SO_2, since the density of its vibrational states is very low, and spin inversion is required for this process as well. Perhaps the apparent intramolecular energy dissipation results as the net effect of a unimolecular rearrangement of the triplet to some thermally unstable, high-energy, isomeric form of sulfur dioxide which reverts nonradiatively to ground-state SO_2 for our conditions. An isomer of sulfur dioxide has been postulated before by Norrish and Oldershaw[24] to explain the disappearance of the sulfur dioxide absorption spectrum immediately following a high-intensity flash of light. They concluded that the isomerization was a thermal reaction induced by the high temperature created in the adiabatic high-energy flash, since added inert gas depressed the temperature rise and eliminated the effect. A third alternative for the mechanism of reaction 7 is the involvement of the unknown $^3A_2$ state of SO_2. This state corresponds to the $^1A_2$ state of SO_2 to which optical transitions from the ground state are somewhat forbidden.[25] If this triplet state lies below the $^3B_1$ state, then conceivably a large fraction of the $^3B_1$ molecules might cross to the $^3A_2$ state and be vibrationally relaxed and trapped in it. Emission from this state would be of very long lifetime and hence very weak, since the transition would be very disallowed.

Further speculation on the mechanism of the unexpected unimolecular nonradiative decay process in isolated $^3SO_2$ molecules must await additional experimental and theoretical studies of the SO_2 system.

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(24) R. G. W. Norrish, and G. A. Oldershaw, *Proc. Roy. Soc., Ser. A*, **249**, 498 (1959).

(25) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

The Triplet Sulfur Dioxide–Carbon Monoxide Reaction Excited within the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ "Forbidden" Band

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Abstract: The physical and chemical quenching reactions of the triplet sulfur dioxide molecule ($^3SO_2$) with carbon monoxide were studied by the direct excitation of $^3SO_2$ through absorption of light within the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band. The lifetimes of $^3SO_2$ were determined in SO_2–CO mixtures using pulsed 3828.8-Å laser excitation. The results are consistent with a competitive $^3SO_2$ quenching mechanism involving CO and SO_2 molecules: $^3SO_2 + SO_2 \rightarrow SO + SO_3$ (8a) $\rightarrow 2SO_2$ (8b), $^3SO_2 + CO \rightarrow SO + CO_2$ (9a) $\rightarrow SO_2 + CO$ (9b). The data give $k_{8a} + k_{8b} = (3.8 \pm 0.3) \times 10^8$ and $k_{9a} + k_{9b} = (8.4 \pm 0.6) \times 10^7$ l./(mol sec) at 25°. In another series of experiments, the excited $^3SO_2$ molecules were formed in a continuous beam of 3530–3970-Å illumination, and the Φ_{CO_2} values were estimated in runs at 30, 84, and 118° and at varied $[SO_2]/[CO]$ ratios. The data fit, within the experimental error, the theoretical rate law $1/\Phi_{CO_2} = (k_{9a} + k_{9b})/k_{9a} + [(k_{8a} + k_{8b})/k_{9a}]([SO_2]/[CO])$. From these data the rate functions of k_{9a} and k_{9b} were evaluated: $k_{9a} = (5.1 \pm 3.2) \times 10^9 e^{-(4.0 \pm 0.7)/RT}$ and $k_{9b} = (5.4 \pm 1.2) \times 10^8 e^{-(1.1 \pm 0.2)/RT}$ l./(mol sec).

Recent studies of sulfur dioxide photochemistry within the first allowed absorption band (3200–2400 Å) have shown that the dominant chemically reactive species is a triplet electronic state of sulfur dioxide ($^3SO_2$). This state is populated by intersystem crossing from the initially formed excited-singlet molecules ($^1SO_2$). Thus, Okuda, *et al.*,[1] found that the suppression of SO_3 formation in SO_2 photolyses on addition of small quantities of biacetyl was consistent with the product formation from reactions involving $^3SO_2$ molecules alone. Timmons[2] studied the photochemistry of sulfur dioxide–hydrocarbon mixtures at 3130 Å. He found that the quantum yield of chemical product formation in excited sulfur dioxide-isobutane mixtures was decreased only slightly by the addition of methane. Since methane quenches $^1SO_2$ molecules effectively and yet excited SO_2 reacts chemically with it only with a very low efficiency, he concluded that the $^3SO_2$ species was the reactive form of SO_2 in the irradiated SO_2–RH mixtures. Very recently, Cehelnik, Spicer, and Heicklen[3] have reported that some common triplet quenchers (biacetyl, nitric oxide, and oxygen) inhibit the chemical reactions of excited SO_2 with carbon monoxide and with perfluoroethylene. They concluded that two triplet states of SO_2 were the major reactive species for these systems. However,

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(1) S. Okuda, T. N. Rao, D. H. Slater, and J. G. Calvert, *J. Phys. Chem.*, **73**, 4412 (1969).

(2) R. B. Timmons, *Photochem. Photobiol.*, **12**, 219 (1970).

(3) E. Cehelnik, C. W. Spicer, and J. Heicklen, private communication to the authors; presented at the 9th Informal Photochemistry Conference, The Ohio State University, Columbus, Ohio, Sept 1970.

in the SO_2–CO system, as much as 13% of the product CO_2 may have come from singlet sulfur dioxide.

Thus in all of the excited SO_2–reactant systems studied to date (SO_2, RH, CO, C_2F_4), there is significant evidence that the major fraction of the chemical change, if not all of it, involves triplet-excited SO_2 molecules. The photochemical studies of SO_2 by our research group and those of others indicate the formidable problems involved in attempting a quantitative treatment of the product rate data from SO_2 mixtures in which singlet SO_2 is formed initially. In these systems triplet formation comes from a bimolecular reaction which may involve either SO_2 or added reactant gas M.

$$\mathrm{SO_2} + h\nu\ (3200\text{–}2400\ \text{Å}) \longrightarrow {}^1\mathrm{SO_2} \tag{I}$$

$${}^1\mathrm{SO_2} + \mathrm{M} \longrightarrow \mathrm{SO_2} + \mathrm{M}\ \text{(or chemical products)} \tag{1}$$

$$\longrightarrow {}^3\mathrm{SO_2} + \mathrm{M} \tag{2}$$

The fraction of singlet-quenching collisions which result in spin inversion, reaction 2, has been estimated to be near 0.1 for the case of $M = SO_2$; $k_2/(k_1 + k_2) = 0.08 \pm 0.01$ (2875 Å),[4] 0.09 (2963 Å),[5] 0.10 (3020 Å).[5] It is not now known what this efficiency is for collision partners other than SO_2. As a consequence, there must be an uncertainty in the rate of triplet generation which prevents a quantitative description of the mechanism of product formation in most systems. The added uncertainty of possible significant rates of product formation from excited-singlet species in one of the parallel paths of reaction 1 complicates all studies of these systems. In view of the difficulties, we have attempted to generate sulfur dioxide triplets directly by excitation of SO_2 within the forbidden $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band.

We have chosen to study the analytically simple reaction of photochemical oxidation of carbon monoxide by triplet SO_2.

$${}^3\mathrm{SO_2} + \mathrm{CO} \longrightarrow \mathrm{SO} + \mathrm{CO_2}$$

This reaction appears to have been first observed only recently by Timmons[2] in experiments at 3130 Å. Cehelnik, *et al.*,[3] have recently studied this system more extensively at the same wavelength. The results of the two studies are very different, and neither is quantitatively consistent with a mechanism description based on the previously proposed reaction scheme for SO_2 photochemistry.[1,4] Timmons found that Φ_{CO_2} from these mixtures showed little variation with altered CO pressure (21–420 Torr) and temperature (25–100°). In contrast, Cehelnik, *et al.*,[3] found that Φ_{CO_2} increased markedly with increasing CO pressure (20–475 Torr), but it was independent of the pressure of SO_2 above 60 Torr. Extrapolation of the previously proposed mechanisms suggests that the product formation (SO_3 and CO_2) should occur largely in the competitive quenching reactions of $^3SO_2$ with SO_2 and CO. If this is the case, the rate of CO_2 formation must be a function of both SO_2 and CO pressures within the pressure range employed by the previous workers.[6] Recognizing this problem, Cehelnik, *et al.*, have proposed that much of the chemistry of irradiated SO_2–CO mixtures involves new nonemitting states of SO_2. The evidence for this postulate is not great, and further definitive work is necessary to elucidate the mechanism of these systems.

In this work, we have succeeded for the first time in generating sufficient $^3SO_2$ species by direct absorption to measure directly the quantum yields of its reaction with CO; we have accomplished this using a high intensity of continuous radiation in the 3530–3970-Å region of the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band. The results are described quantitatively in terms of a simple mechanism which allows evaluation of the rate constants for the reactions

$${}^3\mathrm{SO_2} + \mathrm{CO} \longrightarrow \mathrm{SO} + \mathrm{CO_2}$$

$$\longrightarrow \mathrm{SO_2} + \mathrm{CO}$$

Experimental Section

The Apparatus for Lifetime Measurements. The rate constants for $^3SO_2$ quenching by CO were determined from phosphorescence lifetime measurements employing a 3828.8-Å, 50-kW laser pulse of about 20-nsec duration. This was generated from the output of a 75-MW ruby laser (6943 Å) by Raman shifting (1344 cm^{-1}) using nitrobenzene, followed by frequency doubling. The $^3SO_2$ emission was monitored by a spectrally filtered phototube whose output was traced on an oscilloscope and photographed. A brief description of this equipment has been given,[7] and the details of the equipment and experimental procedures employed are given in a previous publication.[8]

The Apparatus for Φ_{CO_2} Determinations. The photolyses were carried out in a cylindrical Pyrex cell (diameter 5.5 cm, length 60 cm) which was connected in series with an all-glass, magnetically operated circulating pump and was mounted in a thermostatically controlled oven. Pressures were measured using a quartz spiral manometer system. The light sources used were high-pressure xenon arcs (PEK Type X-500 and Osram XBO 450). The light was filtered by passing it through several solution and glass filters in combination: (1) a 10-cm path of solution containing copper sulfate (5.0 g/100 ml of H_2O); (2) a 1-cm path of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate (0.01 g/100 ml of H_2O); (3) a Jena WG 1 1-mm glass plate; (4) a Corning 7-51 (5970), 5-mm glass plate; (5) the Pyrex front window of the photolysis cell. The arc emission and the transmission of the combined filters provided a beam of relatively high intensity ($I_0 = 0.8 \times 10^{16}$–2.0×10^{16} quanta/sec incident at the cell face) and with the energy distribution shown in Figure 1 (the dotted curve). A few experiments were made to test that the filter–arc combination did not excite the SO_2 within the singlet-absorption region which has its onset near 29,400 cm^{-1}. In these experiments, a Jena WG 1 1-mm glass plate and a Corning 0-53 (7740) Pyrex glass plate were added in addition to the filters normally employed. These provided a sharper cutoff of the high-energy end of the envelope of the transmitted light (~27,900 cm^{-1}). There was no detectable difference in the values of Φ_{CO_2} determined using the two different filter combinations, and it was clear that no excitation of SO_2 occurred within the intense singlet band using either of the filter systems.

The extinction coefficient, ϵ [l./(mol cm)] = $\log (I_0/I)/cl$, was determined as a function of $1/\lambda$ by Dr. Charles Badcock of these laboratories using data from a low-resolution Bausch and Lomb 505 spectrophotometer and a 5-cm path of SO_2. It can be seen from these data, summarized in Figure 1, that the beam of light passed by the filter has considerable overlap with the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band.

Estimation of Incident and Absorbed Light Intensities. At the start and finish of each run, a quantitative determination of the incident light intensity was made employing potassium ferrioxalate actinometry.[9] Although the runs were often of 24-hr duration, the incident intensity varied no more than ±5% within each run. The fraction of the incident light absorbed by SO_2 was very low in all

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(4) T. N. Rao, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **91**, 1609 (1969).

(5) T. N. Rao and J. G. Calvert, *J. Phys. Chem.*, **74**, 681 (1970).

(6) This can be shown for the conditions employed by Timmons[2] and Cehelnik, *et al.*,[3] using the ratio of the rate constants for $^3SO_2$ quenching by SO_2[7] to that for CO measured in this work; the ratio of constants equals 4.5 at 25°.

(7) S. S. Collier, A. Morikawa, D. H. Slater, J. G. Calvert, G. Reinhardt, and E. Damon, *J. Amer. Chem. Soc.*, **92**, 217 (1970).

(8) H. W. Sidebottom, C. C. Babcock, J. G. Calvert, G. W. Reinhardt, B. R. Rabe, and E. K. Damon, *ibid.*, **93**, 2587 (1971).

(9) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

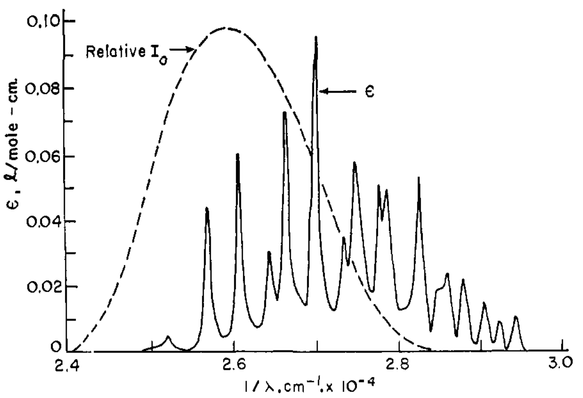

Figure 1. The extinction coefficient, ϵ [l./(mol cm)] = [log (I_0/I)]/cl, for SO_2(g) at 25°; the data were determined by Dr. Charles Badcock using a low-resolution spectrophotometer (solid curve); also shown in the dotted curve is the relative incident intensity of the light from the xenon arc–filter combination used in the quantum yield determinations.

experiments. It varied from 0.0072 to 0.018 for the concentrations of SO_2 employed here. The minor fluctuations in the lamp intensity were sufficient to prevent the direct determination of this fraction in experiments at the pressures of SO_2 employed in the photochemical runs, so an effective average extinction coefficient, $\bar{\epsilon}$, was evaluated for the particular light energy distribution used in these experiments. This was calculated from the I_0 and ϵ functions of Figure 1 by determining the ratio of the integrals $\int_0^\infty I_0\epsilon \mathrm{d}(1/\lambda) \Big/ \int_0^\infty I_0 \mathrm{d}(1/\lambda)$. This procedure gives $\bar{\epsilon} = 0.0170$. The absorbed light intensity was calculated from the limiting form of the Beer–Lambert law: $I_a = I_0(2.303)\bar{\epsilon}[SO_2]l$. The reliability of this method of estimation of I_a was checked in one series of runs; we determined the light intensity by actinometry at the rear of the cell in successive runs with the cell empty and with 765 Torr of SO_2 present. Within the large experimental error, the observed extinction coefficient (0.015 ± 0.002) was equal to that calculated from the $\bar{\epsilon}$ derived by graphical integration methods. The absolute values of Φ_{CO_2} are probably accurate to ±20%; the reproducibility in the quantum yields was usually better than ±10%.

Materials Used and Methods of Analysis. Chemically pure grade carbon monoxide gas from the Matheson Co. was found to contain considerable CO_2 impurity. This was reduced to less than 0.001% by passage of the gas slowly through a 25-ft copper tube of $^1/_8$ in. diameter which was cooled to liquid nitrogen temperature. The carbon monoxide (~400 Torr) was then condensed to a liquid in a glass trap at −196°. It was allowed to distil to a second trap at −196° and then to evaporate slowly into the cell until the desired pressure was reached. The sulfur dioxide used in this study (Matheson Co., anhydrous) was found to contain CO_2 impurity also. In this case, its removal was accomplished by repeated vacuum distillation and the retention of a middle-boiling fraction. The CO_2 impurity in the mixture prepared for photolysis was small, and it was determined accurately before each run so that a correction (usually less than 5%) could be made to determine product rates. Dark runs, identical in duration and experimental conditions with those used in photochemical runs, formed no detectable CO_2 at any of the temperatures used in this work. Before each run, the CO and SO_2 gases were thoroughly mixed using the circulating pump, analysis was made for the impurity CO_2, and then the run was photolyzed. Following the run, the gaseous mixture was pumped very slowly through two glass-helix-packed traps at liquid nitrogen temperature and then through the vpc-injector loop at −196°. When most of the CO had been pumped away, the condensed CO_2 was distilled to the loop and injected into the vpc apparatus. This equipment was a modified Aerograph Model A-700 chromatography system which contained a 12-ft length of $^1/_8$-in. Porapak Q column. Both CO_2 and SO_2 could be estimated quantitatively using this column. Of course the SO_2 showed no detectable loss during the run since the conversion was less than 0.01%, but the relative peak areas of SO_2 from a measured sample before and after the run served as a check on the mixing efficiency which had been achieved prior to the run.

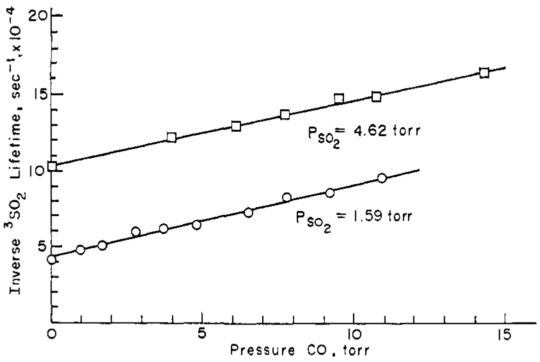

Figure 2. The inverse $^3SO_2$ lifetimes as a function of the CO pressure; data are from 3828.8-Å laser-excited SO_2–CO mixtures at 25°; P_{SO_2} = 4.62 Torr (upper line) and 1.59 Torr (lower line).

Discussion

The present results show that triplet sulfur dioxide molecules, populated by direct excitation within the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ "forbidden" absorption band (see Figure 1), oxidize carbon monoxide effectively. This observation confirms directly the conclusions of previous workers[1–3] who have studied the reactions of excited-singlet sulfur dioxide and have contended that the triplet sulfur dioxide molecules, formed by intersystem crossing, are the chemically active species involved. The present data are consistent with the mechanism suggested in explanation of photochemical studies of singlet-excited SO_2 systems.[1,4,5]

$$SO_2 + h\nu\ (3530\text{–}3970\ \text{Å}) \longrightarrow {}^3SO_2 \qquad \text{(II)}$$

$${}^3SO_2 \longrightarrow SO_2 + h\nu_p \qquad (6)^{10}$$

$$\longrightarrow SO_2 \qquad (7)$$

$${}^3SO_2 + SO_2 \longrightarrow SO_3 + SO \qquad \text{(8a)}$$

$$\longrightarrow 2SO_2 \qquad \text{(8b)}$$

$${}^3SO_2 + CO \longrightarrow SO + CO_2 \qquad \text{(9a)}$$

$$\longrightarrow SO_2 + CO \qquad \text{(9b)}$$

Lifetime Studies of $^3SO_2$ and the Determination of the Rate Constant Sum, $k_{9a} + k_{9b}$. The 3828.8-Å laser-excited $^3SO_2$ phosphorescence from SO_2–CO mixtures (summarized in Table I) follows well the Stern–Volmer relation expected from the proposed mechanism (6–9); see Figure 2. Relation A should hold according to the reaction scheme.

$$-\frac{\mathrm{d}\ln[{}^3SO_2]}{\mathrm{d}t} = \frac{1}{\tau} = k_6 + k_7 + [SO_2](k_{8a} + k_{8b}) + [CO](k_{9a} + k_{9b}) \qquad \text{(A)}$$

In each series of experiments at 25° and at constant SO_2 pressure, the slope of the $1/\tau$ *vs.* P_{CO} plot provides an estimate of $k_{9a} + k_{9b}$. The least-squares equations for the lines determined by the points are: $1/\tau\ (\text{sec}^{-1}) = (4.35 \pm 0.21) \times 10^4 + (4.79 \pm 0.36) \times 10^3 P_{CO}$ (Torr) at 1.59 Torr; $1/\tau = (10.47 \pm 0.21) \times 10^4 + (4.21 \pm 0.25) \times 10^3 P_{CO}$ at 4.62 Torr. The slopes of the plots are equal within the experimental error and give an estimate of $k_{9a} + k_{9b} = (8.4 \pm 0.6) \times 10^7$ l./(mol sec) at 25°.[11] This value checks well with that

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[10] The numbering of the reactions follows that used in the previous studies.[1,4,5]

[11] In every case in this work, the error limits shown represent the 95% confidence limits (twice the standard deviation) as determined by the method of least squares.

Table I. The Reciprocal of Sulfur Dioxide Triplet Lifetimes at Various Carbon Monoxide Pressures[a]

P_{SO_2} = 1.59 Torr		P_{SO_2} = 4.62 Torr	
P_{CO}, Torr	$1/\tau$, sec^{-1}, × 10^{-4}	P_{CO}, Torr	$1/\tau$, sec^{-1}, × 10^{-4}
0.00	4.26	0.00	10.38
0.97	4.78	4.00	12.25
1.70	5.13	6.10	12.95
2.80	6.04	7.75	13.8
3.70	6.17	9.50	14.7
4.80	6.42	10.75	14.9
6.50	7.30	14.3	16.4
7.75	8.35		
9.20	8.65		
10.97	9.60		

[a] Temperature 25°, triplet excitation with a laser pulse at 3828.8 Å.

Table II. Quantum Yields of Carbon Dioxide from the 3530–3970-Å Irradiated Mixtures of SO_2 and CO

P_{SO_2}, Torr	P_{CO}, Torr	$[SO_2]/[CO]$	I_a, quanta/(l. sec) × 10^{-14}	Φ_{CO_2}	$k_{9a}/(k_{9a} + k_{9b})$
		30°			
58.3	216	0.270	1.44	0.028	0.064
58.3	260	0.224	0.54	0.034	0.070
58.3	279	0.209	1.27	0.033	0.065
58.3	284	0.205	1.44	0.035	0.069
58.3	396	0.147	1.44	0.046	0.078
58.3	546	0.107	1.44	0.056	0.084
58.3	606	0.096	1.09	0.064	0.093
93.9	210	0.447	2.32	0.025	0.078
93.9	222	0.423	2.09	0.026	0.078
93.9	239	0.393	1.00	0.024	0.068
93.9	239	0.393	2.31	0.027	0.077
93.9	285	0.329	1.66	0.034	0.087
93.9	310	0.303	2.32	0.029	0.070
93.9	374	0.251	2.31	0.042	0.091
93.9	527	0.178	2.31	0.055	0.101
93.9	552	0.170	2.31	0.063	0.113
145.2	160	0.908	3.61	0.016	0.084
145.2	196	0.741	3.58	0.0205	0.092
145.2	207	0.701	2.76	0.023	0.099
145.2	316	0.459	3.59	0.027	0.085
145.2	346	0.420	3.60	0.031	0.092
145.2	488	0.298	3.58	0.0395	0.095
		84°			
68.7	251	0.274	0.60	0.042	0.117
68.7	255	0.269	0.98	0.042	0.116
68.7	261	0.263	0.61	0.057	0.155
68.7	291	0.236	0.98	0.051	0.130
68.7	315	0.218	0.62	0.062	0.150
68.7	538	0.128	0.59	0.061	0.111
68.7	568	0.121	0.63	0.074	0.132
		118°			
75.1	268.9	0.279	0.91	0.0765	0.238
75.1	281	0.267	0.90	0.0734	0.222
75.1	318	0.236	0.89	0.074	0.206
75.1	406.4	0.185	0.89	0.080	0.192
75.1	606	0.124	0.85	0.121	0.235

estimated independently from triplet SO_2 lifetime studies by Otsuka.[12] He populated the triplet species by intersystem crossing following the flash photolytic generation of excited singlet SO_2. His preliminary results from runs at several temperatures are described by $k_{9a} + k_{9b} = 1.15 \times 10^9 e^{-1.5/RT}$ l./(mol sec). At 25° the data suggest $k_{9a} + k_{9b} = (9.1 \pm 0.8) \times 10^7$ l./(mol sec).

An estimate of $k_{8a} + k_{8b}$ can be made by subtracting the two equations for the lines of Figure 2; this gives $k_{8a} + k_{8b} = (3.8 \pm 0.3) \times 10^8$ l./(mol sec) at 25°. Previously published values for this constant are in good agreement with the present estimate: $k_{8a} + k_{8b} = (3.8 \pm 0.1) \times 10^8$ from laser experiments,[7] $(3.9 \pm 0.7) \times 10^8$ l./(mol sec) from flash studies.[7,12]

Estimation of the Rate Constant Ratio, $k_{9a}/(k_{9a} + k_{9b})$. The fraction of the $^3SO_2$ quenching collisions with CO which result in carbon dioxide formation, $k_{9a}/(k_{9a} + k_{9b})$, can be estimated by two methods using the data of Table II and available rate constant data. The proposed mechanism suggests that relation B determines this ratio.

$$\frac{k_{9a}}{k_{9a} + k_{9b}} = \Phi_{CO_2}\left\{1 + \left(\frac{k_{8a} + k_{8b}}{k_{9a} + k_{9b}}\right)\left(\frac{[SO_2]}{[CO]}\right)\right\} \tag{B}$$

We have determined the rate constant ratio $(k_{8a} + k_{8b})/(k_{9a} + k_{9b}) = 4.42 \pm 0.33$ in this work at 25°. In addition, Otsuka has determined the two quenching constant sums as a function of temperature.[12] The rate constant function for CO quenching was given in the previous section; that for SO_2 quenching is $k_{8a} + k_{8b} = 4.0 \times 10^{10} e^{-2.8/RT}$ l./(mol sec). For 25° these functions give $(k_{8a} + k_{8b})/(k_{9a} + k_{9b}) = 3.9 \pm 0.6$, in reasonable agreement with our present estimate. We have used our value of this rate constant ratio together with the temperature dependence of the functions as found by Otsuka to estimate the ratios at the temperatures employed in this work: $(k_{8a} + k_{8b})/(k_{9a} + k_{9b}) = 4.70 \pm 0.34$ at 30°, 6.54 ± 0.48 at 84°, 7.60 ± 0.55 at 118°. These measured ratios, Φ_{CO_2}, and $[SO_2]/[CO]$ estimates given in Table II can be used to calculate the $k_{9a}/(k_{9a} + k_{9b})$ values; these are given in the last column of Table II. It is seen that for a given temperature the estimates are substantially constant and independent of the $[SO_2]/[CO]$ ratio within the experimental error. The average values derived from these estimates are: $k_{9a}/(k_{9a} + k_{9b}) = 0.083 \pm 0.026$ at 30°, 0.130 ± 0.034 at 84°, and 0.219 ± 0.038 at 118°.

An alternative, less precise method of estimation of $k_{9a}/(k_{9a} + k_{9b})$ can be made using the quantum yield data alone. Function B rearranges to

$$\frac{1}{\Phi_{CO_2}} = \frac{k_{9a} + k_{9b}}{k_{9a}} + \frac{k_{8a} + k_{8b}}{k_{9a}}\frac{[SO_2]}{[CO]} \tag{C}$$

The reciprocal of the intercept of the plot of $1/\Phi_{CO_2}$ *vs.* $[SO_2]/[CO]$ should give the desired ratio directly. A plot of all the quantum yield data is shown in Figure 3. They fit reasonably well the form of (C) expected. The ratios derived from the intercepts of the least-squares lines are $k_{9a}/(k_{9a} + k_{9b}) = 0.068 \pm 0.018$ at 30°, 0.12 ± 0.11 at 84°, and 0.18 ± 0.07 at 118°. The relatively good agreement of the rate constant ratio estimates calculated by the two independent methods is gratifying and lends credence to the mechanism choice and the consistency of the $^3SO_2$ rate data.

These results show the surprising feature that the dominant reaction of quenching of $^3SO_2$ by CO at 30° causes no overall chemistry; the majority of the quenching is "physical" in nature. Although this result is unexpected, it is consistent with the observed $^3SO_2$ quenching by nitrogen; the $^3SO_2$ quenching rate

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(12) K. Otsuka and J. G. Calvert, manuscript in preparation.

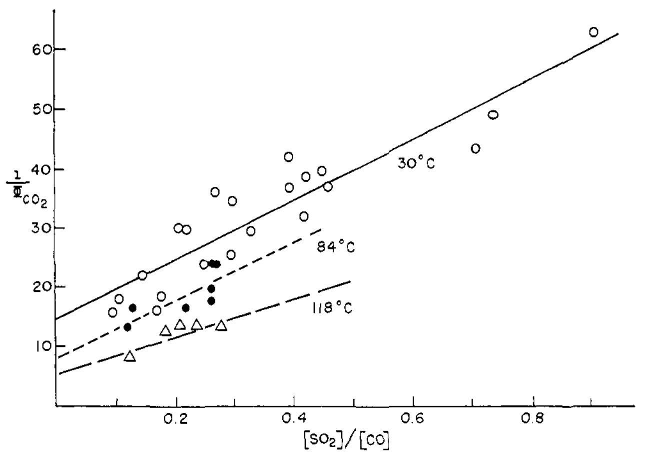

Figure 3. Plot of $1/\Phi_{CO_2}$ *vs.* $[SO_2]/[CO]$ for data obtained in the 3530–3970-Å irradiated SO_2–CO mixtures at 30° (○), 84° (●), and 118° (△).

constant for N_2 at 25° is $(8.5 \pm 1.0) \times 10^7$ l./(mol sec),[13] almost equal to that observed for CO at this temperature [$(8.4 \pm 0.6) \times 10^7$ l./(mol sec)]. N_2 and CO are very similar molecules in the physical sense, and in the case of N_2, no net chemistry would be expected in its $^3SO_2$ quenching since the N_2O product formation would be highly endothermic. Although both CO and N_2 appear to quench $^3SO_2$ largely by some net physical process, from the present data it is not possible to define further the nature of this quenching act.

The Determination of the Rate Constant for the Reaction $^3SO_2 + CO \rightarrow SO + CO_2$ (9a). Three different calculation techniques can be used to extract estimates of k_{9a} from the existing data. (1) The most accurate of these is the use of the $k_{9a}/(k_{9a} + k_{9b})$ ratios, calculated from an average of the data in the last column of Table II, and the estimates of $k_{9a} + k_{9b}$ from lifetime measurements. (2) The k_{9a} estimates can be made using the slopes of the plots in Figure 3: 50 ± 9 at 30°, 48 ± 33 at 84°, and 31 ± 18 at 118°. In theory these are equal to $(k_{8a} + k_{8b})/k_{9a}$; using the measured values of $k_{8a} + k_{8b}$ from lifetime data, one can estimate k_{9a}. (3) The least accurate of the methods is the use of the intercepts of the plots of Figure 3: 14.6 ± 3.8 at 30°, 8.3 ± 7.4 at 84°, and 5.5 ± 4.2 at 118°. These can be used together with lifetime data for $k_{9a} + k_{9b}$ to find k_{9a}. The values obtained using the three methods, respectively, are as follows: $k_{9a} = (7.2 \pm 2.3) \times 10^6$, $(7.6 \pm 1.4) \times 10^6$, and $(6.0 \pm 1.6) \times 10^6$ l./(mol sec) at 30°; $(1.6 \pm 0.4) \times 10^7$, $(1.6 \pm 1.1) \times 10^7$, and $(1.5 \pm 1.3) \times 10^7$ l./(mol sec) at 84°; $(2.7 \pm 0.5) \times 10^7$, $(3.5 \pm 2.0) \times 10^7$, and $(2.8 \pm 2.1) \times 10^7$ l./(mol sec) at 118°. The agreement between the constants calculated by the different means is reasonably good and attests to the self-consistency of the experimental data and the mechanism choice. The best values of k_{9a} (derived from methods 1 and 2 above) together with the rate constant sums $k_{9a} + k_{9b}$ give the following estimates of k_{9b}: $(8.0 \pm 0.6) \times 10^7$ at 30°, $(11.1 \pm 0.9) \times 10^7$ at 84°, $(12.2 \pm 0.9) \times 10^7$ at 118°.

Arrhenius plots of the estimates of the rate constants k_{9a} and k_{9b} (derived from the first two methods) are shown in Figure 4. From the slopes and intercepts of these lines we find [l./(mol sec)]

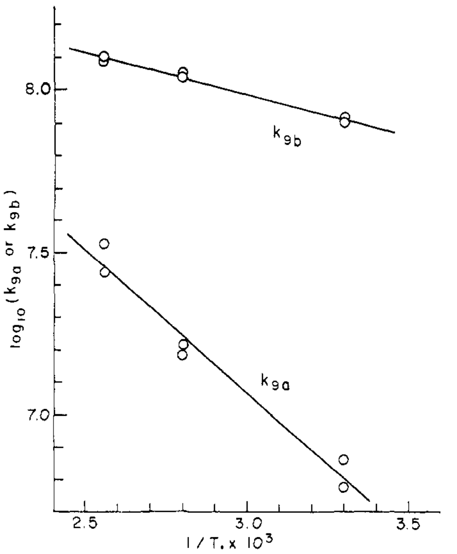

Figure 4. Arrhenius plots of rate constant data for k_{9a} (lower line) and k_{9b} (upper line).

$$k_{9a} = (5.1 \pm 3.2) \times 10^9 e^{-(4.0 \pm 0.7)/RT}$$

$$k_{9b} = (5.4 \pm 1.2) \times 10^8 e^{-(1.1 \pm 0.2)/RT}$$

The rate-determining steps in the two parallel processes of $^3SO_2$ quenching by CO which result in chemical or net physical events do not pass through the same transition state. In the case of the chemical reaction 9a, the transition state is probably of the specific geometry required for O-atom donation by $^3SO_2$

O–S–O–C–O

The reaction also conserves spin since SO must be formed in its ground state. It is very similar in character to the thermal reaction, $NO_2 + CO \rightarrow NO + CO_2$, which has been studied by Johnston, Bonner, and Wilson.[14] The preexponential factor for the NO_2–CO reaction is estimated to be 1.2×10^{10} l./(mol sec). The value of 0.5×10^{10} estimated here for reaction 9a is in reasonable accord with the hypothesis of similar transition states for the NO_2 and SO_2 reactions.

In Table III a summary is given of all of the rate data related to the $^3SO_2$–CO reactions 9a and 9b which we have derived in this work.

Observations on the Mechanism of CO_2 Formation in Excited-Singlet Sulfur Dioxide and CO Mixtures. It is very surprising that the reaction mechanism proposed previously for the singlet-excited SO_2 systems[1,4,5] and found to be adequate in the present work does not fit well the data from recent studies of Timmons[2] and Cehelnik, *et al.*[3] This is especially true since the evidence of these workers points to a major role for triplet sulfur dioxide species in these studies and since there is no measurable difference between the quenching rate constants for the $^3SO_2$ formed by intersystem crossing from excited singlets in the range 2400–3200 Å and those formed by direct laser excitation at 3828.8 Å.[7,12] It is instructive to attempt to fit the simple mechanism of this and previous studies to the recent Φ_{CO_2} data of Timmons and Cehelnik, *et al.* For the conditions they

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[13] H. W. Sidebottom, C. C. Badcock, G. E. Jackson, G. W. Reinhardt, E. K. Damon, and J. G. Calvert, manuscript in preparation.

[14] H. S. Johnston, W. A. Bonner, and D. J. Wilson, *J. Chem. Phys.*, **26**, 1002 (1957).

Table III. Summary of Rate Constant Data Related to the Reactions of $^3SO_2$ Quenching by Carbon Monoxide

Rate constant function	Temp, °C	Exptl values, l./(mol sec)	Method of estimation
$k_{9a} + k_{9b}$	25	$(8.4 \pm 0.6) \times 10^7$	Slope of $1/\tau$ data in Figure 2
	30	$(8.7 \pm 0.6) \times 10^7$	25° data plus Otsuka's temperature dependence
	84	$(12.7 \pm 0.9) \times 10^7$	
	118	$(15.3 \pm 0.9) \times 10^7$	
$k_{9a}/(k_{9a} + k_{9b})$	30	0.083 ± 0.026	Calculated from function B
		0.068 ± 0.018	Intercept of function C plot in Figure 3
	84	0.130 ± 0.034	Calculated from function B
		0.12 ± 0.11	Intercept of function C plot in Figure 3
	118	0.219 ± 0.038	Calculated from function B
		0.18 ± 0.07	Intercept of function C plot in Figure 3
k_{9a}	30	$(7.2 \pm 2.3) \times 10^6$	Ratio from function B; laser $k_{9a} + k_{9b}$
		$(7.6 \pm 1.4) \times 10^6$	Slope, function C, Figure 3; laser $k_{8a} + k_{8b}$
		$(6.0 \pm 1.6) \times 10^6$	Intercept, function C; laser $k_{9a} + k_{9b}$
	84	$(16 \pm 4) \times 10^6$	Ratio from function B; laser $k_{9a} + k_{9b}$
		$(16 \pm 11) \times 10^6$	Slope, function C, Figure 3; laser $k_{8a} + k_{8b}$
		$(15 \pm 13) \times 10^6$	Intercept, function C; laser $k_{9a} + k_{9b}$
	118	$(27 \pm 5) \times 10^6$	Ratio from function B; laser $k_{9a} + k_{9b}$
		$(35 \pm 20) \times 10^6$	Slope, function C, Figure 3; laser $k_{8a} + k_{8b}$
		$(28 \pm 21) \times 10^6$	Intercept, function C; laser $k_{9a} + k_{9b}$
k_{9b}	30	$(8.0 \pm 0.6) \times 10^7$	k_{9a} method I; laser $k_{9a} + k_{9b}$
		$(8.1 \pm 0.6) \times 10^7$	k_{9a} method II; laser $k_{9a} + k_{9b}$
	84	$(11.0 + 0.8) \times 10^7$	k_{9a} method I; laser $k_{9a} + k_{9b}$
		$(11.2 \pm 0.8) \times 10^7$	k_{9a} method II; laser $k_{9a} + k_{9b}$
	118	$(12.5 \pm 0.9) \times 10^7$	k_{9a} method I; laser $k_{9a} + k_{9b}$
		$(11.9 \pm 0.9) \times 10^7$	k_{9a} method II; laser $k_{9a} + k_{9b}$

$k_{9a} = (5.1 \pm 3.2) \times 10^9 e^{-(4.0\pm0.7)/RT}$ l./(mol sec); best estimate, Figure 4
$k_{9b} = (5.4 \pm 1.2) \times 10^8 e^{-(1.1\pm0.2)/RT}$ l./(mol sec); best estimate, Figure 4

employed the first-order radiative and nonradiative decay processes for $^1SO_2$ and $^3SO_2$ must be unimportant.

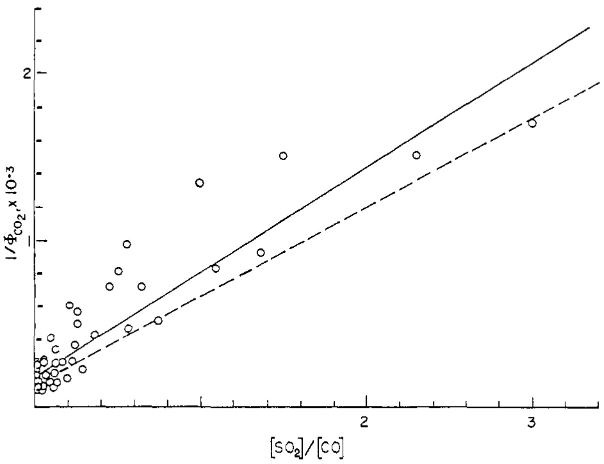

Figure 5. Attempted fit of the recent data of Cehelnik, *et al.*,[3] to relation E. The experimental data are from the 3130-Å photolyses of SO_2 in SO_2–CO mixtures at room temperature (Table V of Cehelnik, *et al.*[3]): — — —, theoretical distribution of the data calculated from relation E; ——, least-squares equation derived from the experimental points.

The following reactions, coupled with reactions 8a, 8b, 9a, and 9b, would be expected to describe the results.

$$SO_2 + h\nu\ (3200\text{–}2400\ \text{Å}) \longrightarrow {}^1SO_2 \quad \text{(I)}$$

$$^1SO_2 + M\ (SO_2, CO) \longrightarrow SO_2 + M\ (SO_2, CO, \text{or products}) \quad (1)$$

$$\longrightarrow {}^3SO_2 + M\ (SO_2, CO) \quad (2)$$

If CO oxidation does not occur in reaction 1, we would predict that Φ_{CO_2} would be given by

$$\Phi_{CO_2} = \left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{k_{9a}}{k_{9a} + k_{9b}}\right) \times \left(\frac{(k_{9a} + k_{9b})[CO]}{(k_{8a} + k_{8b})[SO_2] + (k_{9a} + k_{9b})[CO]}\right) \quad \text{(D)}$$

If one makes the assumption that the ratio $k_2/(k_1 + k_2)$ is the same as it is in the $^1SO_2$–SO_2 interactions, about 0.10 at 3020 Å,[5] then relation D can be evaluated completely from measured rate constant data for 25°; the resulting relation E is obtained.

$$1/\Phi_{CO_2} = (5.4 \times 10^2)([SO_2]/[CO]) + 1.2 \times 10^2 \quad \text{(E)}$$

Relation E can be compared with the recent experimental data from the singlet-SO_2 studies. Timmons reports the following Φ_{CO_2} estimates for experiments at 25° and at the $[SO_2]/[CO]$ ratios shown in parentheses: 0.0052 (0.95), 0.0053 (0.50), 0.0061 (0.18), 0.0074 (0.048). Relation E predicts the following Φ_{CO_2} values for these four runs, respectively: 0.0016, 0.0026, 0.0046, 0.0069. Although the correct order of magnitude of Φ_{CO_2} to match Timmon's results is given by relation E, the predicted trend with $[SO_2]/[CO]$ ratio was not observed.

An attempt to fit the data of Cehelnik, *et al.*,[3] by relation E can be made; see Figure 5. The dotted line is the variation of the $1/\Phi_{CO_2}$ *vs.* $[SO_2]/[CO]$ plot expected theoretically from relation E. The solid line is the least-squares fit of the recent data of Cehelnik, *et al.*[3] Relation E does not describe the variation of the data well, but there is the general trend of $1/\Phi_{CO_2}$ with $[SO_2]/[CO]$ predicted by (E). If one assumes this scatter to originate only in experimental error, then the slope and intercept may be used to estimate $k_2/(k_1 + k_2)$ by using the values of $k_{9a}/(k_{9a} + k_{9b})$ and $k_{9a}/(k_{8a} + k_{8b})$ estimated in this work. Following this procedure, we find that the least-squares slope (193) and intercept (634) of

Figure 5 give $k_2/(k_1 + k_2) \cong 0.10$ and 0.073, respectively. Although the agreement may be fortuitous, these values are in excellent accord with our previous estimates of this quantity for the pure SO_2 system. However, serious problems bar the acceptance of our simple mechanism involving a single $^3SO_2$ reactive species for the 3130-Å excitation of the SO_2–CO mixtures. Thus Cehelnik, *et al.*, found that only very incomplete quenching of the reaction resulted on addition of triplet quenchers. This result cannot be rationalized in terms of our simple mechanism. They also found that Φ_{CO_2} was independent of $[SO_2]$ at pressures above 60 Torr. This observation could be the accidental result of the experimental conditions employed by Cehelnik, *et al.* Light absorption must be very nonuniform in the runs at pressures greater than 60 Torr. The SO_3 product of reaction 8a would be concentrated in a small volume at a distance of only a few millimeters from the cell face. If the reaction $SO_3 + CO \rightarrow SO_2 + CO_2$ occurs significantly for these conditions, then Φ_{CO_2} may appear to be independent of $[SO_2]$.

In any case, it is obvious that the simple mechanism found to be adequate in this work for the SO_2–CO mixture photolyses within the "forbidden" absorption band cannot fit well the photochemistry found for these mixtures irradiated within the first allowed band of SO_2. Further work will be necessary to define better this most interesting and complex system. We will await more definitive proof of the chemical involvement of the two nonemitting states of SO_2 invoked by Cehelnik, *et al.*,[3] before accepting this explanation of their results.

Acknowledgment. The authors acknowledge gratefully the support of this work through a research grant from the National Air Pollution Control Administration, U. S. Department of Health, Education, and Welfare, Public Health Service, Arlington, Va. We are indebted to Mr. George Reinhardt and Mr. Edward Damon for their advice and counsel and for the use of the laser laboratory facilities in the ElectroScience Laboratory, The Ohio State University. We wish to thank Dr. Charles Badcock and Mr. Kenneth Demerjian for the extinction coefficient determinations reported in this work and Professors Julian Heicklen (The Pennsylvania State University) and Richard Timmons (Catholic University of America) for the use of preprints of their work before publication.

A Study of the Viscosity Dependence of Triplet–Singlet Energy Transfer in Solution[1a]

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Abstract: A detailed study of the diffusion effects on triplet–singlet energy transfer in solution confirmed the dipole–dipole nature of this process. The probability of transfer was found to be proportional to $D^{3/4}$ as predicted for dipole–dipole energy transfer by Yokota and Tannimoto. The experimental and theoretical values of the strength of dipole–dipole coupling in the benzophenone–perylene system are compared.

The process of triplet-singlet energy transfer has recently been reported in fluid solution at room temperature by Vaudo and Hercules.[2,3] Investigations into the decay kinetics of the donor–acceptor systems of benzophenone–perylene and phenanthrene–Rhodamine B in fluid solution have shown the ratio of the quenching rate constants for the two systems to be the same as the ratio predicted by the dipole-dipole interaction strength. The kinetic study provided qualitative evidence that triplet-singlet energy transfer in fluid solution procceds *via* a dipole–dipole interaction mechanism. Quantitative confirmation of that conclusion was the aim of the present work.

The effects of diffusion on resonance energy transfer by a dipole–dipole mechanism have been the object of many studies in recent years. Weinreb and Cohen[4] studied the efficiency of singlet–singlet transfer in the naphthalene–anthracene system as a function of the diffusion coefficient, *D*. These authors observed that as *D* approached zero, the energy transfer rate approached the value predicted by Förster's[5] theory of dipole–dipole energy transfer. Similar observations have been reported by Kurskii and Selivanenko,[6] Samson,[7] and Melhuish.[8]

Feitelson and his coworkers[9] in a series of articles from 1966 to 1968 discussed in detail the theoretical and experimental aspects of diffusion on dipole–dipole energy transfer. The observed increase in transfer yield in the naphthalene–anthranilic acid system with

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[1] (a) Taken in part from the Ph.D. thesis submitted by A. F. Vaudo to the Massachusetts Institute of Technology, Cambridge, Mass., June 1970; (b) National Institutes of Health Predoctoral Fellow, 1968–1970.

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