Lifetime of the Lowest Triplet State of Sulfur Dioxide[1]

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Abstract: The lifetime of the first (triplet) excited electronic state of sulfur dioxide has been measured directly and found to have an average value of $(7 \pm 1) \times 10^{-3}$ sec, based on 82 individual measurements. Extreme values of the measurements are about 5 and 10 msec. Measurements were made in a pressure range from 3×10^{-3} to 1.5 mm, but there is no definite evidence that the lifetime depends on pressure. The SO_2 is excited in a pulsed electrodeless discharge, and the decay of optical emission is recorded with a photomultiplier and oscillograph. Experiments which establish the identity of the emitting species are described. The quenching efficiency of various foreign gases was investigated. The quenching efficiency of collisions of SO_2 molecules in the triplet state with SO_2 molecules or with foreign gases is extremely small. The identity of the upper state as a triplet state in fluorescence of SO_2 is supported by spin–orbit interaction calculations.

For many years, SO_2 has been of interest to those concerned with understanding the electronic structure and properties of molecules. It is a prototype of the class of AB_2 triatomic molecules having 18 valence electrons. SO_2 exhibits several discrete absorption systems in conveniently located regions of the spectrum, and it is readily excited to fluorescence.

The determination of transition probabilities is an active area of study in molecular electronic spectroscopy and is of interest in quantum-mechanical calculations of molecular electronic properties. Transition probabilities may be determined from absorption coefficients and from radiative lifetime measurements. The absorption coefficients of the electronic transitions of SO_2 are fairly well known. Much less is known about transition probabilities derived from experimental radiative lifetimes. The lifetime of the lowest energy excited electronic state of SO_2 is of particular interest because of the extremely weak transition between this state and the ground state. This quantity had not been measured directly prior to the start of the present investigation.

In the absorption region between 3900 and 3400 Å, referred to as the first electronic transition, the spectrum shows resolved vibrational structure, and some of the rotational structure associated with these vibrational bands has been partly resolved. The maximum absorption coefficient in this region is about 0.01 cm^{-1} (NTP) (λ_{max} 3740 Å). The origin of this transition appears to be at 3884 Å,[2] and the whole transition is well resolved from other electronic transitions.

The lowest excited electronic state of SO_2 is derived from the following molecular orbital configuration.

$$\ldots (1a_2)^2(3b_2)^2(4a_1)(2b_1)\ {}^{1,3}B_1$$

The symbols refer to a molecule with C_{2v} symmetry such as SO_2. Accumulated evidence,[3,4] including the evidence to be presented in this paper, indicates that the lowest state is ${}^3B_1$ rather than ${}^1B_1$, and we shall refer to it in this way.

The emission spectrum of SO_2 has been studied extensively. Three different methods have been used to produce SO_2 emission: optical excitation, electron bombardment, and shock-tube heating.[5] Work on optical excitation and excitation by electron bombardment has been summarized previously.[6] It should be added that electron bombardment may produce excited SO_2 molecules indirectly through the recombination of SO with oxygen atoms as suggested first by Gaydon[7] and studied in detail by Thrush, *et al.*[8]

The only previous quantitative information on the lifetime of the ${}^3B_1$ state of SO_2 came from measurements of fluorescence decay of the solid[6] at 77°K and from emission in shock-tube experiments[5] at relatively high pressures. Neither of these measurements was obtained under conditions which are favorable for the determination of the lifetime of the ${}^3B_1$ state in the absence of intermolecular interactions.

Optical excitation of SO_2 is preferable to other methods, because the final state reached by optical absorption can be more precisely defined. However, all attempts to use optical excitation in the present work failed. No attempt will be made to give more than the essential reasons for this failure, which are as follows. First, optical excitation to the triplet state requires that a large number of excited molecules be formed to ensure measurement of decay at a workable intensity level. This requirement could be met only with impractically long path lengths or by powerful flashtube sources. When the latter are used, the scattered or extraneous light level is too large for separating the weak fluorescence of the triplet state, with available filters or monochromators. Furthermore, the most significant measurements of a lifetime require low pressures of SO_2, so that extrapolation to zero pressure is possible. The factors mentioned above are inconsistent with the requirement of low pressure.

The method of electron bombardment was chosen. Various forms of this fundamental method have been used successfully for lifetime measurements in other molecular systems.[9-13]

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(1) Part of a dissertation submitted by R. B. Caton to the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy. This work was supported in part by the Office of Naval Research, and their assistance is gratefully acknowledged.

(2) J. B. Coon, R. E. deWames, and C. M. Loyd, *J. Mol. Spectry.*, **8**, 285 (1962).

(3) A. E. Douglas, *Can. J. Phys.*, **36**, 147 (1958).

(4) A. J. Merer, *Discussions Faraday Soc.*, **35**, 127 (1963).

(5) B. P. Levitt and D. B. Sheen, *Trans. Faraday Soc.*, **61**, 2404 (1965); **63**, 540 (1967).

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

(7) A. G. Gaydon, *Proc. Roy. Soc.* (London), **A146**, 901 (1934).

(8) M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, *ibid.*, **A295**, 355 (1966); C. J. Halstead and B. A. Thrush, *ibid.*, **A295**, 363 (1966).

(9) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961).

(10) M. Jeunehomme and A. B. F. Duncan, *ibid.*, **41**, 1692 (1964).

Experimental Details

The SO_2 was Matheson Anhydrous Grade, with a stated purity of 99.998%. It was distilled twice between solid CO_2–acetone and liquid nitrogen traps before admission to a storage bulb. In some of the experiments, other gases were used, all of which were Airco Assayed Research Grade gases supplied by Matheson Co. in Pyrex flasks. Argon had an assay of "no detectable impurities." Helium contained 2 ppm of neon as the only detectable impurity. Oxygen was contaminated by 159 ppm of N_2, 140 ppm of Ar, and 65 ppm of CO_2. A conventional vacuum system was used. Pressures were measured by mercury manometers and McLeod gauges, as well as several electronic gauges which were calibrated against McLeod gauges for each gas which was used. The fluorescence cell was usually a quartz cylinder 25 mm in diameter by 20 cm in length. One end was covered by a plane quartz window, and the other end was drawn into a horn-shaped taper through which connection was made to the vacuum line. In some of the experiments for investigation of wall effects and diffusion processes, a 12-l. Pyrex bulb with a quartz window for observation of the fluorescence was used.

For some of the lifetime measurements, an excitation unit similar to that used by Donovan and Duncan[9] was employed. A high-voltage spark was produced by switching the energy stored in a small capacitor through the primary of a spark coil taken from a Tesla coil leak tester. The switch was an adjustable aluminum sphere air spark gap. The spark gap was usually set to hold off from 2500 to 5000 V, corresponding to an energy input to a 0.08-μF capacitor of about 0.25–1.0 J. The output of this unit was a damped oscillation with a ringing frequency of about 1 Mc/sec. The pulse usually decayed to effectively zero amplitude after about 20 cycles, depending upon the pressure of gas in the cell. This source will be referred to as the spark coil source.

Some of the lifetime measurements were carried out with an EG and G Model TR-69 trigger transformer. With an energy input of 0.09 or 0.20 J, this unit produced a spark of 35,000- or 60,000-V amplitude according to data supplied by the manufacturer. The output was a single critically damped pulse whose rise time was less than 1 μsec. The width of the waveform at half-maximum amplitude was about 20 μsec.

The fluorescence detector was an RCA 1P21 photomultiplier tube powered by a voltage divider across a bank of "B" batteries totaling 900 or 1200 V (90 or 120 V per stage). The output from the photomultiplier was fed to the vertical deflection plates of a Dumont 303 oscilloscope. A load resistor was placed across the oscilloscope input terminals, adjusted to the photomultiplier output current and the decay time to be measured. In most of these experiments, the photomultiplier was switched on a short time after the emission from the discharge appeared. In this way, emission from the second (singlet) excited electronic state of SO_2 and from the recombination of SO and oxygen atoms could be avoided, and the sensitivity could be considerably increased without overloading the photomultiplier. The main component of the delayed detection system was a two-stage Schmitt trigger type of electronic circuit. The output of this unit was a square pulse of about 10-V amplitude and 30-μsec duration. The unit was started by a pulse from a photomultiplier tube which picked up part of the discharge emission. A series of resistor–capacitor combinations made it possible to vary the delay between about 0.002 and 3 msec. The output of this unit was fed through a coupling capacitor to the grid of a 5557 Thyratron switch in the circuit of the detecting photomultiplier voltage divided. The effects of the initial activation of the photomultiplier disappeared in a few microseconds, so that measurements of transient phenomena lasting longer than about 10 μsec were not impaired by the switching device.

The measurement of radiative lifetime was performed as follows. A sample of SO_2 at a pressure between 0.003 and 1.2 mm was introduced into the cell. The discharge was produced by the spark coil or the trigger transformer, and the transient oscilloscope display of the delayed photomultiplier response was photographed by a large aperture, short focal length camera. Delays of up to 2.4 msec were used. The usual delay during measurements of the triplet lifetime was 2 msec. A single trace could be photographed when the decay time of the trace was greater than 10 μsec. Time calibration of the decay traces was accomplished by superimposing on the photograph of the trace a calibrated damped oscillation generated within the oscilloscope. At sweep speeds slower than about 0.2 msec/in., the internal calibration display of the oscilloscope could not be resolved. Under this condition, the signal from a Heath 1G-82 sine wave generator was displayed on the oscilloscope screen and photographed immediately after the decay trace. The timing calibration of the oscilloscope was checked by comparing the internal timing display, the signals from a Knight KG-653 audiogenerator, and the signal from the Heath 1G-82 sine wave generator with the timing marks produced by an Accutronics Multi/Marker. The timing calibration error of the oscilloscope was not greater than 2%. Lifetimes or decay times were derived from the photographs by measuring the intensity as a function of time at ten or more points on a graphical projection of the photographic plate at about 5× magnification. The decays were exponential and the lifetime could be calculated from the slope of the semilogarithmic plot of intensity *vs.* time.

For some of the lifetime measurements, other gases were added to a known amount of SO_2 in order to investigate the relationship between the lifetime and the total pressure for a given number of emitting SO_2 molecules. The added gas was admitted to the cell while the SO_2 was frozen out in a cold finger at 77°K. After evaporating the SO_2, the gases were allowed to mix for a few minutes before any measurements were made. The ratio of the partial pressures of added gas and SO_2 was varied over a wide range. The ratio of Ar/SO_2 was between 0.046 and 33.5 at total pressures between 0.013 and 1.53 mm for several different series of experiments. A series indicates here a group of experiments performed on a single sample of SO_2 in which the pressure was changed by freezing out the SO_2 and expanding the added gas into an evacuated section of the vacuum system. One series of experiments was performed with helium as the added gas for which the ratio He/SO_2 varied between 0.2 and 3.8 at a total pressure of 0.12–0.48 mm. Oxygen was used as the added gas in one experiment for which the ratio O_2/SO_2 was 26.5 at a pressure of 2.20 mm.

Results

Before the results of the lifetime measurements are discussed, some mention should be made of the way in which we concluded that the observed emission decay originated from the $^3B_1$ state of SO_2. Emission spectra of SO_2 show that the triplet band system extends from ~3800 to ~4600 Å. Both discrete and pseudo-continuous emission from the $^1B_1$ state contribute to the spectrum from ~2600 to ~4600 Å. In an electrical discharge there is an additional contribution from a continuum due to the recombination of SO and atomic oxygen in the approximate wavelength region 2600–4600 Å. When the intense, short-lived $^1B_1$ emission from the pulsed discharge was avoided by delaying detection for 0.1 msec, two longer lived decays persisted in the region 3900–4600 Å, as selected by an appropriate filter. According to the above description of the spectrum, these decays must have been due to the triplet emission and the recombination continuum. The decays were both exponential, and their decay times differed by a factor of about 10. The longer lived of these two decays appeared only in the spectral region 3900–4600 Å and disappeared at shorter wavelengths. The shorter lived decay appeared at wavelengths shorter than 3900 Å, as well as in the region 3900–4600 Å. Therefore, we concluded that the longer lived decay must correspond to emission from the $^3B_1$ state of SO_2. This conclusion is further supported by evidence from spectra which were obtained under conditions identical with those for a lifetime measurement. These spectra show that only processes characteristic of the SO_2 system contribute to the emission in the region 3900–4600 Å. The appearance and disappearance of the longest lived decay with changes in wavelength shows in itself that the longest lived decay cannot arise from spurious

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(11) M. Jeunehomme, *J. Chem. Phys.*, 42, 4086 (1965).

(12) R. G. Bennett and F. W. Dalby, *ibid.*, 31, 434 (1959); 32, 1111, 1716 (1960); 36, 399 (1962).

(13) E. H. Fink and K. H. Welge, *ibid.*, 46, 4315 (1967).

electrical phenomena nor from chemical species other than SO_2.

The results of the experimental measurements of the triplet lifetime in pure SO_2 in the small cell are shown in Figure 1, where reciprocal lifetime is plotted *vs.* pressure. These results represent 38 of the 82 individual results which were obtained. The remaining measurements, which were made in mixtures of SO_2 with either Ar or He, are shown in Table I. The results with foreign gases at the same total pressure agree fairly well with the results which are shown in Figure 1. The results from measurements on mixtures of SO_2 and foreign gases in the 12-l. bulb agree very well with the results from similar mixtures at the same total pressure in the small cell.

Table I. Reciprocal Triplet Lifetime in Mixtures of SO_2 with Other Gases[a]

P_{SO_2}	P_M[b]	P_{total}	τ^{-1}, sec^{-1}	Source cell[c]
7	225 A	232	104	S, s
9	65 A	74	91	S, s
	91	100	87	
	115	124	126	
	151	160	116	
	210	219	128	
	250	259	120	
41	55 A	96	138	S, s
	82	123	143	
45	126 A	171	140	S, s
	180	225	152	
	350	395	126	
49	430 A	479	129	S, s
	520	569	128	
	660	709	145	
76	220 A	296	211	T, L
	240	316	199	
	290	366	194	
80	16 A	96	145	S, s
	36	116	139	
	82	162	158	
100	21 H	121	160	T, L
	67 A	167	185	S, s
	95 A	195	179	S, s
	114 H	214	155	T, L
	135 H	235	192	S, s
	197 H	297	156	T, L
	263 H	363	150	T, L
	380 H	480	149	T, L
130	91 A	221	171	T, s
	151 A	281	187	T, s
	256 A	386	178	T, s
	430 A	560	223	T, s
	750 A	880	239	T, s
	1400 A	1530	200	T, s

[a] Pressures in millimeters × 10^3. [b] A = argon; H = helium. [c] Source: S = spark coil; T = trigger transformer. Cell: L = large (12-l. bulb); s = small (25 mm × 200 mm cylinder).

There is no definite pressure dependence of the reciprocal lifetime apparent in Figure 1. If one assumes that there is no pressure dependence, the average of all 82 values of the reciprocal lifetime which were obtained in the pressure range 0.003–1.53 mm is 149 ± 20 sec^{-1}. The average of the low-pressure results for pure SO_2 in Figure 1 is 140 ± 22 sec^{-1}.

The apparent pressure independence of the triplet lifetime suggests that the quenching efficiency of collisions between SO_2 molecules in the triplet state and ground state SO_2 molecules or Ar atoms is very small.

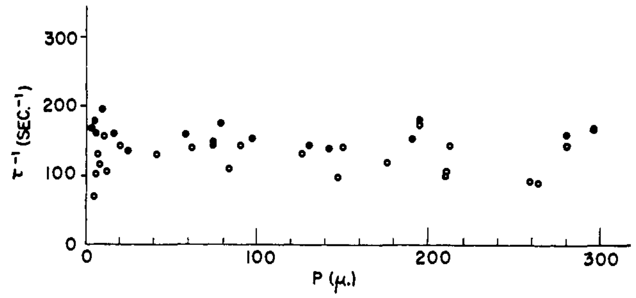

Figure 1.

From the one experiment in which a 20-fold excess of oxygen was used, one concludes that no preferential quenching occurred. By the procedure which was used in that experiment, only a rather large effect of the oxygen could have been detected.

We conclude that the lifetime of the $^3B_1$ state of SO_2 lies between 5 and 10 msec, the extreme values of the measurements in Figure 1 and Table I. The most probable value is 7 ± 1 msec, which is obtained from the reciprocal of the average value of the low-pressure results (Figure 1).

Discussion

The result that the lifetime is independent of pressure is perhaps to be expected. If ideas of spin conservation apply to this situation, then the removal of energy from SO_2 molecules in the $^3B_1$ state by ground state SO_2 molecules is an improbable process. On this basis, the lifetime of triplet SO_2 molecules is expected to be independent of pressure in pressure ranges where collisions are important, as well as in the region where collisions are infrequent. The fact that oxygen shows no preferential quenching of SO_2 triplet molecules merely suggests that the kinds of intermolecular interaction which allow radiationless transfer of energy in collisions of oxygen with some molecules (primarily organic species) are not of sufficient magnitude in collisions between SO_2 and O_2 to cause an observable effect under the conditions of our experiments.

The average value of the lifetime, which apparently does not depend upon pressure, should be a close approximation to the value at zero pressure. The latter value, which is usually obtained by extrapolation, is related to the oscillator strength, f_{nm}, by the equation

$$f_{nm}\tau_n = (\mu c\lambda^2/8\pi^2e^2)(g_n/g_m) \qquad (1)$$
$$= 1.55\lambda^2(g_n/g_m)$$

where λ is the mean wavelength of the transition, and g_n and g_m are the degeneracies of the upper and lower states, respectively. For the present calculation, the degeneracy of the upper state was taken to be unity rather than three, since, as Sidman[14] suggested, on the average only one of the three components of the spin is responsible for the spin–orbit coupling which allows the $^3B_1 \rightarrow {}^1A_1$ (ground state) transition in SO_2. λ in eq 1 may be taken as the wavelength of the absorption maximum, 3740 Å. Mulliken[15] gives two values of the oscillator strength of the $^1A_1 \leftarrow {}^3B_1$ transition in SO_2 which were calculated from different sets of measurements on the absorption spectrum. These values are 1×10^{-6}

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(14) J. W. Sidman, *J. Chem. Phys.*, **29**, 644 (1958).
(15) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

and 1.7×10^{-7}. An independent measurement in this laboratory[6] gave an f value of about 1×10^{-6}. The lifetimes calculated from eq 1 with the above oscillator strengths are 2.2 and 13 msec. The emission lifetimes are longer than the above by the ratio of the squares of the mean wavelengths. The wavelength of the emission maximum in this transition in SO_2 is 4155 Å. Thus, the emission lifetime is expected to be a factor of 1.2 times the above values, that is, 2.6 or 15.5 msec. The measured value of the lifetime from the present work falls between these two values.

Further comparison can be made with the work of Levitt and Sheen.[5] These authors concluded from the results of their examination of the emission from shock-heated SO_2 that the lifetimes of the two lowest excited states of SO_2 are 7×10^{-6} sec for the $^1B_1$ state and 2×10^{-4} sec for the $^3B_1$ state. These authors do not state explicitly what pressures were used, but it can be assumed that in their experiments, the total pressure of SO_2 or of a mixture of SO_2 with Ar or N_2 was between 2 and 12 mm, or at least "a few millimeters." They used the following equation to calculate τ

$$I = \int I_\lambda \, d\lambda = (SO_2^*)/\tau(SO_2)$$

where I is the total emission intensity, and I_λ is the intensity at a particular wavelength (λ). The concentration ratio $(SO_2^*)/(SO_2)$ was calculated from a Boltzmann distribution using an activation energy determined from the temperature variation of the intensity. Levitt and Sheen state that the continuous emission which they observed at 4360 Å and longer wavelengths originated from smeared-out rotational and vibrational structure due to the strong excitation and high pressure inherent in the shock-tube method. The contribution to I_λ from the pseudo-continuous singlet emission in this wavelength region easily could have been underestimated. The contribution of the recombination continuum in this spectral region also may have been underestimated. Comparison of their value of the lifetime with the present value is difficult.

Greenough and Duncan's measurement[6] of the lifetime of the triplet SO_2 emission in solid SO_2 at 77°K should be mentioned. Their value of about 5×10^{-4} sec probably should not be compared with the presently measured value in SO_2 vapor. One would expect the crystal field of the solid lattice as well as other lattice environmental factors to have some effect upon the measured lifetime. Thus, it is felt that the disagreement between the lifetimes measured in the solid and gas phases is not very serious.

Of great interest is the fact that the measured triplet lifetime agrees approximately with that calculated from the integrated absorption coefficient, whereas the lifetime of the singlet state measured by Greenough and Duncan and by Douglas[16] is two orders of magnitude shorter than the value predicted from the integrated absorption coefficient. Douglas suggests that interelectronic level mixing of the $^1B_1$ state with the $^3B_1$ state or with the ground state can account for the discrepancy observed in the case of the singlet state lifetime.

Regardless of the manner in which the $^3B_1$ state is populated, fluorescence occurs only from the (0, 0, 0) and (1, 0, 0) vibrational levels to levels of the $^1A_1$ ground state. One would not expect that the two lowest vibrational levels of the $^3B_1$ state would interact very strongly with the $^1B_1$ state because of the difference in energy (3880 and 3560 cm^{-1}) and the difference in multiplicity. The difference in multiplicity between the $^3B_1$ and $^1A_1$ states could also cause the interaction between these states to be weak. Spin–orbit coupling in both of these cases is expected to be very small. That is, the probability of transferring energy in the (0, 0, 0) or (1, 0, 0) vibrational levels of the $^3B_1$ state to the $^1B_1$ or $^1A_1$ state could easily be small relative to the spontaneous radiation probability. The experimental results described in this paper appear to support this interpretation.

The transition between the $^3B_1$ and $^1A_1$ states of SO_2 presumably is allowed by spin–orbit coupling between the triplet state and a higher singlet state or states. An approximate calculation of this spin–orbit interaction energy was carried out to obtain a theoretical value of the lifetime which could be compared with experiment. Analysis of the rotational structure of the electronic transition to the $^3B_1$ state suggests that the electric moment changes perpendicular to the molecular axis.[4] If this analysis is accepted as correct,[17] a $^1B_2$ state will act as the perturbing state to allow the transition between the $^3B_1$ state and the ground state. Our calculation has been made on this assumption. This $^1B_2$ state arises from the configuration

$$\ldots (1a_2)(3b_2)^2(4a_1)^2(2b_1)\ ^{1,3}B_2$$

We have assumed that this $^1B_2$ state[18] of SO_2 lies at 42,550 cm^{-1}. We have neglected vibronic interactions in this selection. The details of the calculation followed exactly the procedure and formalism which were presented by Sidman[14] in a calculation of spin–orbit interaction in formaldehyde. A formula analogous to Sidman's eq (17) for the σ_z component of electron spin was employed.

The appropriate molecular orbitals for the $^3B_1$ configuration (I) and the $^1B_2$ configuration were chosen as modifications of the MO's of ozone, as reported by Fischer-Hjalmars.[19] The SCF–MO's of SO_2 which were recently reported by Ionov and Porai-Koshits,[20] which included contribution from the sulfur 3d orbitals, were felt not to be necessary for this order-of-magnitude calculation. The AO's which formed the LCAO–MO's were taken to be conventional Slater orbitals, and the corresponding effective screened nuclear potentials were used.

The estimated oscillator strength of the transition between the $^1B_2$ state and the ground state is about 0.1. On this basis, the resulting spin–orbit interaction energy between the $^3B_1$ state and the $^1B_2$ state is 6.7×10^{-3} eV. The oscillator strength of the $^3B_1 \rightarrow {}^1A_1$ transition is then calculated from Sidman's eq (4) to be 6×10^{-7} ($\tau = 4.4 \times 10^{-3}$ sec). Judging from the good agreement between our measured value of the triplet lifetime of SO_2 and the values calculated from the integrated

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(16) A. E. Douglas, *J. Chem. Phys.*, **45**, 1007 (1966).

(17) A referee of this paper has pointed out to us that the analysis in ref 4 may not be correct, and that a more detailed analysis is necessary for identification of the perturbing state; see J. T. Hougen, *Can. J. Phys.*, **42**, 433 (1964). If the transition is of parallel type rather than of a perpendicular type, perturbation by an $^1A_1$ state should be considered. Calculations based on the latter case have not been made.

(18) I. deBois and B. Rosen, *Discussions Faraday Soc.*, **35**, 124 (1963).

(19) I. Fischer-Hjalmars, *Arkiv Fysik*, **11**, 529 (1957).

(20) S. P. Ionov and M. A. Porai-Koshits, *J. Struct. Chem.* (USSR), **7**, 245 (1966).

absorption coefficient and from spin-orbit coupling, the experimental value of the lifetime seems to be reasonable.

The possibility exists that the emission rate process detected by the photomultiplier was not governed by the spontaneous transition probability of the $^3B_1$ state of SO_2 but was instead controlled by a diffusion process. Diffusion processes can be important in optical fluorescence experiments when only a small fraction of the volume of gas is illuminated. In the present experiments, however, the discharge and its resulting emission filled the entire body of either of the two cells. Along the line of vision of the detector, therefore, as many excited molecules would diffuse into view as were diffusing away from view. The population of excited molecules could not be depleted by this process unless the cell wall played a part in deactivation. On the basis of the experiments with the 12-l. bulb, one concludes that wall effects were not important. At all of the pressures which were used in this vessel, the diffusion displacement of an excited molecule was much less than the radius of the bulb. Under this condition the wall would not be expected to participate in quenching. The lifetimes which were measured with this vessel agree well with lifetimes measured in the small cell in the same pressure range. We conclude that diffusion and wall deactivation had no effect upon our experimental results.

Something should be said about the differences in the values of the lifetime obtained by the use of the two different excitation sources. Figure 1 and Table I show that the spark coil unit produced slightly larger values of the lifetime at a given pressure than the trigger transformer. It is believed that there are no fundamental differences in the function performed by the two units. Each provided a high-voltage pulse which decayed to essentially zero amplitude in a very short time relative to the lifetime which was to be measured. No predictable systematic errors could be found in the associated apparatus in the two cases. It is possible that a difference in the voltage output or in the damping characteristics of the two units may have produced an unknown chemical change in the gas which resulted in the small discrepancy in the observed lifetimes. It is very unlikely that physical differences in the makeup of the plasma which was created by the high-voltage spark would have any effect on the lifetime, because nearly all of the triplet emission originates in the lowest vibrational level of the $^3B_1$ state. The lifetime of the vibrationless level of the triplet state should not be affected by the initial energy distribution during excitation. It is felt that the discrepancy is not serious enough to cast doubt upon the validity of the results, but we cannot explain its origin.

In conclusion, we wish to point out that the uncertainty in these measurements is not of unusual magnitude for lifetime measurements in polyatomic systems. For example, a survey of ref 9–13 shows that deviations of 15 to 25% are not unusual for a set of measurements on a given diatomic or polyatomic system. Agreement of the lifetime of a given system obtained by different electron bombardment methods will be seen to be only within a factor of 2 or 3 in many cases. From this point of view, we feel confidence in our results.

Triplet-State Yield of Aromatic Nitro Compounds

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Abstract: Electronic energy-transfer experiments using *cis*-1,3-pentadiene (*cis*-piperylene) indicate that the triplet yields of nitrobenzene and 1-nitronaphthalene are 0.67 ± 0.10 and 0.63 ± 0.10, respectively. The results confirm the rapid deactivation of the nitrobenzene triplet as the prime cause of inefficient photochemistry, whereas with 1-nitronaphthalene a slow hydrogen-abstraction rate constant ($<10^2\ M^{-1}\ \text{sec}^{-1}$) accounts for the lack of photochemical activity in isopropyl alcohol. The rate constants for radiationless decay of the nitrobenzene and 1-nitronaphthalene triplet were estimated to be 10^9 and $<4 \times 10^5\ \text{sec}^{-1}$, respectively. The rate constant for triplet energy transfer from 1-nitronaphthalene to *cis*-piperylene was estimated to be $7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$.

One of the imposing demands of photochemists today is the need to know the triplet-state yield of photoexcited molecules. Lamola and Hammond[1] have devised a triplet-counting method based on the *cis–trans* isomerization of piperylene (1,3-pentadiene). Other methods[2–4] recently reported depend on light emission phenomena and have also been found useful.

Although very little quantitative information is available concerning radiationless processes in aromatic nitro compounds, our recent investigation[5] of the hydrogen-abstraction process by the n,π* triplet of nitrobenzene in pure isopropyl alcohol raised questions concerning the cause of the low photochemical disappearance quantum yield (1.14×10^{-2}). The quantum yield for disappearance of nitrobenzene in isopropyl alcohol is much smaller than the value observed with benzophenone (disappearance yield ranges from 1 to 2).[6–8]

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(3) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

(4) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 234 (1966); *Trans. Faraday Soc.*, **62**, 2785 (1966).

(5) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966).

(6) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).