TABLE OF ATOMIC MASSES OF SELECTED ISOTOPES

Name	Symbol	Atomic no.	Mass no.	Atomic mass	Name	Symbol	Atomic no.	Mass no.	Atomic mass
Hydrogen	H	1	1	1.00782	Promethium	Pm	61	143	142.9110
Deuterium	D	1	2	2.01410				145	144.9128
Tritium	T	1	3	3.01605				147	146.9152
Helium	He	2	3	3.01603	Lead	Pb	82	204	203.9731
			4	4.00260				206	205.9745
Lithium	Li	3	6	6.01512				207	206.9759
			7	7.01600				208	207.9766
Boron	B	5	10	10.0129	Uranium	U	92	233	233.0396
			11	11.0093				234	234.0410
Carbon	C	6	12	12 exactly				235	235.0439
			13	13.0034				236	236.0456
			14	14.0032				238	238.0508
Nitrogen	N	7	14	14.0031	Plutonium	Pu	94	238	238.0496
			15	15.0001				239	239.0522
Oxygen	O	8	16	15.9949				240	240.0538
			17	16.9991				241	241.0569
			18	17.9992				242	242.0588
Sulfur	S	16	32	31.9721				244	244.0642
			33	32.9715	Curium	Cm	96	242	242.0589
			34	33.9679				244	244.0628
			36	35.9671				246	246.0672
								247	247.0704
								248	248.0724

Decay Mechanism of Triplet Sulfur Dioxide Molecules Formed by Intersystem Crossing in the Flash Photolysis of Sulfur Dioxide (2400–3200 Å)

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Abstract: The lifetimes of sulfur dioxide triplet-state molecules ($^3SO_2$) have been measured through phosphorescence intensity–time studies in pure SO_2 at a series of temperatures (25–100°) and pressures (13–366 μ). The $^3SO_2$ species were generated by intersystem crossing from excited singlet molecules ($^1SO_2$) formed in the flash photolysis of SO_2 (2400–3200 Å). The data from runs at pressures above 70 μ give the following rate constant estimates: $^3SO_2 + SO_2 \rightarrow SO + SO_3$ (8a) and $^3SO_2 + SO_2 \rightarrow 2SO_2$ (8b), $\log[k_{8a} + k_{8b}$, l./(mol sec)$] = 10.60 \pm 0.47 - (2.79 \pm 0.68$ kcal/mol)/2.303RT; $^3SO_2 \rightarrow SO_2 + h\nu_p$ (6) and $^3SO_2 \rightarrow SO_2$ (7), $k_6 + k_7 = (1.13 \pm 0.18) \times 10^3$ sec^{-1}, independent of the temperature (25–100°). The existing rate data confirm the inequalities $k_{8a} > k_{8b}$ and $k_7 > k_6$. The Stern–Volmer plot of the $^3SO_2$ lifetime data shows an upward curvature at pressures below about 60 μ. The difference between the reciprocals of the measured lifetime at low pressure and those estimated by the extrapolation of the high-pressure data is found to be proportional to the reciprocal of the SO_2 concentration. It is concluded that a significant fraction of the $^3SO_2$ molecules diffuse to the wall and are deactivated heterogeneously in runs at low pressures.

The demonstrated importance of the excited triplet sulfur dioxide molecule ($^3SO_2$) in the photochemistry of sulfur dioxide[1–4] has stimulated an increased interest in the further characterization of this species. Some reactions of $^3SO_2$ have been deduced recently from phosphorescence lifetime measurements in sulfur dioxide excited by a 3828.8-Å laser pulse which lies within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band.[5,6] Morikawa has studied the reactions of the $^3SO_2$ species formed in very different experiments.[5] He excited singlet sulfur dioxide molecules ($^1SO_2$) by the flash photolysis of sulfur dioxide within the first allowed absorption band (2400–3200 Å). He followed the phosphorescence decay of triplets created by intersystem crossing from the excited molecules. Morikawa found that the $^3SO_2$ molecules formed by this method showed similar reactivity to those

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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.*, in press.

(3) E. Cehelnik, C. W. Spicer, and J. Heicklen, *J. Amer. Chem. Soc.*, submitted for publication.

(4) G. Jackson and J. G. Calvert, *ibid.*, **93**, 2593 (1971).

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

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

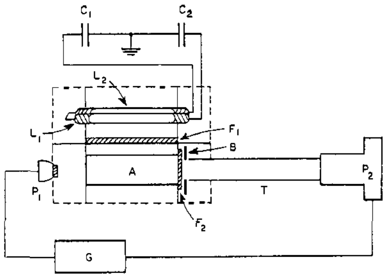

Figure 1. Diagram of the equipment used in the flash photolytic study of the $^3SO_2$ phosphorescence lifetimes; see the text for the explanation of the components.

created directly by absorption within the singlet–triplet band. This result was somewhat surprising, since the flash photolytic experiments generated triplets initially with as much as 15–44 kcal/mol of energy excess over those formed directly by 3828,8-Å laser excitation.

In this work we have repeated and extended the flash studies initiated by Morikawa. We have confirmed his findings and have obtained significant new information on the quenching reactions of the $^3SO_2$ species: (1) the bimolecular rate constant for $^3SO_2$ quenching by SO_2 has been evaluated as a function of temperature for the first time; (2) estimates have been made of the rate constants for the first-order $^3SO_2$ decay reactions in isolated $^3SO_2$ molecules at several temperatures; and (3) a heterogeneous mode of triplet decay has been observed in experiments at low pressures (P_{SO_2} = 13–60 μ).

Experimental Section

The apparatus employed was constructed in our laboratory. Much of the original work was done by Dr. Akira Morikawa. Some elements of the equipment are shown in Figure 1. Two flash lamps (L_1 and L_2) were placed above and slightly to the sides of the photolysis cell A. They were fabricated locally from Suprasil quartz (10 mm in diameter, 140 mm long) with heavy-duty tungsten metal electrodes sealed to the ends. Each flash lamp had a side arm through which evacuation and recharging with xenon gas (20 Torr) could be effected when necessary. The lamps were triggered by a high-voltage pulse applied to a loop of small copper wire placed around both of the lamps. The flash lamps were connected in electrical series, and in turn these were in series with two 10-μF, low-impedance, General Electric capacitors, C_1 and C_2 in Figure 1. The flash energy of 10–30 J created a burst of light of less than 10-μsec half peak time. The lamps were housed in a light-tight box made of Bakelite plates coated with black Formica. Light reaching the cell A (2400–4000 Å) passed through a Corning 7-54 (9863) glass filter, F_1 in Figure 1; the beam of light illuminated the entire cell volume quite uniformly.

The photolysis cell A was constructed of Suprasil quartz (50 mm in diameter, 100 mm long). The temperature of the cell was controlled within ±0.3° by a large thermostated box which surrounded the flash lamp and photolysis systems.

Emission from the cell was monitored by two detectors, P_1 and P_2. The flash produced a signal from the photodiode, P_1 in Figure 1, which activated the delayed-pulse generator G. About 200 μsec following the flash, the pulse from G activated the cathode-first dynode circuit of the photomultiplier P_2 (EMI 6275B) by means of a solid-state switch. The emission from the cell A arrived at the photomultiplier P_2 after passage through the filter F_2 (Schott and Jena glass filter, WG-1, sharp transmission cutoff for $\lambda < 3600$ Å), the aperture B (40 mm in diameter), and the collimation tube T. The tube (400 mm long, 40 mm in diameter) was coated inside with flat black paint, as were all of the exposed surfaces in the cell and photomultiplier housings. With the combination of filters and the geometrical arrangement of the parts, light seen by the photomultiplier was restricted to the range above 3600 Å and originated largely from excited-molecule emission within the cell volume. The emission decay signal from the photomultiplier was fed to an oscilloscope (Tektronix Model 3B3 scope, 3A1 dual-trace amplifier). The sweep of the oscilloscope was triggered after a 300-μsec delay following the flash, and the trace of the phosphorescence intensity was monitored and photographed. A small and very reproducible signal resulted from the tail of the flash-lamp emission, scattered largely from the left-hand window of the cell A in Figure 1. A reference signal was recorded with the cell empty prior to each lifetime determination. This trace on the oscilloscope was used as the baseline for the phosphorescence signal obtained in the sequential run with added SO_2.

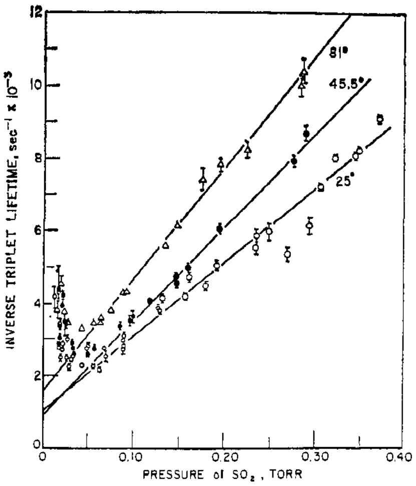

Figure 2. Stern–Volmer plot of phosphorescence lifetime data from the flash photolytic excitation of SO_2 in experiments at three temperatures: O, 25°; ●, 45.5°; Δ, 81°.

The observed phosphorescence intensity followed closely an exponential dependence on time. The relative intensities (I_p) at several times were determined accurately from the decay curves, and log I_p *vs.* time data were fitted by a least-squares linear program. The reciprocal lifetimes were determined from the slopes of these lines.

The reagent SO_2 gas employed was obtained from Matheson Corp. and was further purified by vacuum distillation. The pressure of the SO_2 was determined with a calibrated transducer–digital voltmeter combination.

Discussion

The $^3SO_2$ Quenching Reaction Mechanism. The quenching reactions of the excited triplet sulfur dioxide molecules ($^3SO_2$) have been studied in this work using flash photolytic excitation. The excited singlet molecules ($^1SO_2$) are formed directly by light absorption within the first allowed electronic absorption band of sulfur dioxide (2400–3200 Å). The triplet molecules are generated in secondary thermal reactions of the excited singlet molecules. The $^1SO_2$ and $^3SO_2$ species decay by a rather complex reaction scheme which was proposed in previous studies.[7,8] It is instructive to consider the present lifetime data in terms of the following mechanism.

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

$$^1SO_2 + SO_2 \longrightarrow (2SO_2) \qquad (1)$$

$$\longrightarrow {}^3SO_2 + SO_2 \qquad (2)$$

$$^1SO_2 \longrightarrow SO_2 + h\nu_f \qquad (3)$$

$$\longrightarrow SO_2 \qquad (4)$$

$$\longrightarrow {}^3SO_2 \qquad (5)$$

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

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

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

Table I. Reciprocal Lifetimes of $^3SO_2$ Excited in Flash Photolyses of SO_2 (2400–3200 Å) at Various Pressures and Temperatures

P_{SO_2}, μ	$1/\tau$, sec^{-1} × 10^{-3}	P_{SO_2}, μ	$1/\tau$, sec^{-1} × 10^{-3}	P_{SO_2}, μ	$1/\tau$, sec^{-1} × 10^{-3}	P_{SO_2}, μ	$1/\tau$, sec^{-1} × 10^{-3}
25°						81°	
366	9.12	156	4.64	22	4.18	288	10.38
348	8.25	143	4.18	21.1	3.41	286	10.34
345	8.07	102	3.53	21.0	3.92	285	10.03
322	8.02	95	3.31	19.7	4.09	225	8.24
296	7.23	84	2.92	18.0	3.04	195	7.82
295	6.15	81	2.99	17.6	2.86	175	7.40
270	5.39	55	2.64	17.1	4.38	148	6.13
250	5.99	37	2.48	17.0	4.22	135	5.57
236	5.86	22	2.79			90	4.29
235	5.53	21	3.67	50°		89	4.29
192	5.05	18	2.94	315	9.37	88	4.29
180	4.48	15.6	3.23	282	8.70	75	3.78
162	4.72			252	7.83	65	3.57
158	4.16	45°		201	6.05	64	3.47
132	4.10	315	7.91	200	6.20	57	3.44
129	3.80	240	6.54	182	5.94	43.5	3.27
128	3.83	215	5.28	160	5.29	29	3.49
90.1	3.07	195	6.21	147	4.76	24	3.77
90.0	3.12	175	5.19	110	3.84	21	4.50
89.7	2.87	157	4.38	99	3.32	20	4.30
89.6	2.98	125	4.35	98	3.84	17	3.78
89.5	2.94	103	3.71	82	3.51	16	4.17
89.2	2.74	88	3.26	80	3.06		
89.0	2.62	74	3.04	55	2.52	100°	
80.0	2.74	72	2.87	39	2.34	330	16.53
70.0	2.52	51	2.57	28	2.55	272	12.98
63.0	2.15	50	2.80	21	2.80	211	9.99
56.0	2.24	24	3.46	19.7	2.27	196	9.32
43.5	2.26	18.5	3.35			168	8.11
34.0	3.00			60°		161	7.57
32.0	2.45	45.5°		270	8.74	85.2	4.87
29.0	2.21	290	8.68	212	7.00	85.0	4.34
28.0	3.06	275	7.91	186	6.08	81	5.07
27.0	2.47	195	6.05	181	6.23	80.2	4.92
23.0	2.84	160	4.96	180	5.87	80.0	4.60
21.0	2.69	148	4.48	155	5.53	66	4.21
20.0	2.49	147	4.72	99	3.89	62	4.06
19.5	3.39	118	4.04	96	4.22	49	4.00
17.8	2.73	100	3.62	78	3.47	39	3.77
17.0	4.29	96	3.46	73	3.21	32	3.12
13.0	4.11	89	3.22	55	3.00	27.7	3.86
40°		85	3.36	41	2.82	25.1	4.11
360	9.83	68	2.73	27	3.21	25.0	4.29
280	7.97	58	2.74	25.8	3.28	24.8	4.21
270	7.26	50	2.71	20.1	3.57	21.0	4.59
204	5.83	36	2.61	20.0	3.65	20.4	3.59
203	5.58	34	2.73	19.2	3.39	20.3	4.31
158	4.60	32	2.84	19.0	4.89	17.2	3.40
157	4.31	26	3.39	17.5	4.63	16.8	4.86
				14.3	5.15	14.3	4.77
						14.2	4.07

$$^3SO_2 \longrightarrow SO_2 \qquad (7)$$

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

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

Lifetimes of phosphorescence decay were measured in 190 different experiments at 8 temperatures (25–100°) and over a range of pressures of sulfur dioxide (13–366 μ). The data are given in Table I. Stern–Volmer plots of the typical lifetime data from three temperatures are shown in Figure 2. For the range of pressures above about 60 μ, the data fit well the linear form of relation A anticipated from the above mechanism. However, an unexpected and very interesting

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

result is seen for runs at pressures below about 60 μ; there is an increasingly serious deviation of the $1/\tau$ values from the linear form of the high-pressure data. The previous laser studies were made at higher pressures than those used here ($P_{SO_2} \geq 160$ μ), so this effect has not been observed previously. It is important that we evaluate the possible influence of this effect on the estimation of the rate constant sums, $k_{8a} + k_{8b}$ and $k_6 + k_7$. The parameters that control the low-pressure phenomenon were discovered by estimating the difference between the reciprocals of the observed lifetimes and the corresponding predicted values found from an extrapolation of the linear portion of the Stern–Volmer plot, $(1/\tau_{obsd}) - (1/\tau_{ext})$. These differences are plotted versus $1/[SO_2]$ in Figure 3. Within the necessarily large uncertainty in the differences, they appear to be independent of the temperature and proportional to the reciprocal of the sulfur dioxide con-

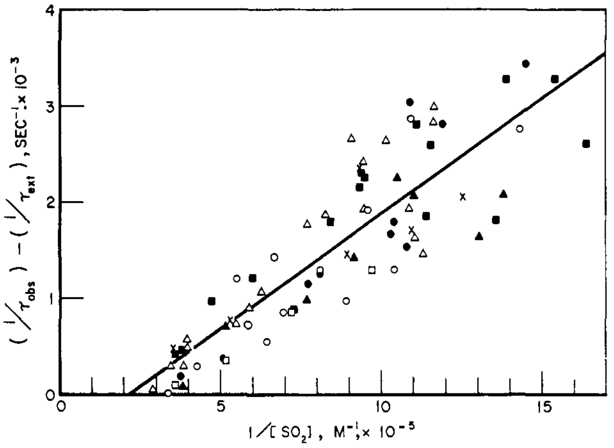

Figure 3. Plot of $1/[SO_2]$ *vs.* the difference between the reciprocals of the observed lifetime of $^3SO_2$ at low SO_2 pressures and that found by extrapolation of the linear portion of the Stern–Volmer plots at high SO_2 pressures ($P_{SO_2} \geq 70\ \mu$): ○, 25°; ×, 40°; △, 45.5°; □, 50°; ●, 60°; ▲, 81°; ■, 100°.

centration for $[SO_2] \leq 3 \times 10^{-6}\ M$. Several possible explanations of this effect must be evaluated.

(1) It is possible that our experiments are complicated by the appearance of significant fluorescence emission among the phosphorescence at low pressures of sulfur dioxide. Observations of emission were started after a 300-μsec delay following the initiating flash. The delay was designed to avoid other sources of emission within the triplet phosphorescence region (3600–4900 Å). The flash had a less than 10-μsec half-peak decay time, but the long tail of emission, characteristic of the xenon flash source, gave some scattered light within the $^3SO_2$ emission region at times less than 300 μsec. Furthermore the filter used to key the photomultiplier response to the triplet phosphorescence could not discriminate well against the excited singlet emission, since there is an extensive overlap of the fluorescence and phosphorescence envelopes. It is fortunate for the success of our experiments that the singlet quenching reactions 1 and 2 occur at rates commensurate with the number of $^1SO_2$–SO_2 collisions per liter per second, while triplets are quenched much less effectively.[7,9–11] Thus the 300-μsec delay in starting the emission measurements was important to ensure the near-total decay of the $^1SO_2$ molecules formed in the flash. We can evaluate the extent of the interference of the fluorescence emission in these experiments using the best estimates for the rate constants for reactions 1–8.[5,7] Of course the interference will be a maximum at the lowest pressures employed ($P_{SO_2} = 13\ \mu$), since the rate of quenching of singlets and the rate of formation of triplets are both minimized for these conditions. At $P_{SO_2} = 13\ \mu$, 99% of the singlets formed in the flash have decayed in 118 μsec, and all but 1% of the total triplets to be formed in the experiment have appeared at this time. After 300 μsec at $P_{SO_2} = 13\ \mu$, the intensity of phosphorescence to that of fluorescence $\cong$ 207. At $P_{SO_2} = 70\ \mu$, the ratio is 9.4×10^{10}. Of course the filter system employed removes preferentially about 64% of the fluorescence emission so that the lowest ratio of intensities of phosphorescence to fluorescence seen by the phototube is about 323 for runs at the lowest pressure, $P_{SO_2} = 13\ \mu$. It is clear that interference from fluorescence emission in the recorded phosphorescence emission signal at 300 μsec, and at later times following the flash, is negligible for our conditions. This theoretical conclusion has been borne out by the observed kinetics of the emission followed in this work. The linear correlation coefficients for the plots of the logarithm of the intensity *vs.* time data were usually better than 0.998 even in runs at the lowest pressures. Obviously we were not studying the decay of emission from two excited sulfur dioxide species with different lifetimes. The observed data must apply to the phosphorescence emission of the $^3SO_2$ species for all the conditions used here, and the deviation of the lifetime data from the Stern–Volmer relation at low pressures can in no way result from the interference from excited-singlet molecule emission.

(2) Deviations from the Stern–Volmer relation at low pressures have been observed previously in experiments in which only a small fraction of the total volume of the fluorescence cell was illuminated by the light and the emission from the same small volume was monitored by the photomultiplier.[12] In many such cases the effect can be accounted for quantitatively by the postulate that an increasing fraction of the excited molecules diffuse from the monitored volume element as the pressure is decreased in successive experiments. However, in the present case the molecules within the entire cell volume are excited rather homogeneously, and no appreciable concentration gradients should exist, except for those volume elements very near the cell wall. This mechanism cannot be important in the present work.

(3) The alternative mechanism which we feel is responsible for the low-pressure deviations from the Stern–Volmer relation involves the removal of $^3SO_2$ molecules at the wall in the experiments at low pressure. Note that the mean free path of the triplet molecule is about 0.08 cm at the point of detectability of the effect: $[SO_2] = 3 \times 10^{-6}\ M \equiv P_{SO_2} = 56\ \mu$ (25°). At the lowest pressure employed here, $P_{SO_2} = 13\ \mu$, the mean free path of the $^3SO_2$ molecule is about 0.34 cm. At 25° the average distance the $^3SO_2$ molecule will diffuse during its lifetime will be about 0.8 cm at 56 μ and 2.1 cm at 13 μ.[13] These facts suggest qualitatively that diffusion of the excited triplets to the wall during their lifetimes can be important for the low-pressure conditions. If the triplets reaching the wall are quenched with a reasonably high efficiency and the pressure is such that a significant fraction of the triplets formed in the cell reach the wall during their lifetimes, then the observed effect can be rationalized at least qualitatively by adding reaction 9 to the homogeneous reaction mechanism.

$$^3SO_2 + \text{wall} \longrightarrow SO_2 + \text{wall} \qquad (9)$$

One would expect the rate to be limited by the rate of triplet encounters with the wall, and this would be

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

(10) H. D. Mettee, *J. Chem. Phys.*, 49, 1784 (1968).

(11) S. J. Strickler and D. B. Howell, *ibid.*, 49, 1947 (1968).

(12) For one example, see G. M. Almy and S. Anderson, *ibid.*, 8, 805 (1940).

(13) In making this estimate we have used the approximation given by S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 446, that the time required for a molecule to diffuse a distance x (cm) $= x^2/D$; D is the diffusion constant, calculated as $80.6/P_{SO_2}$ (Torr) cm^2/sec, using $\sigma_{SO_2} = 4.04$ Å.

proportional to the inverse of [SO_2] for those molecules for which the mean free path is considerably less than their distance from the wall. For the pressure range we have employed, this condition is met. A more quantitative theoretical treatment of these low-pressure data is not in order here. However, it is important to the determination of accurate homogeneous reaction rate constants to judge the extent of the heterogeneous reaction of the $^3SO_2$ molecules from the actual experimental data by using the least-squares equation derived to fit the data of Figure 3

$$1/\tau_{\text{obsd}} - 1/\tau_{\text{ext}} = -0.519 \times 10^3\ \text{sec}^{-1} + 0.239 \times 10^{-2}\ M\ \text{sec}^{-1}/[SO_2]$$

From this equation it can be shown that the normal lifetime of $^3SO_2$ molecules which decay only by homogeneous reactions is altered by less than 3% by the occurrence of the wall reaction for runs in which $P_{SO_2} \geq 70\ \mu$. It is evident that we can derive accurate rate parameter estimates for the homogeneous reactions from runs in the pressure range above 70 μ.

Determination of the Rate Constants for the $^3SO_2$ Quenching Reactions with Sulfur Dioxide. Estimates of the rate constants for the homogeneous quenching reactions of the excited triplet sulfur dioxide reactions 8a and 8b can be derived from the lifetime data of Table I for runs at pressure of sulfur dioxide above 70 μ. The slopes of the least-squares lines derived from the $1/\tau$ *vs.* P_{SO_2} plots (as in Figure 2) gave the estimates of $k_{8a} + k_{8b}$ for several temperatures which are summarized in Table II. The following temperature-dependent function for $k_{8a} + k_{8b}$ was estimated from the least-squares fit of the Arrhenius plot of these rate constants (Figure 4).

Table II. Summary of Rate Constant Estimates for $^3SO_2$ and the Lifetimes of Isolated $^3SO_2$ Molecules at Several Temperatures

Temp, °C	$k_{8a} + k_{8b}$, l./(mol sec) × 10^{-8}	$k_6 + k_7$, $\text{sec}^{-1} \times 10^{-3}$	Lifetime of $^3SO_2$, sec × 10^4 ($P_{SO_2} = 0$)
25	3.61 ± 0.28[b]	1.12 ± 0.27	9.0 ± 2.2
27[a]	3.9 ± 0.7	1.27 ± 0.27	7.9 ± 1.7
40	4.80 ± 0.28	0.82 ± 0.23	12.2 ± 3.4
45	4.03 ± 0.58	1.55 ± 0.43	6.5 ± 1.8
45.5	5.12 ± 0.28	0.96 ± 0.22	10.4 ± 2.4
50	5.58 ± 0.30	0.97 ± 0.24	10.3 ± 2.6
60	5.54 ± 0.40	1.30 ± 0.34	7.7 ± 2.0
81	6.70 ± 0.34	1.61 ± 0.26	6.2 ± 1.0
100	10.50 ± 0.80	0.85 ± 0.54	11.8 ± 6.4

[a] Data of Morikawa.[5] [b] 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.

$$\log [k_{8a} + k_{8b}, \text{l./(mol sec)}] = 10.60 \pm 0.47 - (2.79 \pm 0.68\ \text{kcal/mol})/2.303RT$$

The only previous estimates of this rate constant sum come from experiments near room temperature. The first 3828.8-Å laser experiments carried out at 25° with P_{SO_2} in the range 1–25 Torr,[5] and the more recent laser study at 25° over a wider range of pressures (0.16–18 Torr),[6] gave the values $k_{8a} + k_{8b} = (3.8 \pm 0.1) \times 10^8$ and $(3.9 \pm 0.1) \times 10^8$ l./(mol sec), respectively. The earlier flash studies[5] at 27° gave $k_{8a} + k_{8b} = (3.9 \pm 0.7) \times 10^8$ l./(mol sec). Our results are in excellent agreement with these estimates; $k_{8a} + k_{8b} = (3.6 \pm 0.3) \times 10^8$ and $(3.7 \pm 0.3) \times 10^8$ l./(mol sec) for 25 and 27°, respectively.

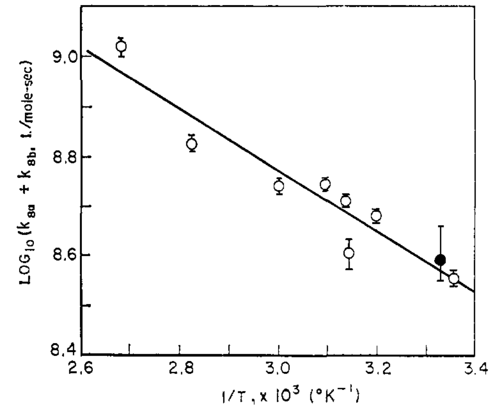

Figure 4. Arrhenius plot of the rate constant sum $k_{8a} + k_{8b}$; ●, from the experiments of Morikawa at 27°.[5]

From existing data it is possible to estimate the relative importance of reactions 8a and 8b. If we accept the observation that SO_3 is derived primarily in reaction 8a with little, if any from reaction 1,[1] then for experiments at SO_2 pressures above 5 Torr, the rate constant ratio $k_{8a}/(k_{8a} + k_{8b})$ should be given by relation B. The fraction of bimolecular $^3SO_2$–SO_2

$$k_{8a}/(k_{8a} + k_{8b}) = \Phi_{SO_3}[(k_1 + k_2)/k_2] \qquad \text{(B)}$$

quenching collisions which result in intersystem crossing, $k_2/(k_1 + k_2)$, has been estimated to be 0.080 ± 0.014 at 2875 Å,[7] ~0.09 at 2963 Å,[14] and ~0.10 at 3020 Å.[14] There is a very limited quantity of data for the quantum yields of SO_3 formation in SO_2 photolyses at 25°. Hall's data for a single run at 3130 Å with $P_{SO_2} = 12.7$ and $P_{O_2} = 10.6$ Torr gave $\Phi_{SO_3} = 0.036$;[15] for these conditions only 82% of the triplets are quenched by SO_2. Since the efficiency of SO_3 formation from the quenching reaction with O_2 is not known, the data are of little quantitative value for our purposes. In preliminary experiments at both 3130 and 2537 Å Warneck found $\Phi_{SO_3} \cong 0.05$ for pure SO_2.[16] Okuda, Rao, Slater, and Calvert reported an average value of $\Phi_{SO_3} = 0.08 \pm 0.02$ from runs in pure SO_2 (740 Torr) using a band of wavelengths (2537–3130 Å). The limited results show no wavelength dependence on either $k_2/(k_1 + k_2)$ and Φ_{SO_3}, so we may estimate averages from the available data: $k_2/(k_1 + k_2) = 0.09 \pm 0.01$ and $\Phi_{SO_3} = 0.065 \pm 0.015$ for SO_2 photolyses (2400–3200 Å) above 5 Torr. From these quantities we estimate the desired ratio.

$$k_{8a}/(k_{8a} + k_{8b}) \cong (0.065 \pm 0.015)/(0.09 \pm 0.01) \cong 0.72 \pm 0.18$$

The extent of chemical quenching of $^3SO_2$ by SO_2 seems to outweigh that for physical quenching. Furthermore, the absence of apparent curvature in the Arrhenius plot of $k_{8a} + k_{8b}$ in Figure 4 suggests either

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

(15) T. C. Hall, Jr., Ph.D. Thesis, University of California, Los Angeles, 1953.

(16) P. J. Warneck, GCA Technology Division, Bedford, Mass., personal communication to one of the authors.

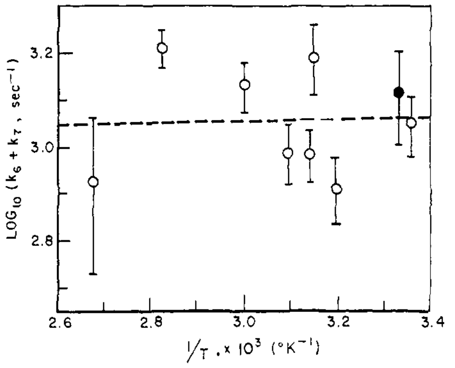


Figure 5. Arrhenius plot of the rate constant sum $k_6 + k_7$; ●, from experiments of Morikawa at 27°.[5]

that reactions 8a and 8b must have near the same activation energy or one of them, presumably k_{8a}, dominates for the temperature range used in this study, 25–100°. In view of all of the experimental results, it appears likely to us that $k_{8a} \cong k_{8a} + k_{8b}$, and we may interpret the rate constant sum measured here in terms of its applicability to reaction 8a.

It is instructive to compare the present rate data for reaction 8a with that for the similar thermal reactions, 10–12. All of these reactions involve an O-atom

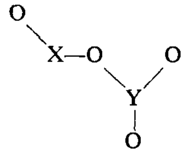
$$SO_2 + {}^3SO_2 \longrightarrow SO({}^3\Sigma) + SO_3 \qquad (8a)$$

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \qquad (10)$$

$$NO_2 + SO_2 \longrightarrow NO + SO_3 \qquad (11)$$

$$SO_2 + SO_2 \longrightarrow SO({}^3\Sigma) + SO_3 \qquad (12)$$

transfer from one triatomic molecule to another, and one would expect them to have transition states of very similar geometry



Although the chemical nature and the masses of atoms X and Y vary in the reaction series, they are similar, and one anticipates that the preexponential factors for reactions 8–12 would be about the same. For the first three reactions, this conclusion seems to be borne out by the experimental facts: log [A_{8a}, l./(mol sec)] $\cong$ 10.6 ± 0.5; log $A_{10} \cong 8.9 \pm 0.3$;[17] log $A_{11} \cong 11.1$.[18] However, reaction 12, the one of the series which appears most similar to (8a) at first glance, seems to be least like it: log $A_{12} \cong 12.0$; activation energy, $E_{12} \cong 70 \pm 7$ kcal/mol.[19a] The rate data in this case do not fit the mechanism suggested by reaction 12. The very high preexponential factor is inconsistent both with the relative complexity of the transition state involved in this series of reactions and the fact that a spin inversion is required if the product molecule SO is formed in its ${}^3\Sigma$ ground state. It may be noted that the activation energy, $E_{12} \cong 70 \pm 7$ kcal/mol, is equal within experimental error to the energy separation between the first excited triplet state of SO_2 and the ground state, $E_T = 73.7$ kcal/mol. It is probable that the rate data do not correspond to reaction 12 but to the rate-determining step[19]

$$2SO_2 \longrightarrow SO_2 + {}^3SO_2 \qquad (13)$$

Triplets so formed would react quantitatively by (8a) for the 3000–4000°K temperature range employed by Olschewski, Troe, and Wagner. The net result of the sequence of reactions 13 and 8a would fit the experimental results quite well. If this mechanism choice is correct, then triplet formation with spin inversion (reaction 13) must result on nearly every collision for which the necessary 73.7 kcal of energy is available. This may not be an unrealistic requirement; about 10% of the collisions of excited-singlet sulfur dioxide with ground-state SO_2 result in spin inversion.[7,14]

It is interesting to compare the observed activation energy for reaction 8a, $E_{8a} \cong 2.8$ kcal/mol, with the minimum barrier possible for the analogous thermal reaction 12; $\Delta H_{12} \cong 48$ kcal/mol. Obviously, there is considerable weakening of the S–O bonds in ground-state sulfur dioxide on being excited to the triplet state.

Estimate of the Rate Constant Sum, $k_6 + k_7$; the Intrinsic Lifetime of the ${}^3SO_2$ Molecule at Zero Pressure. Estimates of the theoretically important lifetime of the isolated sulfur dioxide triplet molecule can be made from the results obtained in this work. The intercepts of the Stern–Volmer plots from each of the eight series of experiments at different temperatures provide estimates of $k_6 + k_7$. The effects of the heterogeneous decay path of the ${}^3SO_2$ molecules were eliminated by using only the data for runs with $P_{SO_2} \geq 70\ \mu$. These results are summarized in Table II. Within the error limits of the estimates there is no obvious trend of the values with change in temperature. The least-squares fit of the Arrhenius plot of these data in Figure 5 gives an apparent activation energy $E = -0.07 \pm 1.7$ kcal/mol, or zero within experimental error. Thus the first-order radiative and nonradiative decay processes appear to be temperature independent. The weighted average of the nine values provides the best estimate of $k_6 + k_7$

$$k_6 + k_7 = (1.13 \pm 0.18) \times 10^3\ \text{sec}^{-1}$$

From the reciprocal of this rate constant sum, the best estimate is had of the intrinsic lifetime of the isolated SO_2 molecule at zero pressure

$$\tau_0 = 1/(k_6 + k_7) = (0.88 \pm 0.14) \times 10^{-3}\ \text{sec}$$

The estimate of τ_0 compares well with that found by Sidebottom, *et al.*,[6] $\tau_0 = (1.02 \pm 0.71) \times 10^{-3}$ sec. Their estimate came from the ${}^3SO_2$ lifetime data obtained from the 3828.8-Å laser-excited SO_2 experiments at 25° and at SO_2 pressures in the range 0.16–2.04 Torr.

The present work confirms the conclusion reached recently by other workers that the intrinsic lifetime of the ${}^3SO_2$ species is unexpectedly short.[5,6] Estimates of the *radiative* lifetime of the triplet are considerably higher than the experimentally observed lifetimes at zero pressure: $\tau_{rad} = (1/k_6) = 1.7 \times 10^{-2}$ (from integrated absorption data),[6] 0.85×10^{-2} (from ϕ_p of ${}^3SO_2$ at $P_{SO_2} = 0$, and τ_0 estimates from the 3828.8-Å

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(17) P. G. Ashmore and M. G. Burnett, *Trans. Faraday Soc.*, **58**, 253 (1962).

(18) G. K. Boreskov and V. V. Illarionov, *Zh. Fiz. Khim.*, **14**, 1428 (1940).

(19) (a) H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Z. Phys. Chem. (Frankfurt am Main)*, **44**, 173, (1965); (b) A. G. Gaydon, G. H. Kimbell, and H. B. Palmer, *Proc. Roy. Soc., Ser. A*, **276**, 461 (1963).

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.

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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]

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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).