laser experiments),[6] and 0.68 × 10^{-2} sec (from steady-state phosphorescence studies[7] and lifetime data[6]). An abundance of evidence now exists which suggests that the unexpected shortness in the observed lifetime of $^3SO_2$ results from the significant role of reaction 7 in the decay of isolated $^3SO_2$ molecules.[6,7]

There is excellent agreement between the $k_{8a} + k_{8b}$ and $k_6 + k_7$ rate constant estimates found in this flash photolysis work, in which triplets were derived by intersystem crossing, and those reported from the very different study in which triplets were formed by the direct excitation using the 3828.8-Å beam.[5,6] At first sight this may seem unusual, since the triplets formed in the present flash experiments could have an energy excess as great as 15–44 kcal/mol over the $^3SO_2$ entity formed directly in the laser experiments. This may be in part an artifact of the method used here. The 300-μsec delay period we have employed before observing the triplet emission would allow vibrational relaxation of the triplets to be accomplished even in the runs at the lowest pressure used here; at $P_{SO_2} = 13\ \mu$ the $^3SO_2$ molecules undergo about 30 collisions on the average during the 300-μsec delay period. Thus the present system is well suited to the study of the thermal reactions of the triplet sulfur dioxide molecules. Furthermore, when one considers the magnitude of the A factor for reaction 8a, he would not expect any significant difference between the reactivity of the triplets observed here and those formed immediately after the flash: vibrational relaxation of the $^3SO_2$ formed by intersystem crossing would be the normal result of a collision, since only a fraction of the collisions (0.3–0.09) would occur with the specific orientation of the colliding partners necessary to form the transition state of reaction 8a. The reasonable agreement between the $^3SO_2$ rate constant data reported here and that estimated from steady-state emission studies supports this thesis.[20]

Our studies with this system are being extended to determine the temperature dependence of the $^3SO_2$ quenching rate constants for a wide variety of compounds in the hope of delineating better the nature of the quenching reactions of the triplet sulfur dioxide molecules.

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 wish to thank Dr. Akira Morikawa, for his design and construction of the major portion of the flash equipment used in this work, and Mr. John Richter, for his help with the electrical component design. We appreciate the kindness of Professors Julian Heicklen (Pennsylvania State University) and Richard Timmons (Catholic University of America), who provided us with reprints of their work before publication.

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(20) For example, the data from the steady emission studies of Strickler and Howell,[11] as recalculated by Rao, Collier, and Calvert,[7] give $(k_6 + k_7)/(k_{8a} + k_{8b}) = (0.577 \pm 0.084) \times 10^{-5}\ M$. Using our data for $k_6 + k_7$, we estimate $k_{8a} + k_{8b} = (2.0 \pm 0.4) \times 10^8$ l./(mol sec).

A Study of the Decay Processes in the Triplet Sulfur Dioxide Molecule Excited at 3828.8 Å[1]

Howard W. Sidebottom, Charles C. Badcock, Jack G. Calvert,*
George W. Reinhardt, Blaine R. Rabe, and Edward K. Damon

Contribution from the Department of Chemistry and the ElectroScience Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received September 17, 1970*

Abstract: Triplet sulfur dioxide molecules ($^3SO_2$) were generated by the absorption of a 3828.8-Å laser light pulse within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band. The lifetimes of the $^3SO_2$ species were determined over a wide range of pressures (0.16–17.6 Torr) in experiments at 25°. The data fit well a Stern–Volmer quenching mechanism and lead to the following rate constant data: $^3SO_2 + SO_2 \rightarrow SO_3 + SO$ (8a), $^3SO_2 + SO_2 \rightarrow 2SO_2$ (8b), $k_{8a} + k_{8b} = (3.9 \pm 0.1) \times 10^8$ l./(mol sec); $^3SO_2 \rightarrow SO_2 + h\nu_p$ (6), $^3SO_2 \rightarrow SO_2$ (7); $k_6 + k_7 = (9.8 \pm 6.8) \times 10^2\ \text{sec}^{-1}$. In another set of experiments, comparative phosphorescence emission intensities were measured in pure SO_2 and from biacetyl–cyclohexane mixtures. The data provide an estimate of the quantum yield of phosphorescence of $^3SO_2$ at zero pressure: $(\phi_p)_{SO_2} = k_6/(k_6 + k_7) = 0.12 \pm 0.09$. These and all other pertinent data give the surprising result that the isolated sulfur dioxide triplet molecule undergoes some form of nonradiative decay, the net reaction 7, with higher efficiency than the radiative reaction 6. Possible mechanisms of this process are considered.

An increased interest in the study of the sulfur dioxide triplet molecule ($^3SO_2$) has developed with the recent discovery that these molecules are the major chemically reactive species in sulfur dioxide photolysis within the first allowed absorption band (3200–2400 Å).[2] Previous attempts to characterize the reactions of the $^3SO_2$ have met with only limited success.[3-6] The difficulty in obtaining reliable $^3SO_2$

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(1) A communication on one aspect of this work was published previously: S. S. Collier, A. Morikawa, D. H. Slater, J. G. Calvert, G. Reinhardt, and E. Damon, *J. Amer. Chem. Soc.*, **92**, 217 (1970); presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

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

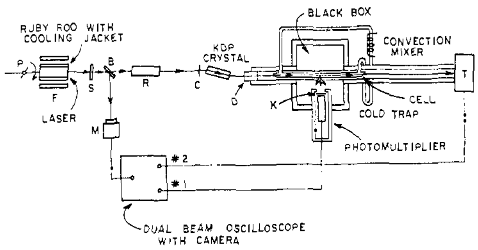

Figure 1. Schematic diagram of the 3828.8-Å laser system used to excite the triplet sulfur dioxide and determine phosphorescence lifetimes in this work; see the text for the detailed description.

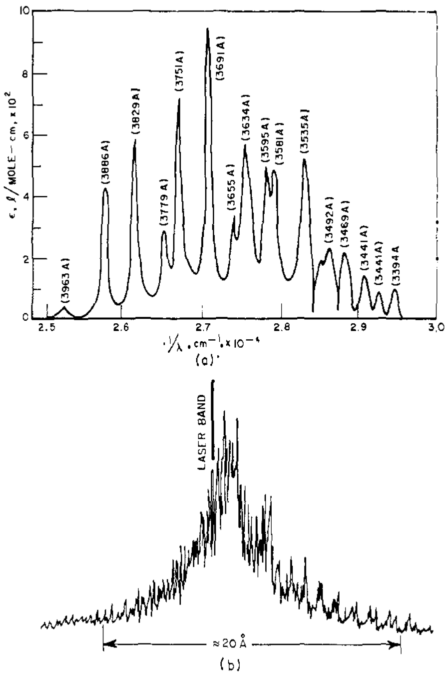

Figure 2. (a) The extinction coefficient of sulfur dioxide as a function of $1/\lambda$ for the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ "forbidden" band; the approximate wavelengths (Å) are shown for the maxima of the vibrational bands (calculated from the absorption data determined at several pressures using a low-resolution recording spectrophotometer, temperature 25°). (b) Microdensitometer tracing of the high-resolution absorption spectrum of the $SO_2(^1A_1, 0, 0, 0) \rightarrow SO_2(^3B_1, 0, 1, 0)$ vibrational band near 3828 Å.

reaction rate constant estimates from these systems results from their very great complexity. Among the many problems are the uncertainty in the rate of triplet formation by intersystem crossing from the excited singlet molecules and the extensive overlap of the triplet and singlet emission envelopes.

We have found that is is possible to excite the $^3SO_2$ species directly in SO_2 gas irradiated by a short laser light pulse at 3828.8 Å, within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band. A preliminary report of lifetime studies of $^3SO_2$ excited in this manner has been published previously.[1] Since the completion and the report of that work, the intensity and the reproducibility of the 3828.8-Å laser system and the sensitivity of the detection system have been improved significantly. With the present system it has been possible to extend the $^3SO_2$ lifetime data to much lower pressures than previously employed (0.16 Torr). In addition to obtaining more accurate quenching rate data, a meaningful estimate of the intrinsic lifetime of $^3SO_2$ at zero pressure now has been possible.

In a new, as yet unreported, series of experiments, comparative emission intensity studies were made using pure sulfur dioxide and biacetyl–cyclohexane mixtures. From these data we have been able to estimate the quantum yield of triplet sulfur dioxide emission. All of the results confirm the interesting yet unexpected previous finding that a first-order, nonradiative decay of triplet sulfur dioxide is more important than radiative decay for the isolated molecule at low pressures.[5]

Experimental Section

Apparatus. Sulfur dioxide triplets were excited in this work using a 3828.8-Å laser beam in experiments at 25°. Figure 1 shows schematically the apparatus employed. The entire optical apparatus was rigidly attached to a flat granite bench. The laser source was a ruby rod which was excited by a 4000-J flash from a helical xenon flash lamp F; it was Q switched by a rotating prism P (24,000 rpm). The wavelength of the laser beam was temperature tunable, 0.055 Å/deg. The stability of the emission wavelength was enhanced by thermostatically controlling the temperature of the ruby rod at 15°; this was accomplished by pumping a water–methanol mixture through a glass jacket which surrounded the rod. The sapphire etalon S with a reflectivity of 26% completed the laser cavity. The laser beam intensity as measured at the first beam splitter B was 75 MW at a wavelength of 6943 Å. The doubled ruby frequency is a very poor match for the bands of the SO_2 singlet–triplet absorption region. However, it was observed that the Raman-shifted (1344 cm^{-1}) ruby frequency obtained using nitrobenzene liquid gave a frequency when doubled which was an excellent match for a triplet band at 3828.8 Å. The collimated beam exiting from the Raman cell R included the original ruby line and first Stokes-shifted line (7658 Å) and weaker higher order Stokes and anti-Stokes lines. Any flash-lamp ultraviolet was filtered from the beam by a Corning CS 2-59 filter (C in Figure 1). Frequency doubling of only the first Stokes line was effected using a precisely oriented potassium dihydrogen phosphate (KDP) crystal. The arrangement employed formed about 50 kW of power at 3828.8 Å and a half-intensity peak duration of 20 nsec. An aqueous copper sulfate solution filter D, placed before the sample cell, removed any red and infrared radiations from the beam.

The reaction cell was constructed from a Pyrex tube (25 mm in diameter, 60.3 cm long) with Brewster angle windows of Suprasil quartz sealed to the ends with low-vapor pressure epoxy resin.

The intensity of phosphorescence was monitored at right angles to the excitation beam. The emission beam was filtered (Kodak Wratten gelatin 2B, K in Figure 1) so that only light of the wavelengths within the phosphorescence emission band was transmitted. Scattered light originating from the laser beam was largely eliminated with this arrangement. An RCA 7265 photomultiplier was used to detect emission. The light from the beam splitter B, by use of the phototube monitor M, triggered the oscilloscope which recorded the response. An ITT F 4000 phototube T, placed at the end of the cell, was used to measure the transmitted laser intensity. The output from both detectors was traced on a dual-beam, fast-scanning oscilloscope (Fairchild 777) and photographed using a Polaroid camera. The decay curves were digitzed by means of a modified x–y plotter. The data were punched onto paper tape which was fed directly into a computer for least-squares linear treatment of the logarithm of the phosphorescence intensity *vs.* time data. A correction was automatically made for skewed placement of the photograph on the plotter.

Samples of the gases were prepared in a mercury-free, grease-free, vacuum line. Low-pressure measurements were made by use of a calibrated pressure transducer (Whittaker Model P7D). Higher pressures were determined on a mercury manometer separated from the line by a spiral gauge. Mixing of the mixtures of cyclohexane and biacetyl was accomplished using a simple convection pump.

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(3) H. D. Mettee, *J. Chem. Phys.*, **49**, 1784 (1968); *J. Phys. Chem.*, 73, 1071 (1969).

(4) S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, **49**, 1957 (1968).

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

(6) T. N. Rao, S. S. Collier, and J. G. Calvert, *ibid.*, **91**, 1616 (1969).

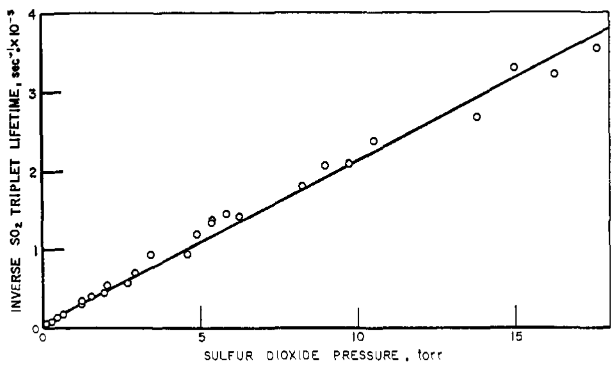

Figure 3. Stern–Volmer plot of $^3SO_2$ lifetime data; experiments at high SO_2 pressures; temperature, 25°; 3828.8-Å laser excitation; the rate constant sum, $k_{8a} + k_{8b}$, was derived from the slope of this plot.

Determinations of the wavelength of the laser beam and the high-resolution absorption spectrum of SO_2 (Figure 2) were made on a Jarrell-Ash 3.4-m Ebert spectrograph. Wavelengths from an iron arc were used for calibration. The low-resolution singlet–triplet absorption spectrum was determined using a Bausch and Lomb Spectronic 505 with SO_2 at pressures over 1 atm in a 10-cm cell.

Materials. The sulfur dioxide was the anhydrous grade of the Matheson Chemical Co. It was further purified and degassed by vacuum distillation. Biacetyl (Fluka, puriss) was distilled in the vacuum system; the fraction volatile at −63° ($CHCl_3$ melt) was rejected, a portion which distilled at −23° (CCl_4 melt) was retained, and the residue was rejected. The retained portion was thoroughly degassed by bulb-to-bulb distillation at −196°. Cyclohexane (top grade, 99.1%, from Chemical Samples Co.) was degassed and distilled in the vacuum line with the retention of a middle-boiling fraction.

Discussion

Although light absorption by sulfur dioxide at ordinary pressures within the forbidden $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band is rather weak (see Figure 2a), it was evident that the use of incident light of a suitable matching wavelength and of laser intensities could populate triplets in sufficient number to allow readily their detection and study through phosphorescence intensity measurements. However, the commonly employed laser frequencies do not match well those of the triplet absorption band. Thus the doubled-ruby laser line at 3471 Å (28,810 cm^{-1}) lies in a valley between two vibrational bands of the triplet absorption region. It was found that a useful 3828.8-Å line was generated by frequency doubling of the Raman-shifted, ruby-laser fundamental frequency; the 20-nsec pulse of this system was of sufficient power (about 50 kW) to excite readily detectable SO_2 triplet phosphorescence. From Figure 2a it is seen that the 3828.8-Å line enters the second major vibrational band of the triplet absorption region,[7] in which the excited molecule possesses 1 quantum of the fundamental bending frequency; thus the transition involved in SO_2 excited at 3828.8 Å appears to be $SO_2(^1A_1, 0, 0, 0) \rightarrow SO_2(^3B_1, 0, 1, 0)$. The fine rotational structure of this vibrational band is apparent in the high-resolution absorption spectrum shown in Figure 2b. It was taken from a microdensitometer tracing of the spectrographic plate on which the absorption of the "forbidden" band was photographed.

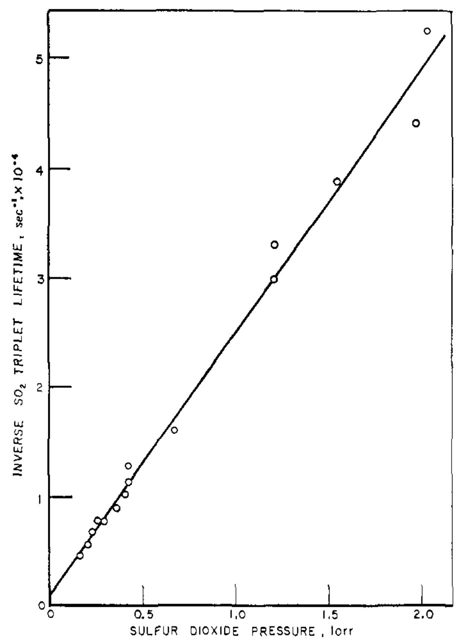

Figure 4. Stern–Volmer plot of $^3SO_2$ lifetime data; experiments at low SO_2 pressures; temperature, 25°; 3828.8-Å laser excitation; the rate constant sum, $k_6 + k_7$, was derived from the intercept of this plot.

The laser frequency was tuned to match well that of one of the rotational lines. This was accomplished by varying the temperature of the thermostated water–methanol mixture pumped through the glass jacket which surrounded the ruby laser rod, until a maximum was observed in the intensity of the phosphorescence emission on pulsing the laser.

Sulfur Dioxide Triplet Lifetime Data; the Estimation of the Rate Constants for $^3SO_2$ Decay. All of the results of the present study are described well in terms of the previously proposed mechanism for triplet sulfur dioxide quenching reactions.[1,2,5,6]

$$SO_2(^1A_1) + h\nu\ (3828.8\ \text{Å}) \longrightarrow SO_2(^3B_1)\ (\text{designated } ^3SO_2 \text{ here}) \qquad (I)$$

$$^3SO_2 \longrightarrow SO_2 + h\nu_p \qquad (6)^8$$

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

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

$$\longrightarrow 2SO_2 \qquad (8b)$$

The triplet lifetime data of Table I fit well the Stern–Volmer quenching mechanism suggested by these reactions; see Figures 3 and 4. In terms of the mechanism, the lifetime of triplet molecules will be described by the function

$$-d[^3SO_2]/dt[^3SO_2] = 1/\tau = k_6 + k_7 + (k_{8a} + k_{8b})[SO_2] \qquad (A)$$

The least-squares treatment of the data obtained from the entire range of SO_2 pressures (17.6–0.16 Torr), shown in Figure 3, gives the slope = (20.5 ± 0.8) × 10^3 $Torr^{-1}$ sec^{-1} and intercept, (7.9 ± 5.3) × 10^3 sec^{-1} The data taken only from the low-pressure region (0.16–2.04 Torr), shown in Figure 4, give the slope = (24.0 ± 1.4) × 10^3 $Torr^{-1}$ sec^{-1} and intercept, (9.8 ± 6.8) ×

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(7) A. J. Merer, *Discuss. Faraday Soc.*, **35**, 127 (1963); the small band centered at 3963 Å appears to be an anti-Stokes band involving 1 quantum of the fundamental bending mode in the absorbing molecule: $SO_2(^1A_1, 0, 1, 0) \rightarrow SO_2(^3B_1, 0, 0, 0)$.

(8) The numbering of reactions follows that used in our previous studies[1,2,5,6] and in the accompanying paper: K. Otsuka and J. G. Calvert, *J. Amer. Chem. Soc.*, 93, 2581 (1971).

Table I. The Inverse SO_2 Triplet Lifetimes as a Function of Pressure of SO_2[a]

P_{SO_2}, Torr	$1/\tau$, $sec^{-1} \times 10^{-3}$	P_{SO_2}, Torr	$1/\tau$, $sec^{-1} \times 10^{-3}$
17.6	354	2.70	56.9
16.3	322	2.04	52.4
15.0	328	1.97	44.1
13.8	267	1.55	38.8
10.5	238	1.21	32.9
9.73	209	1.21	29.8
8.98	207	0.679	16.0
8.25	182	0.432	12.8
6.26	142	0.431	11.2
5.81	145	0.405	10.1
5.36	134	0.363	8.87
5.34	135	0.288	7.68
4.92	119	0.255	7.73
4.58	95.2	0.230	6.62
3.46	93.4	0.202	5.52
2.94	69.9	0.157	4.48

[a] Laser excitation at 3828.8 Å; temperature, 25°.

10^2 sec^{-1}.[9] The most reliable estimate of the slope and the rate constant sum, $k_{8a} + k_{8b}$, are obtained from the results over the entire pressure range

$$k_{8a} + k_{8b} = (3.9 \pm 0.1) \times 10^8 \text{ l./(mol sec)}$$

This estimate checks remarkably well with those reported recently from lifetime measurements in the preliminary laser and flash photolysis experiments carried out by others in our laboratory:[1] $k_{8a} + k_{8b} = (3.8 \pm 0.1) \times 10^8$ in 3828.8-Å laser experiments and $(3.9 \pm 0.7) \times 10^8$ l./(mol sec) in flash experiments. Previous estimates of $k_{8a} + k_{8b}$ were derived from SO_2 steady-state emission studies[3-6] together with the $^3SO_2$ lifetime data of Caton and Duncan[10] in which there is considerable question as to the assignment of the observed lifetime to the lowest sulfur dioxide triplet state. It is probably incorrect; see the discussion in the following section. Using the τ_0 values derived in this work, $(1.02 \pm 0.71) \times 10^{-3}$ sec, the older steady-state results give the following corrected estimates of $k_{8a} + k_{8b}$: $(1.7 \pm 1.2) \times 10^8$ calculated from Stickler and Howell's results;[4,5] $(0.33 \pm 0.58) \times 10^8$, $(0.90 \pm 1.3) \times 10^8$, and $(0.72 \pm 1.12) \times 10^8$ l./(mol sec) from Rao, Collier, and Calvert's data.[5,6] Although estimates for $k_{8a} + k_{8b}$ from the older data still show deviation from the recent laser values, the use of the presently determined lifetime for $^3SO_2$ brings them in line with the more accurate data of the present work.

The Lifetime of $^3SO_2$ at Zero Pressure of Sulfur Dioxide. The improved accuracy and the extended low-pressure range of the present laser results allow a realistic intercept determination in the Stern-Volmer plot of Figure 4. This was not possible in the previous laser work.[1] The intercept gives

$$k_6 + k_7 = (9.8 \pm 6.8) \times 10^2 \text{ sec}^{-1}$$

From the reciprocal of this rate constant sum, the intrinsic lifetime of the excited $^3SO_2$ molecule is estimated

$$\tau_0 = (1.02 \pm 0.71) \times 10^{-3} \text{ sec}$$

The results of Caton and Duncan[10] gave a much higher estimate for this lifetime: $\tau_0 = (7 \pm 1) \times 10^{-3}$ sec. These workers excited SO_2 in an electric discharge and studied the decay of the emission. The one of several emitting species present in this system, which they picked as the lowest triplet of sulfur dioxide, showed no measurable quenching by SO_2. Our data require a large change in lifetime over the pressure range which they employed (0.003–1.5 Torr); thus it is highly likely that their lifetime data do not apply to the $SO_2(^3B_1)$ state.

Our present lifetime data are in reasonable agreement with the values estimated recently by several other workers: $\tau_0 = (0.79 \pm 0.17) \times 10^{-3}$ sec by Morikawa using lifetime measurements from the flash photolytic generation of $^3SO_2$;[1] $\tau_0 = (0.76 \pm 0.16) \times 10^{-3}$ sec by McKenzie and Thrush using chemiluminescence from excited SO_2 formed on O-atom association with SO at a wall;[11] $\tau_0 = 0.2 \times 10^{-3}$ sec by Levitt and Sheen[12] from shock tube studies of SO_2; and $\tau_0 = (0.50 \pm 0.10) \times 10^{-3}$ sec by Greenough and Duncan[13] from the optical excitation of SO_2 triplets in solid SO_2 at 77°K. The fair agreement of our recent estimate of τ_0 with those derived in nonoptical SO_2-excitation experiments may be fortuitous since these systems are very much more complicated than that used here, and neither rate constant data for the quenching reaction nor other information is available to allow a good comparison of these states with the one produced in our work.

The best estimate of $\tau_0 = (1.02 \pm 0.71) \times 10^{-3}$ sec, derived in this work, shows a surprisingly short lifetime for the isolated $^3SO_2$ species. The radiative lifetime of $^3SO_2$ predicted from the integrated absorption data is $\tau_0 = 1/k_6 = 1.7 \times 10^{-2}$ sec.[14] Of course, the Strickler and Berg relation used to make this estimate holds strictly for allowed transitions only;[15] however, reasonably good checks exist between observed and calculated triplet lifetimes for many molecules.[16] If the theoretical lifetime is near correct, then one finds the surprising result that $k_6 < k_7$. This unexpected conclusion is reached also using measured rate constant ratios reported previously by Rao, Collier, and Calvert,[5] who found

$$k_9k_{10}/k_6(k_{10} + k_{11}) = (1.4 \pm 0.4) \times 10^8$$

These rate constants refer to the reactions

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

$$^3SO_2 + (CH_3CO)_2 \longrightarrow SO_2 + {}^3(CH_3CO)_2 \qquad (9)$$

$$^3(CH_3CO)_2 \longrightarrow (CH_3CO)_2 + h\nu_p \qquad (10)$$

$$\longrightarrow (CH_3CO)_2 \qquad (11)$$

From previous data, $k_{10}/(k_{10} + k_{11}) = 0.149 \pm 0.009$[17]

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[9] 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.

[10] R. B. Caton and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **90**, 1949 (1968).

[11] A. McKenzie and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **308**, 133 (1968).

[12] B. P. Levitt and D. P. Sheen, *Trans. Faraday Soc.*, **63**, 540 (1967).

[13] K. F. Greenough and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **83**, 555 (1961).

[14] The value was calculated using the data of Figure 1 and the method of Strickler and Berg;[15] the ratio of degeneracy of the final state to that of the initial state was taken as 3.

[15] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

[16] S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 40.

and $k_9 = (1.4 \pm 0.1) \times 10^{11}$ l./(mol sec),[18] we estimate $k_6 = (1.5 \pm 0.5) \times 10^2$ sec^{-1}. Since $k_6 + k_7 = (9.8 \pm 6.8) \times 10^2$ sec^{-1} as measured in this work, the evidence suggests again that $k_6 < k_7$. Because of the theoretical interest in the unexpected importance of nonradiative processes in an isolated molecule as simple as SO_2, further experiments were designed to determine more directly the ratio $k_6/(k_6 + k_7)$. This work is described in the following section.

The Determination of the Quantum Yield of Phosphorescence of $^3SO_2$ at Zero Pressure. The theoretically important ratio of $k_6/(k_6 + k_7)$ is equal to the quantum yield of phosphorescence emission from 3828.8-Å-excited SO_2 triplets, extrapolated to zero pressure, $(\phi_p)_{SO_2=0}$. This quantum yield was measured in the present system using the intensity of biacetyl emission as a standard in sequential experiments with pure SO_2. For our experiments the quantum yield of phosphorescence of triplet sulfur dioxide molecules will be related to that for biacetyl phosphorescence by

$$(\phi_p)_{SO_2} = (\phi_p)_{Ac_2}\left(\frac{(I_p)_{SO_2}{}^T}{(I_p)_{Ac_2}{}^T}\right)\left(\frac{(I_a)_{Ac_2}{}^T}{(I_a)_{SO_2}{}^T}\right) \qquad (B)$$

Here $(I_a)_{SO_2}{}^T$ and $(I_a)_{Ac_2}{}^T$ represent the total numbers of 3828.8-Å quanta absorbed per cubic centimeter by the SO_2 and Ac_2 gases, respectively, in consecutive experiments, and $(I_p)_{SO_2}{}^T$ and $(I_p)_{Ac_2}{}^T$ are the total numbers of phosphorescence quanta emitted per cubic centimeter from SO_2 and Ac_2, respectively, following the laser pulse.

The ratio of the quanta absorbed by the two gases is rather easily evaluated in the present study. The pressures of SO_2 and Ac_2 were kept low in the phosphorescence experiments, below 8 Torr for SO_2 and below 0.2 Torr for Ac_2. This ensured $\epsilon_{SO_2}[SO_2]l$ and $\epsilon_{Ac_2}[Ac_2]l \leq 0.02$, and for these conditions the limiting form of the Beer–Lambert law applies. Furthermore, by careful control of the optical and electrical components of the laser system, it was possible to repeat the incident laser intensity at 3828.8 Å from consecutive phases within a reproducibility of ±5%. Thus for our conditions the desired ratio for relation B is given by

$$((I_a)_{Ac_2}{}^T/(I_a)_{SO_2}{}^T) = (\epsilon_{Ac_2}[Ac_2]/\epsilon_{SO_2}[SO_2]) \qquad (C)$$

The needed ratio for relation B involving the phosphorescence intensities will be described by the ratio of the integrals in relation D. Of course the triplet

$$\left(\frac{(I_p)_{SO_2}{}^T}{(I_p)_{Ac_2}{}^T}\right) = \frac{\int_0^\infty (I_p)_{SO_2}{}^t \mathrm{d}t}{\int_0^\infty (I_p)_{Ac_2}{}^t \mathrm{d}t} \qquad (D)$$

lifetimes for SO_2 and Ac_2 for our conditions are sufficiently long so that a negligible fraction of the triplets excited in the 20-nsec laser pulse actually decay during the laser pulse. It can be shown readily from the reaction mechanism that relations E and F should give the time dependence of the intensities of phosphorescence (quanta/cm^3) of $^3SO_2$ and $^3Ac_2$ following the pulse. $(I_p)_{SO_2}{}^0$ and $(I_p)_{Ac_2}{}^0$ are the intensities for SO_2 and Ac_2, respectively, at $t = 0$ after the laser pulse. The rate

$$(I_p)_{SO_2}{}^t = (I_p)_{SO_2}{}^0 e^{-\{k_6 + k_7 + (k_{8a} + k_{8b})[SO_2]\}t} \qquad (E)$$

$$(I_p)_{Ac_2}{}^t = (I_p)_{Ac_2}{}^0 e^{-(k_9 + k_{10} + k_{11}[Ac_2] + k_{12}[C_6H_{12}])t} \qquad (F)$$

constants k_{11} and k_{12} of function F correspond to the electronic quenching reactions of $^3Ac_2$ with Ac_2 and cyclohexane, respectively. (Cyclohexane was added in the Ac_2 runs to prevent dissociation of vibrationally excited Ac_2 molecules.)

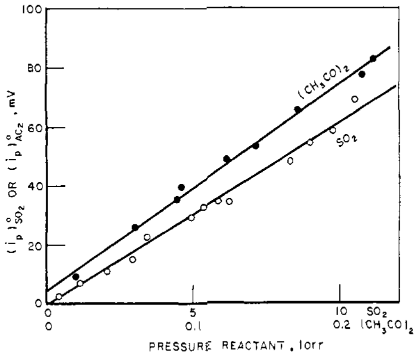

Figure 5. Plot of the intensity of phosphorescence (phototube response) for SO_2 and $(CH_3CO)_2$ gases at time = 0 after the laser pulse at 3828.8 Å *vs.* the pressure of the reactant; in all $(CH_3CO)_2$ runs, 85.1 Torr of cyclohexane was present.

$(I_p)_{SO_2}$ and $(I_p)_{Ac_2}$ values cannot be measured directly in this work, but the deflections of the oscilloscopic trace caused by the phototube response to the phosphorescence signals from SO_2 and Ac_2 were monitored, $(i_p)_{SO_2}{}^t$ and $(i_p)_{Ac_2}{}^t$. These quantities are proportional to the desired phosphorescence intensities.

$$(I_p)_{SO_2}{}^t = \alpha(i_p)_{SO_2}{}^t \qquad (I_p)_{Ac_2}{}^t = \beta(i_p)_{Ac_2}{}^t \qquad (G)$$

The final working equation H is derived for the desired quantum yield of $^3SO_2$ phosphorescence from relations B–G.

$$(\phi_p)_{SO_2} = (\phi_p)_{Ac_2}\left(\frac{(i_p)_{SO_2}{}^0}{[SO_2]}\right)\left(\frac{[Ac_2]}{(i_p)_{Ac_2}{}^0}\right)\left(\frac{\epsilon_{Ac_2}}{\epsilon_{SO_2}}\right) \times \left(\frac{k_9 + k_{10} + k_{11}[Ac_2] + k_{12}[C_6H_{12}]}{k_6 + k_7 + (k_{8a} + k_{8b})[SO_2]}\right)\left(\frac{\alpha}{\beta}\right) \qquad (H)$$

The methods of determination of the various ratios required to evaluate $(\phi_p)_{SO_2}$ should be considered briefly here. An evaluation of the ratios $(i_p)_{SO_2}{}^0/[SO_2]$ and $(i_p)_{Ac_2}{}^0/[Ac_2]$ can be made from the measured phosphorescence data. Values of $(i_p)_{SO_2}{}^t$ and $(i_p)_{Ac_2}{}^t$ were measured as a function of time in experiments using different pressures of pure SO_2 or Ac_2 in cyclohexane (85.1 Torr). The exponential decay curves were converted to the linear logarithmic form and extrapolated to zero time to give $(i_p)_{SO_2}{}^0$ and $(i_p)_{Ac_2}{}^0$ for each run. The desired ratios were then estimated from the slopes of the plots of the $(i_p)^0$ quantities *vs.* the reactant pressure; see Figure 5. The least-squares treatment of the data give: $(i_p)_{SO_2}{}^0/[SO_2] = 6.27 \pm 0.38$ mV/Torr and $(i_p)_{Ac_2}{}^0/[Ac_2] = 350 \pm 20$ mV/Torr.

The evaluation of the ϵ_{SO_2} and ϵ_{Ac_2} values involved a series of somewhat unique experiments. Since there

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[17] S. S. Collier, D. H. Slater, and J. G. Calvert, *J. Photochem. Photobiol.*, 7, 737 (1968).

[18] H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, manuscript in preparation; the value was determined from lifetime measurements of $^3SO_2$ excited by a 3828.8-Å laser pulse in experiments with added small concentrations of biacetyl.

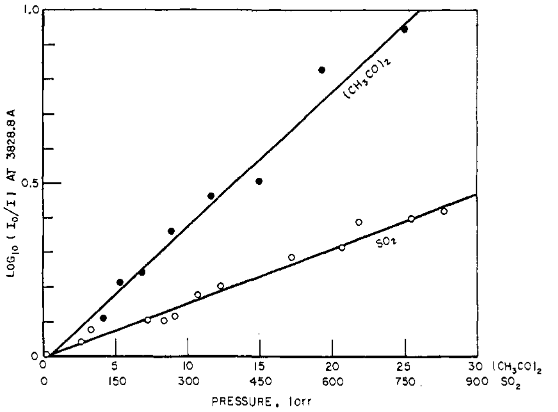

Figure 6. Plot of the absorbance at the laser wavelength of 3828.8 Å as a function of pressure for SO_2 and $(CH_3CO)_2$ gases at 25°; the pathlength was 60.3 cm; these data were used to estimate ϵ_{SO_2} and ϵ_{Ac_2}.

is extensive rotational structure in the triplet absorption band in the region of the laser line, it is necessary to measure ϵ_{SO_2} under the exact conditions used in the phosphorescence emission experiments. This was accomplished by splitting the laser beam into two components; one went to the detector directly and the other to a similar detector after transmission through the 60.3-cm path absorption cell. The two detectors were balanced with the cell empty. From the ratios of the heights of the two signals from experiments at varied pressures of pure SO_2 or Ac_2, the data of Figure 6 were obtained. The linearity of the log (I_0/I) *vs.* pressure plots shows that the absorption followed the Beer–Lambert law quite well for the incident 3828.8-Å laser beam. The least-squares lines which describe the data best are: log $(I_0/I) = [(5.26 \pm 0.46) \times 10^{-4}]$ P_{SO_2} (Torr) $+ (6.6 \pm 105) \times 10^{-4}$ and log $(I_0/I) = [(3.92 \pm 0.37) \times 10^{-2}]P_{Ac_2}$ (Torr) $- (1.8 \pm 4.8) \times 10^{-2}$; the intercepts are equal to zero within the experimental error as expected. The slopes give: $\epsilon_{SO_2} = 0.16 \pm 0.02$ and $\epsilon_{Ac_2} = 12.1 \pm 1.1$ l./(mol cm) at 3828.8 Å. It is not surprising that the estimate for SO_2 is considerably higher than the value suggested by the low-resolution data of Figure 2a. The laser beam absorption has been carefully matched to one of the rotational lines in the fine structure, and such structure is washed out by the low resolution of the recording spectrophotometer used to obtain the Figure 2a data. The value for Ac_2 is in fair agreement with an estimate made using a conventional spectrophotometer and standard technique ($\epsilon_{Ac_2} \simeq 9.6$ l./(mol cm) at 3829 Å). This region of biacetyl shows little structure, and the degree of agreement between the two values lends some confidence to the laser technique employed.

The rate function, $k_9 + k_{10} + k_{11}[Ac_2] + k_{12}[C_6H_{12}]$, which appears in relation G, can be evaluated directly from the $^3Ac_2$ lifetime data. For the conditions employed here, constant cyclohexane pressure at 85.1 Torr, the reciprocal lifetime is independent of the $[Ac_2]$ over the range of concentrations employed in this work. Hence the average of our measured values[19] $1/\tau = (6.78 \pm 0.26) \times 10^2$ sec^{-1} $= k_9 + k_{10} + k_{11}[Ac_2] + k_{12}[C_6H_{12}]$ for our conditions. Collisional deactivation of the electronic energy in $^3Ac_2$ by added cyclohexane or Ac_2 has been shown to be relatively unimportant,[20] so as one expects, the lifetime found here is similar to that reported for pure biacetyl excited in the 4000-Å region: $1/\tau = 6.1 \times 10^2$;[21] 5.6×10^2 sec^{-1}.[22] The other rate constant function in relation H, $k_6 + k_7 + (k_{8a} + k_{8b})[SO_2]$, can be fully evaluated from our present data.

The phosphorescence quantum yield falls below 0.15 in 3660-Å photolyses of Ac_2 at low pressures, presumably due to the dissociation of vibrationally excited Ac_2 molecules; a similar though less marked effect would be expected for our experiments at 3828.8 Å. However, Ishakawa and Noyes[20] found that added cyclohexane at pressures greater than 45 Torr restored $(\phi_p)_{Ac_2}$ to its long-wavelength value, 0.15. Hence in this work we have employed biacetyl–cyclohexane mixtures to ensure the conditions leading to $(\phi_p)_{Ac_2} = 0.15$.[17,23]

The ratio of the proportionality factors, α/β, in relation H is not unity. The phototube response is wavelength dependent and is somewhat different for the two spectral regions of emission by SO_2 and Ac_2. There are minor differences in the fractions of the incident envelopes of phosphorescence of $^3SO_2$ and $^3Ac_2$ which are transmitted by the filter system placed in front of the phototube. Also the detector sees only a fraction of the total solid angle of emission from the excited triplets, but this fraction is exactly the same for the two emitters and cancels out in the α/β ratio in H. From the characteristics of the filters, the emission envelopes, and the phototube's response as a function of wavelength, we estimate $\alpha/\beta = 0.86$ for our conditions.

Now all of the required quantities in relation H have been evaluated and may be substituted into the relation to estimate $(\phi_p)_{SO_2}$. The value at $[SO_2] = 0$ gives

$$(\phi_p)_{SO_2=0} = k_6/(k_6 + k_7) = 0.12 \pm 0.09$$

Within experimental error this checks well with the estimate $(\phi_p)_{SO_2=0} = k_6/(k_6 + k_7) = 0.15 \pm 0.11$, derived in the previous section from the steady-state phosphorescence studies. It is also in qualitative accord with the integrated extinction coefficient data for k_6; using our measured $k_6 + k_7$ this gives $(\phi_p)_{SO_2=0} \simeq 0.06$.

All of the available data suggest that the isolated sulfur dioxide triplet molecule undergoes some form of nonradiative decay with relatively high efficiency. The presence of the forbidden antisymmetric stretching frequency in the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ transition indicates a strong vibrationally induced spin–orbit coupling with another electronic state of SO_2.[7] It is reasonable to suppose that such a strong perturbation can give rise to such a nonradiative decay. Several possible mechanisms for this process must be considered in view of our present limited knowledge. Process 7 may involve simply the intersystem crossing of the triplet molecule to the isoenergetic vibrational levels of the ground state. However, one expects this process to be very slow for such a simple molecule as

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(19) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, manuscript in preparation.

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(21) G. M. Almy and S. Anderson, *ibid.*, **8**, 805 (1940).

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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 $^3\mathbf{B}_1$ state, then conceivably a large fraction of the $^3\mathbf{B}_1$ 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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The Triplet Sulfur Dioxide–Carbon Monoxide Reaction Excited within the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ "Forbidden" Band

George E. Jackson and Jack G. Calvert*

Contribution from the Department of Chemistry and the ElectroScience Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received September 8, 1970*

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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