficients of the different gases used in the photolysis and actinometer runs were measured at the different wavelengths and temperatures which were used. In all cases the data followed the regular straight line Beer's law plot. The values obtained are given in Table 1.

TABLE 1

ABSORPTION COEFFICIENTS OF THE REACTANT GASES^a

λ (Å)	ϵ_{SO_2} (cm ⁻¹ Torr ⁻¹)	$\epsilon_{\text{CF}_4\text{I}}$ (cm ⁻¹ Torr ⁻¹)	$\epsilon_{\text{acetone}}$ (cm ⁻¹ Torr ⁻¹)	ϵ_{OCS} (cm ⁻¹ Torr ⁻¹)
3261 (300 K)	1.00×10^{-4}	6.06×10^{-5}	—	—
3130 (300 K)	2.67×10^{-3}	2.95×10^{-4}	—	—
2537 (300 K)	2.28×10^{-3}	6.50×10^{-3}	—	1.17×10^{-4}
3130 (415 K)	2.26×10^{-3}	—	1.54×10^{-4}	—
3130 (520 K)	1.85×10^{-3}	—	1.55×10^{-4}	—

^a Absorption coefficients are to base 10.

For the 3130 Å studies a Hanovia 200 W No. 654A36 medium pressure mercury lamp was used in conjunction with a Corning CS 0-54 filter to remove wavelengths shorter than 3130 Å. The filter passed 35% of the 3130 Å radiation.

The longer wavelengths which were transmitted were not appreciably absorbed by either SO_2 or any of the actinometry gases. This lamp was also used for the later runs reported by Cehelnik *et al.*¹⁸. (They report using a Hg U-tube lamp, type 30620, but this lamp was used only for the early runs.)

For the 3261 Å study, two Phillips cadmium resonance lamps Type 93107E15 were placed one at each end of the reaction cell. Corning CS 0-53 filters removed wavelengths shorter than 3261 Å but passed 80% of the 3261 Å line. Again the longer wavelengths had no effect as a result of low absorption.

For the 2537 Å study a Hanovia 924210 low pressure mercury lamp was used. A Corning CS 9-30 filter removed wavelengths shorter than 2200 Å but passed 83% of the 2537 Å line. In addition, a Cl_2 filter, made from a 5 cm long by 5 cm diameter quartz cell filled with 700 Torr of Cl_2 gas, was used to absorb all the lines between 2537 Å and the visible part of the spectrum.

$\text{CF}_3\text{I}-\text{O}_2$ mixtures were used for actinometry. The product of the photolysis in the reaction cell is CF_2O . This, however, is converted quantitatively on the gas chromatographic column to CO_2 . Heicklen²⁴ found that $\Phi\{\text{CO}_2\}$ for this reaction was unity at 3130 Å. This was checked against the well-known high-temperature acetone photolysis where $\Phi\{\text{CO}\}$ is known to be unity²⁵. Within 5%, $\Phi\{\text{CO}_2\}$ at 3130 Å was indeed unity. It was assumed that it would be unity at 3261 Å also.

At 2537 Å the $\text{CF}_3\text{I}-\text{O}_2$ actinometry was checked against the photolysis of OCS where $\Phi\{\text{CO}\}$ has been reported to be 1.8²⁶. It was found, however, that $\Phi\{\text{CO}_2\}$ was 0.5 instead of unity when checked against OCS. A value of $\Phi\{\text{CO}_2\}$ equal to 0.5 ± 0.05 was also found when checked against the photolysis of HBr at 2537 Å²⁷, where $\Phi\{\text{H}_2\}$ is known to be 1²⁸.

In reference to the CF_3I actinometry, in all cases $\Phi\{\text{CO}_2\}$ was found to be independent of pressure, intensity, and length of exposure. The only effect seems to be a wavelength effect on the primary process giving CO_2 as a final product. Once the quantum yield of this primary process is known, the $\text{CF}_3\text{I}-\text{O}_2$ system can be used as an actinometer.

All actinometry was performed at absorbances matched to the particular SO_2 pressure being used. This eliminated any corrections which would have to be made due to the uncertainty in the path length of the absorbing species.

RESULTS

In order to determine the effect of the wavelength on the SO_2-CO system, a series of experiments was carried out using 2537 and 3261 Å radiation. The SO_2 pressures were varied from 3.38 to 200 Torr. The CO pressures were varied from 10.5 to 767 Torr at 2537 Å, and from 98 to 461 Torr at 3261 Å. The results are shown in Figs. 1 and 2, respectively. The trends in the quantum yields of CO_2 production, $\Phi\{\text{CO}_2\}$, are similar to those at 3130 Å¹⁸. $\Phi\{\text{CO}_2\}$ is independent of the absorbed intensity, I_a , and the irradiation time. At high SO_2 pressures,

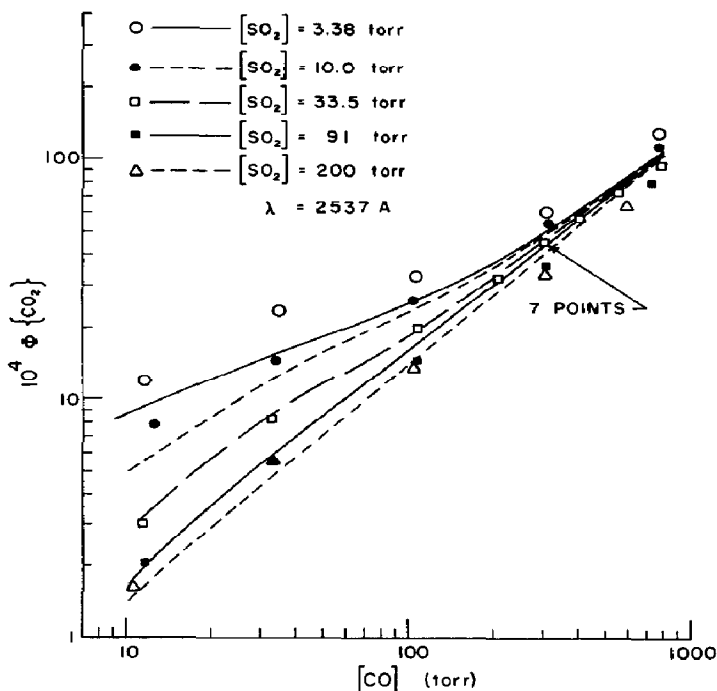


Fig. 1. Log-log plots of $\Phi\{\text{CO}_2\}$ vs. CO pressure in the photolysis of SO_2 in the presence of CO at 2537 Å and 300 K for various SO_2 pressures. The lines are computed from the mechanism and the rate constant ratios listed in Table 6.

$\Phi\{\text{CO}_2\}$ is directly proportional to the CO pressure and nearly independent of SO_2 pressure. At lower SO_2 pressures, $\Phi\{\text{CO}_2\}$ increases with decreasing SO_2 pressure for a given CO pressure. However, the quantitative results are somewhat different at the three wavelengths. This is shown for the data with 30–36 Torr of SO_2 in Fig. 3, where it can be seen that at high CO pressures, $\Phi\{\text{CO}_2\}$ is about a factor of two greater at 3261 Å than at 2537 Å, with the values at 3130 Å lying in between. At low CO pressures, $\Phi\{\text{CO}_2\}$ is essentially the same at all wavelengths.

Tables 2–4 show the results when N_2 , O_2 or NO is added to the SO_2 –CO system at the three wavelengths. NO is a known triplet quencher²⁹, and N_2 quenches $^1\text{SO}_2$ effectively⁸. Thus the addition of these two gases helps to sort out the states responsible for the chemistry. In a manner similar to the results obtained at 3130 Å, the addition of NO quenches part, but not all, of the reaction, thus showing both singlet and triplet contributions. The addition of N_2 removes part of the reaction at low CO pressures, but almost none at high CO pressures. Therefore $^1\text{SO}_2$ plays some role at low [CO], but is not important at high [CO].

At 3130 Å, experiments were done at 520 and 415 K in order to test for a temperature effect. Separate dark runs at these temperatures gave no CO_2 . Acetone photolysis was used as an actinometer for these runs ($\Phi\{\text{CO}\} = 1.00$). The results are given in Table 5. Runs were performed with 5–60 Torr of SO_2 and 60–405 Torr

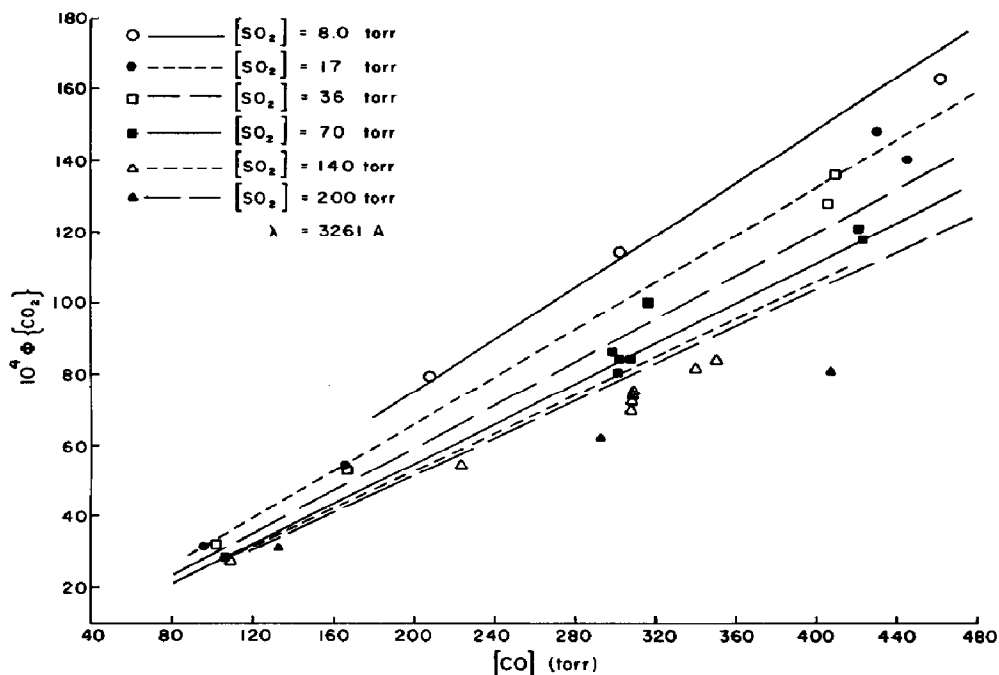


Fig. 2. Plots of $\Phi\{\text{CO}_2\}$ vs. CO pressure in the photolysis of SO_2 in the presence of CO at 3261 Å and 300 K for various SO_2 pressures. The lines are computed from the mechanism and the rate constant ratios listed in Table 6.

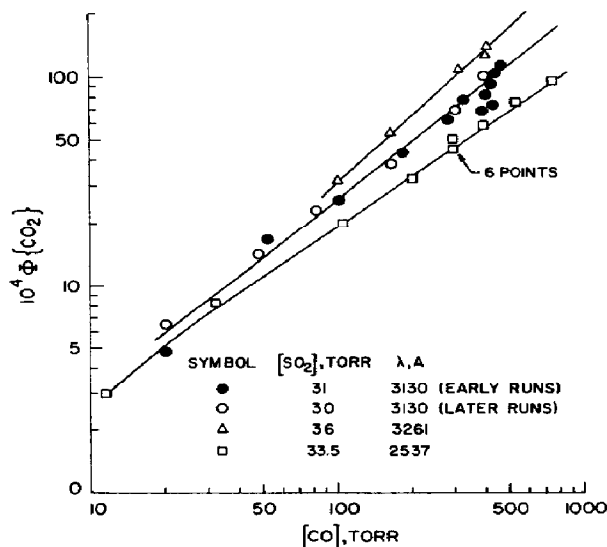


Fig. 3. Log-log plots of $\Phi\{\text{CO}_2\}$ vs. CO pressure in the photolysis of SO_2 in the presence of CO at 300 K and various wavelengths for $[\text{SO}_2] = 30\text{--}36$ Torr. The data for 3130 Å are from Cehelnik *et al.*¹⁸, those of the Early Runs are scaled up by a factor of 1.26.

of CO. When compared on a molar basis, there is no temperature effect, as can be seen from Fig. 4.

TABLE 2

PHOTOLYSIS OF SO₂ IN THE PRESENCE OF CO AND OTHER GASES AT 2537 Å AND 300 K

[CO] (Torr)	[X] (Torr)	<i>I_a</i> (mTorr/min)	Irradiation time (min)	10 ⁴ Φ{CO ₂ }	
				obs.	calc.
X = N ₂ , [SO ₂] = 3.38 Torr					
34.2	0.0	18.2	750	23.0	15.2
34	742	18.2	660	5.67	4.81
304	0.0	18.2	289	59.6	50.3
300	486	18.2	297	47.2	42.0
X = N ₂ , [SO ₂] = 33.5 Torr					
32.5	0.0	122	293	8.15	7.52
35	700	110	212	5.15	4.90
301	0.0	110	72	44.8	47.0
300	460	110	68	42.3	41.5
X = O ₂ , [SO ₂] = 33.5 Torr					
301	0.0	110	72	44.8	—
301	31	110	60	40.0	—
300	72	110	86	34.0	—
300	121	110	120	29.0	—
X = NO, [SO ₂] = 3.38 Torr					
34.2	0.0	18.2	750	23.0	15.2
36	6.35	18.2	760	7.9	9.4
304	0.0	18.2	289	59.6	50.3
300	8.1	18.2	742	13.4	14.7
X = NO, [SO ₂] = 10.0 Torr					
33.9	0.0	46.0	187	14.6	11.8
36.4	0.54	46.0	180	8.53	9.60
36.7	5.27	46.0	261	5.96	7.34
36.0	8.04	46.0	198	5.58	6.76
301	0.0	46.0	111	54.1	49.2
300	8.24	46.0	182	12.5	14.0
X = NO, [SO ₂] = 33.5 Torr					
32.5	0.0	110	293	8.15	7.52
36	0.84	110	257	4.60	5.13
36	8.38	110	679	2.94	3.70
300	0.0	110	120	45.0	46.8
300	0.19	110	60	32.6	34.1
300	0.99	110	159	19.0	20.1
300	3.31	110	159	12.9	14.1
302	8.31	110	180	10.2	11.9
X = NO, [SO ₂] = 91 Torr					
33.7	0.0	164	137	5.55	5.68
36.5	7.65	164	227	2.43	1.88
302	0.0	164	77	36.1	43.9
300	8.10	164	134	8.23	8.95
X = NO, [SO ₂] = 200 Torr					
303	0.0	188	55	33.6	41.3
300	7.97	188	129	8.72	6.35

TABLE 3

PHOTOLYSIS OF SO₂ IN THE PRESENCE OF CO AND OTHER GASES AT 3261 Å AND 300 K

[CO] (Torr)	[X] (Torr)	<i>I_a</i> (mTorr/min)	Irradiation time (min)	10 ⁴ Φ{CO ₂ }	
				obs.	calc.
X = N ₂ , [SO ₂] = 17 Torr					
316	0.0	3.06	503	100	104.8
307	493	2.16	523	98.7	101.8
X = N ₂ , [SO ₂] = 70 Torr					
105	0.0	10.85	840	28.6	29.1
108	604	8.10	301	30.5	30.0
302	0.0	8.10	165	84.5	83.8
302	423	8.10	160	84.8	83.8
X = N ₂ , [SO ₂] = 200 Torr					
133	0.0	23.8	120	31.2	34.6
140	401	21.1	440	31.2	36.5
294	0.0	23.8	95	62.2	76.6
298	390	21.1	139	61.5	77.6
X = O ₂ , [SO ₂] = 17 Torr					
316	0.0	3.06	503	100	—
305	28	2.20	251	70.7	—
304	40	2.20	660	68.2	—
304	73	2.20	347	63.4	—
X = O ₂ , [SO ₂] = 70 Torr					
301	0.0	7.95	141	80.5	—
302	25	7.95	103	65.4	—
302	38	7.95	125	60.9	—
304	71	7.95	347	51.5	—
X = NO, [SO ₂] = 17 Torr					
316	0.0	3.06	503	100	104.8
306	0.58	2.10	450	45.7	53.6
307	1.60	2.10	900	27.5	38.7
303	8.00	2.10	820	22.2	27.8
X = NO, [SO ₂] = 70 Torr					
307	0.0	7.89	240	84.4	85.2
307	0.22	7.89	180	55.4	55.4
306	0.55	7.89	195	42.4	38.0
305	1.05	7.89	310	31.0	27.3
306	2.25	7.89	780	18.8	18.6
302	5.00	7.89	675	13.8	13.2
304	10.0	7.89	421	11.4	10.9
X = NO, [SO ₂] = 140 Torr					
307	0.0	14.6	130	74.5	81.2
302	0.060	17.3	105	59.5	68.8
307	0.36	17.3	630	38.4	42.2
307	1.40	17.3	125	21.8	19.8
303	3.10	17.3	321	12.5	12.1
307	9.00	17.3	360	7.69	7.35
X = NO, [SO ₂] = 200 Torr					
294	0.0	23.8	95	62.2	76.6
300	10.0	23.8	1020	5.0	5.66

TABLE 4

PHOTOLYSIS OF SO₂ IN THE PRESENCE OF CO, NO, AND N₂ AT 3130 Å AND 300 K^a

[NO] (Torr)	[N ₂] (Torr)	Irradiation time (min)	10 ⁴ $\Phi\{\text{CO}_2\}$	
			obs.	calc.
[SO ₂] = 5.8 Torr, I _a = 35.0 mTorr/min				
0.0	737	255	14.6	13.2
8.2	0.0	196	15.7	12.9
8.0	760	623	6.53	6.2
[SO ₂] = 20.0 Torr, I _a = 124.5 mTorr/min				
0.0	751	135	9.46	10.5
7.90	0.0	217	6.16	6.3
8.05	748	540	4.19	3.4
[SO ₂] = 60.0 Torr, I _a = 173 mTorr/min				
0.0	704	132	9.07	8.7
8.10	0.0	210	4.97	2.4
8.20	724	665	2.78	1.6
[SO ₂] = 200 Torr, I _a = 223 mTorr/min				
0.0	0.0	127	9.19	7.9
0.0	578	126	8.67	7.8
9.45	0.0	270	3.61	0.8
9.25	589	645	2.55	0.7

^a [CO] = 41 Torr.

TABLE 5

EFFECT OF TEMPERATURE ON THE SO₂-CO SYSTEM AT 3130 Å

[SO ₂] (Torr)	[CO] (Torr)	I _a (mTorr/min)	Irradiation time (min)	10 ⁴ $\Phi\{\text{CO}_2\}$	10 ⁴ [SO ₂] (mol/l)	10 ⁴ [CO] (mol/l)	10 ⁶ I _a (Einstein/ l-min)
Temp. = 520 K							
5.72	62	38.2	240	16.6	1.77	19.2	1.18
5.65	156	38.2	142	38.5	1.75	48.4	1.18
5.50	404	38.2	60.0	82.1	1.72	125	1.18
17	62	106.5	180	15.8	5.27	19.2	3.30
17	156	106.5	95.0	27.8	5.27	48.4	3.30
17	405	106.5	72.0	62.1	5.27	126	3.30
60	64	141	119	12.3	18.6	19.8	4.37
60	158	141	60.0	24.3	18.6	49.0	4.37
60	405	141	45.0	52.1	18.6	125	4.37
Temp. = 415 K							
5.10	61	23.8	186	34.7	1.98	23.6	0.925
5.18	155	23.8	185	57.5	2.02	60.3	0.925
5.08	405	23.8	110	121	1.97	157	0.925
15	57	68.7	225.0	22.8	5.83	22.1	2.67
15	153	68.7	100.0	41.2	5.83	59.5	2.67
15	404	68.7	90.0	84.6	5.83	157	2.67
45	59	132	100	15.4	17.5	22.9	5.13
45	152	132	95.0	33.3	17.5	59.0	5.13
45	402	132	53.0	67.0	17.5	156	5.13

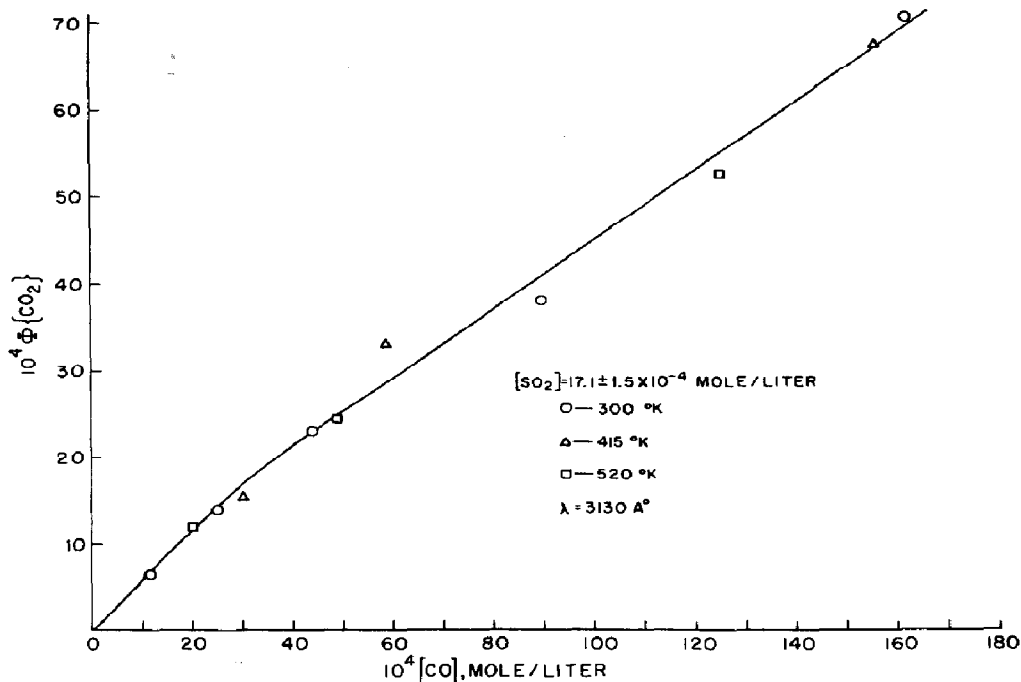


Fig. 4. Plot of $\Phi\{\text{CO}_2\}$ vs. CO concentration in the photolysis of SO_2 in the presence of CO at 3130 \AA and various temperatures for $[\text{SO}_2] = (17.1 \pm 1.5) \times 10^{-4} \text{ M}$. The data at 300 K are from the Later Runs of Cehelnik *et al.*¹⁸.

DISCUSSION

There are two new pieces of evidence in this work which demonstrate that the chemically active triplet state is not the emitting triplet state. The first is the lack of a temperature effect on $\Phi\{\text{CO}_2\}$, even though the NO quenching experiments show that most of the reaction comes from a triplet state. When the emitting triplet state is excited directly at 3829 \AA , CO_2 is produced with an activation energy of 4.0 kcal/mol ³⁰. Thus the chemically active triplet state in the present study must be a different state.

The second piece of evidence comes from the NO quenching experiments. With about 8 Torr of NO, the triplet states are efficiently removed. Thus the remaining CO_2 must come from singlet states. If this amount is subtracted from the total CO_2 yield at lower NO pressures, the triplet yield, $\Phi_{\text{T}}\{\text{CO}_2\}$, is obtained. Furthermore, any mechanism will predict a linear Stern-Volmer quenching mechanism of the form:

$$(\Phi_{\text{T}}\{\text{CO}_2\})^{-1} [\text{CO}] = a + b[\text{NO}] \quad (\text{I})$$

where a and b are constants for a given SO_2 and CO pressure. The Stern-Volmer

plots at both 2537 Å and 3261 Å are shown in Figs. 5 and 6, respectively. Also shown are the corresponding plots with O₂ as the quenching gas. All four plots can be fitted with good straight lines. The intercept a is directly proportional to the quenching of triplet SO₂ in the absence of NO. For the emitting triplet, ³SO₂, a should increase linearly with [SO₂]. The data in Fig. 6 show no such effect for either NO or O₂. Consequently the triplet state must be removed mainly by first-order processes, and it cannot be ³SO₂. The relative quenching constants for the chemically active triplet state, SO₂** , for NO and O₂ are given by the ratio of the slopes of the respective curves. For NO these values are 463 and 250 respectively at 2537 and 3261 Å. These values can be compared with that of 426 at 3130 Å¹⁸. The two values at 2537 and 3130 Å are in good agreement. The reason for the low value at 3261 Å is not clear.

More definitive evidence on the existence of SO₂* is given by the experiments (Table 4) in the presence of NO to remove the triplet states. When excess N₂ is

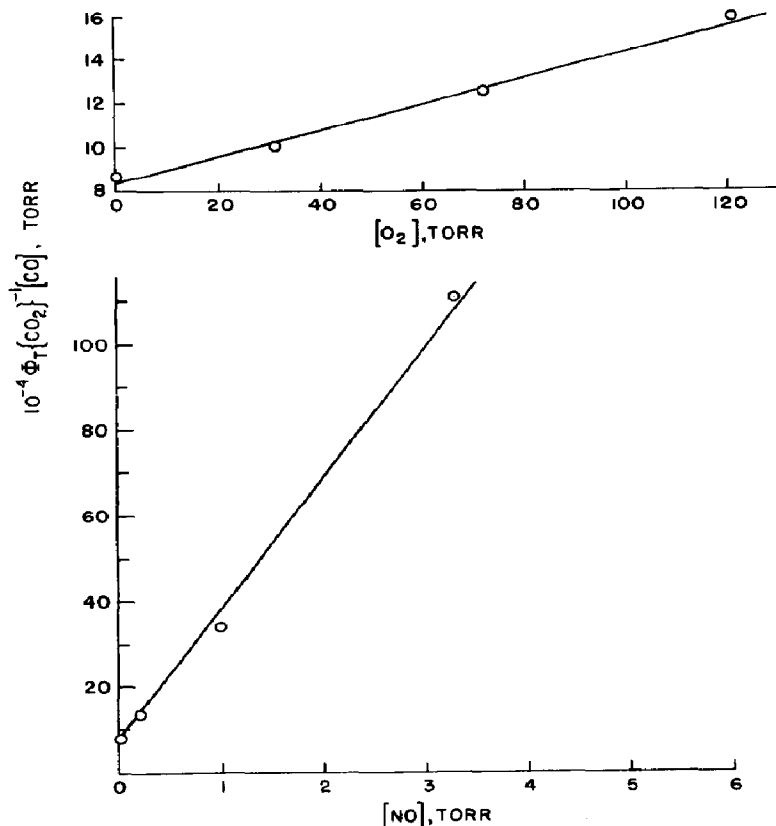


Fig. 5. Plots of $\Phi_T\{\text{CO}_2\}^{-1} [\text{CO}]$ vs. $[\text{M}]$ for $\text{M} = \text{NO}$ or O_2 in the $\text{SO}_2\text{-CO-M}$ system at 2537 Å and 300 K for an SO_2 pressure of 33.5 Torr. $\Phi_T\{\text{CO}_2\}$ is the quantum yield of CO_2 arising from triplet states of SO_2 .

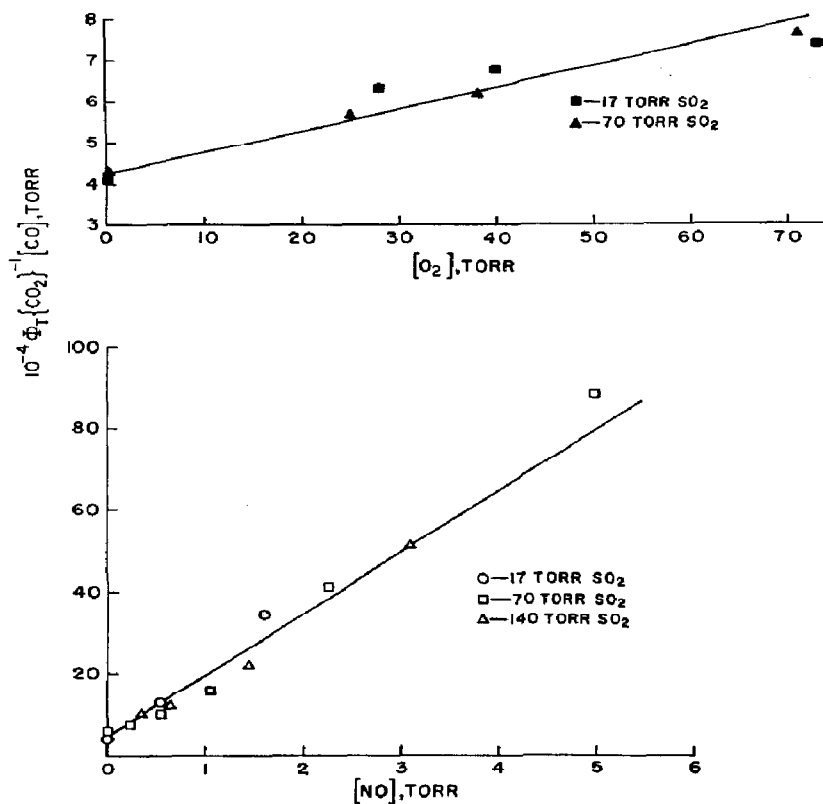
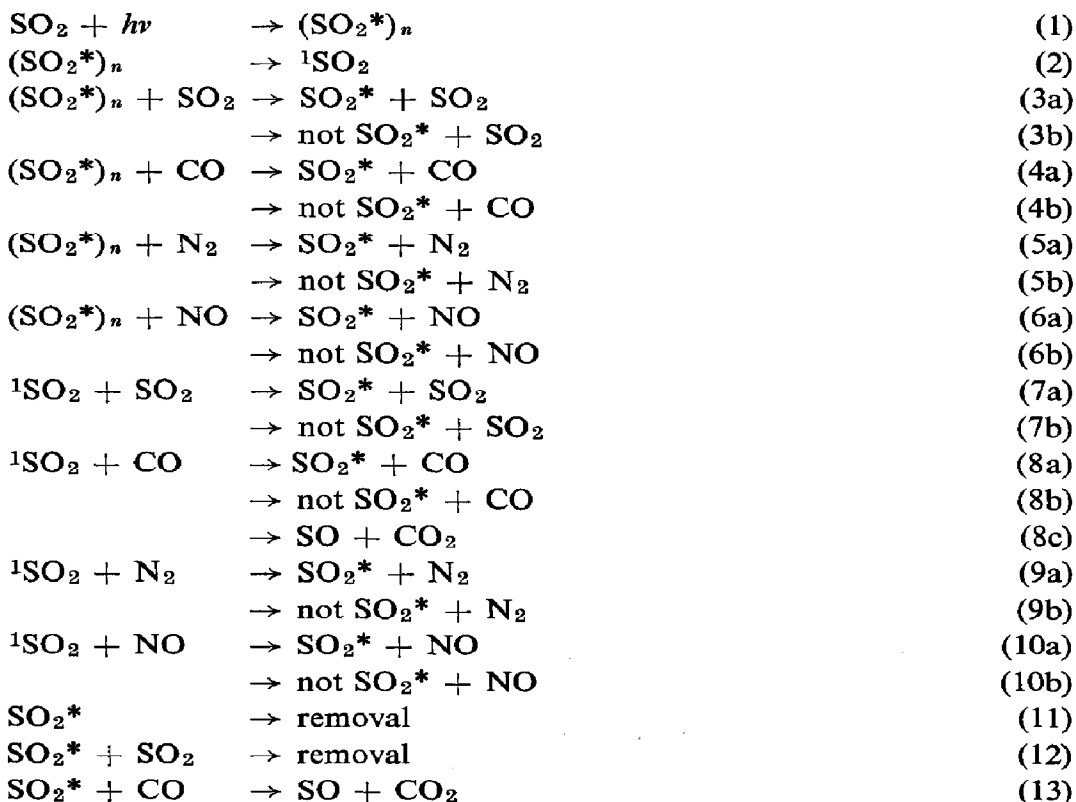


Fig. 6. Plots of $\Phi_T\{\text{CO}_2\}^{-1} [\text{CO}]$ vs. $[\text{M}]$ for $\text{M} = \text{NO}$ or O_2 in the $\text{SO}_2\text{-CO-M}$ system at 3261 Å and 300 K for various SO_2 pressures. $\Phi_T\{\text{CO}_2\}$ is the quantum yield of CO_2 arising from triplet states of SO_2 .

also added to quench the emitting singlet state, $^1\text{SO}_2$, $\Phi\{\text{CO}_2\}$ does not drop to zero, thus indicating that some other singlet state, not quenched by N_2 , enters into chemical reaction with CO . Similar results have been obtained by Wampler *et al.* with benzene replacing NO as the triplet quencher¹⁷.

The mechanism developed by Cehelnik *et al.*¹⁸ incorporated the then prevailing idea that the emitting singlet $^1\text{SO}_2$ was the state produced by absorption of the radiation. However, the results of Stockburger *et al.*²⁰ have since shown that $^1\text{SO}_2$ cannot be the state produced by absorption of the radiation, and the mechanism must be modified. To conform to those results, we now propose that the absorption of radiation produces vibrationally excited levels of SO_2^* , that this state can pass by first-order processes to $^1\text{SO}_2$ or be collisionally deactivated to low vibrational levels of SO_2^* , which presumably are below the energy of $^1\text{SO}_2$ and thus can no longer pass to that state. Both $^1\text{SO}_2$ and the low vibrational levels of SO_2^* can react with CO to produce CO_2 . The reaction steps needed to explain the reactions involving singlet states are



where $(\text{SO}_2^*)_n$ represents upper vibrational levels of SO_2^* and SO_2^* without a subscript represents low vibrational levels of SO_2^* . These low vibrational levels are removed by first order processes, by collision with SO_2 , or reaction with CO. The data require that SO_2^* not be removed to any significant extent by collision with N_2 , CO, or NO. First-order removal steps for ${}^1\text{SO}_2$ have been omitted since they are negligible under our conditions^{7, 10}.

The above mechanism leads to the predicted quantum yield expressions:

$$\Phi^1\{\text{CO}_2\} = \frac{k_2 k_{8c} [\text{CO}]/(k_7[\text{SO}_2] + k_8[\text{CO}] + k_9[\text{N}_2] + k_{10}[\text{NO}])}{(k_2 + k_3[\text{SO}_2] + k_4[\text{CO}] + k_5[\text{N}_2] + k_6[\text{NO}])} \quad (\text{II})$$

$$\Phi^*\{\text{CO}_2\} = \alpha k_{13} [\text{CO}]/(k_{11} + k_{12} [\text{SO}_2]) \quad (\text{III})$$

where $\Phi^1\{\text{CO}_2\}$ and $\Phi^*\{\text{CO}_2\}$ are the quantum yield contributions from ${}^1\text{SO}_2$ and SO_2^* , respectively. The quantity α is the fraction of the time that SO_2^* is produced; in general it could be a complex function of the various gas pressures. In the denominator of eqn. (III), the term $k_{13} [\text{CO}]$ has been omitted to reflect the experimental fact that it is negligible compared to the other two terms.

A great amount of information is known about the rate constant ratios needed to evaluate eqn. (II). The ratios k_8/k_7 , k_9/k_7 , and k_{10}/k_7 are known to be 0.35, 0.29, and 0.59, respectively, from fluorescence quenching measurements^{8,20}. At 3130 Å, the data of Stockburger *et al.*²⁰ show that 30 Torr of either CO or N₂ has an effect equal to 2 Torr of SO₂ in quenching (SO₂^{*})_n. If we make the reasonable assumption that SO₂ is about 3 times as efficient as either CO or N₂ in quenching (SO₂^{*})_n, then $k_3/k_2 = 0.12 \text{ Torr}^{-1}$, and $k_4/k_2 = k_5/k_2 = 0.04 \text{ Torr}^{-1}$. NO probably has a similar efficiency, and we assume this to be so, though the data are very insensitive to [NO], since no more than 16 Torr was ever used. Consequently there is only one parameter to be evaluated to determine $\Phi^1\{\text{CO}_2\}$. This is k_{8e}/k_7 , which can be dependent on the incident wavelength of the radiation.

At 2537 Å, the vibrational energy in (SO₂^{*})_n must be much higher than at 3130 Å. Consequently deactivation will be slower, and ¹SO₂ will be produced more readily. In fact, with 2537 Å radiation, there is probably so much vibrational energy that deactivation never occurs at our pressures. The data are well fitted by assuming that ¹SO₂ is produced all the time, *i.e.*, k_3 , k_4 , k_5 , and k_6 are unimportant. On the other hand, at 3261 Å the reverse is true and ¹SO₂ is probably never produced to any significant extent at our pressures. Again, the data can be fitted with this assumption.

The expression for $\Phi^*\{\text{CO}_2\}$ depends on two parameters, $\alpha k_{13}/k_{11}$ and k_{12}/k_{13} . The ratio k_{12}/k_{13} must be the same at all incident wavelengths, since low vibrational levels of SO₂^{*} are involved in reactions (12) and (13). However, α is a wavelength-dependent function. The data are best fitted by setting $\alpha = 0$ at 2537 Å. At this wavelength ¹SO₂ is produced all the time, so presumably quenching of ¹SO₂ does not give SO₂^{*}. On the other hand, low vibrational levels of SO₂^{*} are probably produced all the time at 3261 Å, so that $\alpha = 1$. The same value of $\alpha k_{13}/k_{11}$ fits the data at both 3130 Å and 3261 Å. Presumably only a small amount of ¹SO₂ is produced at 3130 Å, and SO₂^{*} is produced almost all the time.

Our conclusion concerning the likelihood of formation of ¹SO₂ or SO₂^{*} is supported by direct spectroscopic observations. Wampler *et al.*³¹ have excited SO₂ at 2662 Å, and have found that the fraction of the time that ³SO₂ is formed depends on the ratio of gas pressures, a result to be expected if ¹SO₂ is the precursor state. On the other hand, Stockburger *et al.*²⁰ found that with 3130 Å radiation the fraction of triplet formed was independent of the ratio of gas pressures, a result inconsistent with ¹SO₂ being the precursor state.

Let us now turn our attention to the role of triplet SO₂ in producing CO₂. The data require that ³SO₂ does not provide an important contribution (*i.e.*, < 10%). This is not to say that ³SO₂ does not react with CO to give CO₂: the experiments of Jackson and Calvert³⁰ have shown that ³SO₂ reacts readily with CO to produce CO₂ and these results have been confirmed in our laboratory¹⁹. The fact that ³SO₂ is not important in our system means that it is produced only to an insignificant extent by absorption into the band at 2400–3400 Å.

Essentially all of the CO₂ produced from triplet SO₂ comes from SO₂***. The reactions of this latter state are:



Then the contribution to $\Phi\{\text{CO}_2\}$ from this state, $\Phi^{***}\{\text{CO}_2\}$, is

$$\Phi^{***}\{\text{CO}_2\} = \beta k_{15} [\text{CO}] / (k_{14} + k_{16} [\text{NO}]) \quad (\text{IV})$$

where the contribution of $k_{15} [\text{CO}]$ to the denominator of eqn. (IV) has been neglected since it is always small. The ratio k_{16}/k_{14} is 2.9 Torr⁻¹, independent of exciting wavelength, but β , which is the fraction of the time SO₂** is produced, can depend on both the incident wavelength and the gas pressures. Our data are best fitted by assuming a slight wavelength dependence, but no pressure dependence. At this time it is not clear why this form of β should prevail.

The total quantum yield, $\Phi\{\text{CO}_2\}$, is just the sum of the three contributions from ¹SO₂, SO₂*, and SO₂***. Only one parameter is needed to fit $\Phi^1\{\text{CO}_2\}$, two parameters to fit $\Phi^*\{\text{CO}_2\}$, and two parameters to fit $\Phi^{***}\{\text{CO}_2\}$. These parameters which best fit the data are listed in Table 6.

TABLE 6

RATE CONSTANT RATIOS AT 300 K

Ratio	Units	Value at			Source
		3261 Å	3130 Å	2537 Å	
10 ⁴ k _{8e} /k ₇	None	—	15	5.0	This work
10 ⁴ αk ₁₃ /k ₁₁	Torr ⁻¹	0.22	0.22	0	This work
k ₁₂ /k ₁₁	Torr ⁻¹	0.1	0.1	0.1	This work
10 ⁴ βk ₁₅ /k ₁₄	Torr ⁻¹	0.25	0.18	0.12	This work
k ₁₆ /k ₁₄	Torr ⁻¹	2.9	2.9	2.9	Cehelnik <i>et al.</i> ¹⁸ and this work
k ₈ /k ₇	None	0.35	0.35	0.35	Stockburger <i>et al.</i> ²⁰
k ₉ /k ₇	None	0.29	0.29	0.29	See text
k ₁₀ /k ₇	None	0.59	0.59	0.59	See text
k ₉ /k ₂	Torr ⁻¹	∞	0.12	0	See text
k ₄ /k ₂	Torr ⁻¹	∞	0.04	0	See text
k ₅ /k ₂	Torr ⁻¹	∞	0.04	0	See text
k ₆ /k ₂	Torr ⁻¹	∞	0.04	0	See text

The fit of the data at 2537 and 3261 Å in the absence of N₂ or NO is shown in Figs. 1 and 2, respectively. The computed values using the rate constants listed in Table 6 are shown as lines in the Figures. For both sets of data, the fit is reasonably good. The only discrepancies are at low SO₂ and CO pressures at 2537 Å, and high SO₂ and CO pressures at 3261 Å. These discrepancies, which are less than 50% for the few points involved, may be due to the assumption that β is

pressure-independent. Possibly there is a small pressure dependence on β to give more SO_2^{**} at low pressures at 2537 Å and less SO_2^{**} at high pressures at 3261 Å. In any event the discrepancy is not large, and must reflect the oversimplification of the proposed mechanism.

In the presence of N_2 or NO , the values for $\Phi\{\text{CO}_2\}$ computed with the rate constant ratios listed in Table 6 are listed next to the observed values in Tables 2–4. At both 2537 and 3261 Å the agreement is excellent. At 3130 Å (Table 4), agreement is good at low SO_2 pressures, but at high SO_2 pressures in the presence of NO , the calculated values are too low. The experimental values cannot be attributed to an excess contribution from $^1\text{SO}_2$, since with a large excess of N_2 to quench $^1\text{SO}_2$, the discrepancy still exists. At 3130 Å and high SO_2 pressures, there must be an extra source of SO_2^* (or some other singlet state not quenched by N_2). Possibly the fraction α increases at 3130 Å at high SO_2 pressures. Why this should occur at 3130 but not at 3261 Å is not clear.

TABLE 7

PHOTOLYSIS OF SO_2 IN THE PRESENCE OF CO AND OTHER GASES AT 3130 Å AND 300 K
(LATER RUNS)^{a,b}

[CO] (Torr)	[X] (Torr)	Irradiation time (min)	$10^4 \Phi\{\text{CO}_2\}$ obs.	calc.
X = N_2				
42	0.0	153.0	36.3	28.0
46	108	256.0	17.5	18.5
44	407	250.0	15.6	16.2
302	0.0	130.0	101	112.4
302	86	295.0	107	111.3
303	461	264.0	105	110.2
299	493	248.0	116	108.7
X = NO				
42	0.0	153.0	36.3	28.0
49	6.0	540.0	18.7	18.7
81	0.0	155.0	39.8	38.2
87	7.0	368.0	26.4	23.7
81	16.0	385.0	~35	21.0
164	0.0	410.0	56.3	64.6
170	7.0	240.0	46.5	37.0
184	7.0	240.0	42.4	39.4
281	0.0	120.0	96	105.0
314	7.0	235.0	57.8	62.6
312	8.0	428.0	~42	61.9
311	13.0	422.0	59.2	60.8
400	0.0	70.0	150	147.1
391	7.0	155.0	92	76.8

^a $[\text{SO}_2] = 2.1$ Torr, $I_a = 7.8 \pm 0.3 \mu\text{m}/\text{min}$.

^b From Cehelnik *et al.*¹⁸.

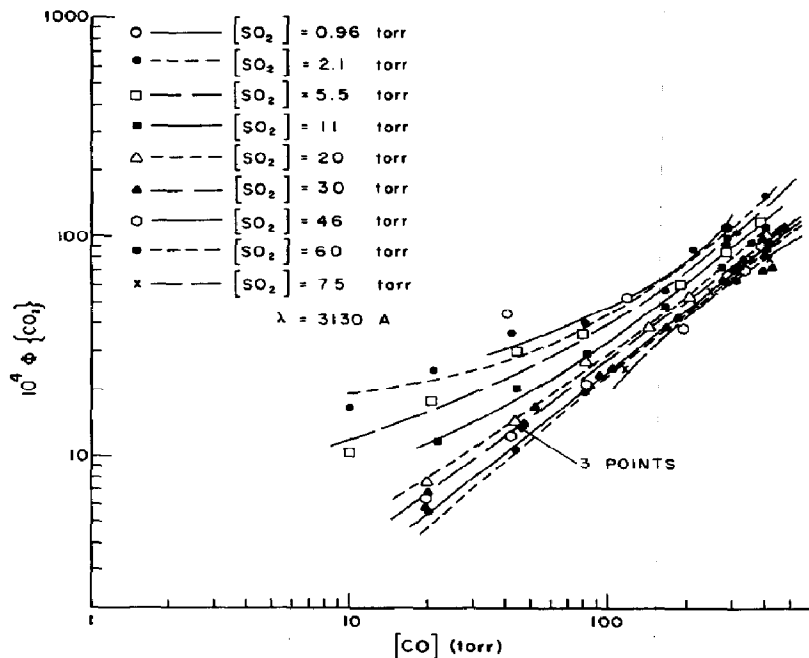


Fig. 7. Log-log plots of $\Phi\{\text{CO}_2\}$ vs. CO pressure in the photolysis of SO₂ in the presence of CO at 3130 Å and 300 K for various SO₂ pressures. The data are from Cehelnik *et al.*¹⁸, those of the Early Runs are scaled up by a factor of 1.26. The lines are computed from the mechanism and the rate constant ratios listed in Table 6.

It was also of interest to see if the data of Cehelnik *et al.*¹⁸ at 3130 Å could be fitted by the mechanism. There was a slight constant discrepancy between the Later Runs and the Early Runs of Cehelnik *et al.* Most of the Early Runs (which are less reliable in absolute magnitude owing to insufficient purification of the CF₃I used as an actinometer) can be fitted to the Later Runs with multiplication by a scale factor of 1.26. This has been done and plots of the data in the absence of NO or N₂ are shown in Fig. 7. The values computed with the rate constant ratios listed in Table 6 are given by the lines in Fig. 7, and they excellently reproduce the data. The results at higher temperatures can, of course, be fitted by the same parameters, since there is no temperature effect. For the Later Runs of Cehelnik *et al.*¹⁸ with NO or N₂ added, the observed and calculated values are listed in Table 7, and the fit is good.

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