Lifetime Studies of the Biacetyl Excited Singlet and Triplet States in the Gas Phase at 25°

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Abstract: The lifetimes of excited biacetyl triplet (^3A) and first-excited singlet (^1A) molecules have been determined in vapor phase experiments at 25°. Biacetyl was excited with a low-energy laser pulse of monochromatic light of wavelengths 3471, 3829, and 4365 Å. Within the experimental error the lifetime of the triplet [$\tau = (1.52 \pm 0.26) \times 10^{-3}$ sec] is independent of the exciting wavelength and the pressure of biacetyl or added cyclohexane for experiments above some minimum pressure. With excitation at 4365 Å and at pressures below about 0.6 Torr, the observed triplet lifetimes decrease with decreasing pressure. However, the quantum yields of triplet formation are independent of the pressure of biacetyl over a wide range of pressures, 11.4–12,500 μ. These data prove unambiguously the contention of Parmenter and Poland[11] that biacetyl behaves in the "large molecule" limit of the theories of radiationless transitions. The lifetime of the first-excited singlet biacetyl formed with a 3829-Å laser pulse was found to be $\tau = (2.4 \pm 0.4) \times 10^{-8}$ sec, independent of the pressure (24–105 Torr). The present data and published quantum yield data allow the estimation of the following rate constants for gas phase reactions at 25°: $^1A_0 \rightarrow h\nu_f + A$ (5), $k_5 = (9.8 \pm 2.8) \times 10^4$ sec^{-1}; $^1A \rightarrow {}^3A$ (4), $^1A \rightarrow A$ (6), $k_4 \cong k_4 + k_6 = (4.3 \pm 0.8) \times 10^7$ sec^{-1}; $^3A_0 \rightarrow A + h\nu_p$ (8), $k_8 = (1.0 \pm 0.2) \times 10^2$ sec^{-1}; $^3A_0 \rightarrow A$ (9), $k_9 = (5.6 \pm 1.3) \times 10^2$ sec^{-1}; $^3A_0 + M \rightarrow A + M$ (11), M = biacetyl or c-C_6H_{12}, $k_{11} \cong 4 \times 10^3$; M = SO_2, $k_{11} = (4.5 \pm 0.8) \times 10^3$; M = O_2, $k_{11} = (5.5 \pm 0.2) \times 10^8$ l./(mol sec).

Over the past two decades extensive studies have been made on both the liquid and vapor phase photochemistry of biacetyl. The basic mechanisms of the photochemical and photophysical processes have been summarized in several reviews.[1,2] The continued interest in biacetyl photochemistry is related largely to its use as a gas phase emission standard and as a triplet energy acceptor in the study of the triplet molecule participation in the photochemistry of other molecules. Its attractiveness lies in its several rather unique properties; it has a relatively high quantum yield of phosphorescence ($\phi_p = 0.145 \pm 0.03$,[3] 0.149 ± 0.009[4]); ϕ_p is essentially constant over a range of exciting wavelengths (3650–4400 Å) and pressures;[5–7] furthermore the relatively low triplet energy of biacetyl (E_T = 57 kcal/mol) allows efficient triplet energy transfer from a variety of molecules of photochemical interest.[8]

The photochemistry of biacetyl is probably as well established today as that of any compound, largely as a result of the research efforts of Noyes and his coworkers. However several key problems in the mechanism remain unresolved and hamper the extended use of the biacetyl both as a standard for emission and in quantitative energy transfer experiments.

Recent work of Garabedian and Dows[9] suggested that the rate of biacetyl triplet quenching by biacetyl or added "inert" gases is significant at the usual pressures employed. The long-accepted conclusions of Almy and Gillette,[3] Okabe and Noyes,[6] Heicklen,[10] Parmenter and Poland,[11] and others, that the phosphorescence yield of biacetyl excited near 4300 Å was independent of the pressure, have been open to question. The magnitude of the quenching observed by Garabedian and Dows is such that they concluded that the ϕ_p reported by Almy and Gillette[3] (0.143 ± 0.03) should be increased to 0.17 for biacetyl at zero pressure. In view of these conclusions, one must question the accuracy of data obtained using biacetyl as an emission quantum yield reference. For example, we have assumed the unimportance of the collisional quenching of triplet biacetyl by SO_2 in our previous work[12] in which the quantum yield of intersystem crossing in excited singlet SO_2 was determined. In another study we have assumed ϕ_p to be independent of the pressure of added cyclohexane gas.[13] In order to check the reliability of these assumptions we have reinvestigated in this work the effect of increased biacetyl pressure, added cyclohexane, SO_2, and O_2 on the lifetime of triplet biacetyl.

An additional question of considerable interest remains unanswered. What is the efficiency of intersystem crossing for the isolated, excited biacetyl molecule? Parmenter and Poland[11] found that there was a marked decrease in both the quantum efficiency of biacetyl phosphorescence emission and the lifetime of the triplet in experiments to low pressures ($p < 0.1$ Torr). They suggested that the sole factor responsible for these effects was the increased importance of biacetyl triplet diffusion and deactivation at the cell wall at low pressures. They concluded that the efficiency

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of intersystem crossing in excited singlet biacetyl is the same for the isolated molecule at low pressures as in experiments at high pressures. However, it appears to us that the effect of a significant decrease in the efficiency of intersystem crossing at low pressures could have been masked well by the observed "diffusion" effect; further study is necessary to establish unambiguously the rates of intersystem crossing in the isolated singlet biacetyl molecule. We report in this work the findings of further definitive experiments which bear on this important question.

In the present study we have employed the very short pulse of a low-intensity laser beam to excited biacetyl at 3471, 3829, and 4365 Å. Both excited singlet and triplet biacetyl lifetime data were determined under a much wider range of experimental conditions than had been possible in the older studies.

Experimental Methods and Results

Laser Excitation Systems. A 20-nsec pulse of laser light was used to excite biacetyl to its first excited singlet state. The ruby laser was tuned to enable excitation at three different wavelengths: 3471, 3829, and 4365 Å. The basic laser system and the associated equipment for the measurement of emission lifetimes have been described in detail previously.[13] The techniques for production of the various wavelengths from the ruby fundamental are of interest and are described here. Frequency doubling of the ruby fundamental (6943 Å) was effected using a precisely oriented potassium dihydrogen phosphate crystal. With this system about 10,000 ergs of 3471 Å radiation was available in the laser beam per pulse. In this work the beam was attenuated to about 100 ergs per pulse through the use of neutral density filters to avoid high concentrations of biacetyl triplet and to ensure the unimportance of the triplet–triplet annihilation reactions. A Kodak Wratten 2B filter was positioned in front of the emission detection photomultiplier to remove any scattered laser light of wavelengths less than 3900 Å.

The Raman-shifted (1344 cm^{-1}) ruby frequency, obtained using nitrobenzene liquid, was doubled to form a beam of 3829 Å with a maximum energy of 5000 ergs per laser pulse. In triplet lifetime studies this beam was attenuated to an energy less than 100 ergs per pulse. A Wratten 2B filter was employed again to remove any scattered laser light from the phosphorescence light seen by the detector. In singlet lifetime studies the full 5000 ergs per pulse was used directly and a Corning CS 7-59 filter was added to remove phosphorescence emission from the detector.

The 4365-Å beam was generated using acetonitrile to effect a Raman shift (2945 cm^{-1}) of the ruby frequency, and this was again frequency doubled. The best results in this case were obtained when the acetonitrile cell was placed directly in the laser cavity. This positioning had the useful side effect of reducing the pulse time to 10 sec. The full intensity of the laser pulse in this case was about 2000 ergs; this was attenuated again to reduce the power to less than 50 ergs per pulse. A Wratten 4 filter was employed to remove scattered laser light from the detector.

Lifetime Studies. The sample cell and phototubes were the same as those employed previously.[13] The emission was monitored at right angles to the cell, and the emission detection photomultiplier was positioned to view a 3.5-cm horizontal portion of the 88-cm length of the cell and the full vertical height of the cell (2.5-cm diameter). The laser formed a parallel beam of light which was directed through the center of the cell. The cross section of the beam showed a rather complex intensity distribution which is of little interest in this study of first-order decay reactions. It is important in the consideration of bimolecular triplet decay reactions, and we describe it in detail in the following paper. The full intensity of the laser beam at the three wavelengths employed created a sufficient concentration of triplet molecules so that the bimolecular triplet–triplet annihilation reaction was very important. The deviation of the triplet emission intensity from the simple exponential decay gave evidence of this. At the low intensities employed in the present work, decays

Table I. Inverse Triplet Lifetimes of Biacetyl Vapor Excited by Low-Intensity Laser Pulses at 3471, 3829, and 4365 Å and 25°

Pressure, Torr		
Biacetyl	Cyclohexane	$1/\tau$, sec^{-1}, $\times\ 10^{-2}$
(a) Excitation at 3471 Å (Laser Pulse Energy ≤ 100 Ergs)		
7.79	0.0	6.00
29.1	0.0	5.75
29.6	84.8	6.42
(b) Excitation at 3829 Å (Laser Pulse Energy ≤ 100 Ergs)		
0.205	85.1	6.73
0.0602	85.1	7.95
0.0891	85.1	6.22
0.0911	85.1	6.75
0.122	85.1	7.58
0.177	85.1	6.24
0.215	85.1	6.00
5.20	85.1	5.66
8.77	85.1	6.07
14.7	85.1	6.23
24.1	0.0	6.36
31.4	0.0	6.02
(c) Excitation at 4365 Å (Laser Pulse Energy ≤ 50 Ergs)		
0.0114	0.0	50.3
0.0114	0.0917	15.3
0.0114	0.157	12.5
0.0114	0.254	11.6
0.0114	0.550	9.63
0.0167	0.0	39.6
0.0280	0.0	33.4
0.0470	0.0	23.5
0.0858	0.0	15.2
0.0858	9.98	5.76
0.144	0.0	11.8
0.241	0.0	11.1
0.315	0.0	10.1
0.400	0.0	10.3
0.486	0.0	8.42
0.486	8.76	6.89
0.603	0.0	7.99
0.815	0.0	7.25
1.07	0.0	7.19
1.07	10.5	6.53
1.07	17.1	7.52
1.07	28.8	6.27
1.07	41.0	7.17
1.07	85.1	6.83
1.37	0.0	6.73
1.70	0.0	6.67
2.29	0.0	6.90
5.06	0.0	5.98
12.5	0.0	6.88
17.2	0.0	7.14
24.0	0.0	6.64
28.7	0.0	6.99
31.4	0.0	6.31

of phosphorescence and fluorescence emission were clearly exponential in character over several lifetimes. Shown in Table I are the measured lifetimes of triplet biacetyl at 3471, 3829, and 4365 Å and at various pressures of biacetyl and added cyclohexane.

The short pulse time and the high intensity of the laser system make it possible to detect accurately the fluorescence emission from initially formed, excited-singlet-state biacetyl molecules. It was deemed desirable to use the 3829-Å excitation in order to minimize the possibility of any scattered laser light from interfering with the fluorescence signal passed selectively by the Corning 7-59 and Wratten 2B filters. This filter combination allowed only fluorescence emission to reach the detector. Since the lifetime of the excited singlet state is very short, there was a significant decay of the singlet molecules even within the short 20-nsec period of the laser pulse. However, the intensity of the laser was sufficiently high that the singlet concentration remained at an easily detectable level after the laser pulse and its associated scattered light had disappeared. Measurements of the intensity of the singlet emission were taken after a 40-nsec delay following the laser pulse. The observed singlet lifetime data are summarized in Table II.

Table II. Inverse Singlet Lifetime of Biacetyl Vapor Excited by Laser Pulse (Maximum Incident Energy, 5000 Ergs/Pulse) at 3829 Å and 25°

Pressure of biacetyl, Torr	$1/\tau$, sec^{-1}, $\times 10^{-7}$
(a) Pressure of Cyclohexane Added, 85.1 Torr	
5.20	4.57
5.20	4.41
8.77	3.70
8.77	3.82
8.77	3.60
14.7	4.17
14.7	4.48
14.7	4.46
14.7	4.32
19.4	4.49
19.4	4.31
19.4	4.38
19.4	4.71
(b) No Cyclohexane Added	
24.1	4.83
24.1	4.46
24.1	4.73
24.1	4.71
31.4	3.92
31.4	3.63
31.4	3.97
31.4	3.83

The quenching of biacetyl triplets by oxygen and sulfur dioxide gases was studied in a series of experiments, and the data are given in Table III.

Materials. 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 degassed thoroughly by bulb-to-bulb distillation at −196°. Cyclohexane (Top Grade, 99.9%, from Chemical Samples Co.) was degassed and distilled in the vacuum line with the retention of a middle-boiling fraction. Both SO_2 and O_2 were research grade chemicals of the Matheson Co.

Table III. Inverse Triplet Lifetime of Biacetyl as a Function of Pressure of Added Oxygen and Sulfur Dioxide Gases[a]

Pressure of added gas, Torr	Inverse triplet lifetime, sec^{-1}, $\times 10^{-3}$
(a) Oxygen	
0.0	0.614
0.957	31.5
2.31	72.8
3.81	120
5.47	174
8.27	233
9.20	275
10.4	321
12.3	367
(b) Sulfur Dioxide	
0.0	0.669
93.5	0.670
188	0.661
297	0.745
406	0.750
527	0.777
653	0.800
781	0.855
910	0.867
(c) Sulfur Dioxide	
0.0	4.70
0.0450	2.32
0.092	1.68
0.267	1.10
0.511	0.934
1.04	0.770

[a] Laser excitation of biacetyl at 4365 Å; incident energy = 50 ergs/pulse; temperature, 25°; pressure of biacetyl, 2.41 Torr in series a, 2.90 Torr in series b, 0.0118 Torr in series c.

The gaseous mixtures were prepared in a mercury-free system using a Pyrex spiral manometer as a null instrument for pressure measurement. A thermal gradient pump in series with the cell was used to mix the reactants.

Discussion of the Results

The primary processes in the photolysis of biacetyl can be discussed conveniently in terms of the following mechanism which is largely the result of the work of Noyes and coworkers.[1,5–7]

$$A + h\nu \longrightarrow {}^1A_n \qquad \text{(I)}$$

$${}^1A_n \longrightarrow \text{products} \qquad (1)$$

$$\longrightarrow A \qquad (2)$$

$${}^1A_n + M \longrightarrow {}^1A_0 + M \qquad (3)$$

$${}^1A_0 \longrightarrow {}^3A_m \qquad (4)$$

$$\longrightarrow A + h\nu_f \qquad (5)$$

$$\longrightarrow A \qquad (6)$$

$${}^3A_m + M \longrightarrow {}^3A_0 + M \qquad (7)$$

$${}^3A_0 \longrightarrow A + h\nu_p \qquad (8)$$

$$\longrightarrow A \qquad (9)$$

$${}^3A_0 + {}^3A_0 \longrightarrow A + A^* \qquad (10)$$

$${}^3A_0 + M \longrightarrow A + M \qquad (11)$$

$${}^3A_0 + \text{wall} \longrightarrow A + \text{wall} \qquad (12)$$

A represents a ground-state biacetyl molecule; ${}^1A_n$ and ${}^3A_m$ are excited first-singlet and triplet biacetyl molecules, respectively, in upper vibrational levels; ${}^1A_0$ and

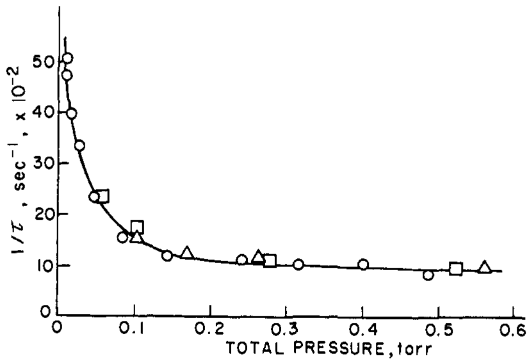

Figure 1. Plot of the inverse triplet lifetime of biacetyl *vs.* the total pressure: excitation at 4365 Å; incident energy ≤ 50 ergs per laser pulse; temperature, 25°; pure biacetyl (circles); biacetyl at 11.8 μ with added SO_2 (squares); biacetyl at 11.4 μ with added cyclohexane (triangles).

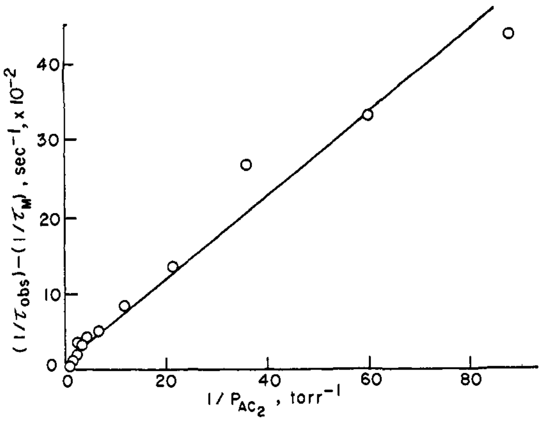

Figure 2. Plot of the reciprocal of the pressure of biacetyl *vs.* the difference between the reciprocals of the observed lifetime (τ_{obsd}) of the triplet biacetyl at low pressures ($P < 1$ Torr) and the constant triplet lifetime (τ_M) characteristic of the 1.4–31.4-Torr range.

$^3A_0$ are the corresponding vibrationally relaxed states; A* may be a higher excited singlet state which, in any case, leads to dissociation products.[14]

Effects of Exciting Wavelength and Pressure on the Lifetime of Triplet Biacetyl Molecule. In terms of the presently accepted mechanism for biacetyl photolysis, reactions I–12, one expects that there will be at least three different reactions which can alter the phosphorescence emission intensity or lifetime if the wavelength or the pressure is changed, 3, 11, and 12. Two other potential sources can be excluded. (1) The relatively long lifetime of the triplet ensures its complete vibrational equilibration in reaction 7 even in experiments at the lowest pressures employed,[15] and no influence of pressure is expected from this reaction. (2) An indirect effect of increased biacetyl pressure is expected at high incident light intensities; the absorbed light intensity and the concentration of triplets may increase with pressure to the point where the triplet–triplet annihilation reaction 10 becomes significant. At full laser beam intensities this effect was important in the present work as evidenced by the nonexponential decay of the triplets for these conditions. For the results presented from runs at greatly attenuated beam intensities, reaction 10 was unimportant. Thus, in terms of the accepted mechanism, the only significant pressure or wavelength effects are expected to arise in reactions 3, 11, and 12 for our conditions. In addition, there is major interest in the possible influence of pressure on reaction 4, but this cannot be evaluated unambiguously before one can describe the effects of 3, 11, and 12 in a quantitative fashion. If the excited singlet biacetyl molecule is truly in the large molecule limit as Parmenter and Poland conclude, then, of course, the first-order character of (4) will be maintained to very low pressures.

There is abundant evidence of the influence of pressure and wavelength on reaction 3 which has been published.[1,5–7] Excitation of biacetyl at 4365 Å generates the first-excited singlet state with practically no excess vibrational energy.[16] Absorption of low intensity 4365-Å radiation (59 kcal/mol) does not decompose biacetyl where for the ground-state molecule about 70 kcal/mol is necessary to rupture the weakest bond [$(CH_3CO)_2 \rightarrow 2CH_3CO$]. However vibrationally excited singlet molecules are formed by excitation of biacetyl at 3650 Å (78 kcal/mol), and significant molecular decomposition is observed at low pressures.[1,6,7] As the pressure is increased, and vibrational equilibration of the singlet suppresses the decomposition, a concurrent increase in the quantum yield of emission is seen. At pressures greater than about 45 Torr (for experiments at 3650 Å), the quantum yield for emission reaches a constant value equal to that found at 4358 Å.[7] In low-pressure runs at both 3471 (82 kcal/mol) and 3829 Å (75 kcal/mol), we have observed these same effects qualitatively. We found that at pressures above 1 Torr, where, although the triplet lifetime was near equal to its high-pressure value, the quantum efficiency of phosphorescence emission was significantly below the constant value characteristic of similar experiments at higher pressures. As one might expect, the effect was most noticeable in runs at 3471 Å. Since the ratio of the quantum yield of fluorescence to that of phosphorescence is independent of the exciting wavelength (3650–4358 Å)[6] and, for pressures above 1 Torr, the triplet lifetime is also independent of the exciting wavelength (3471–4365 Å), both intersystem crossing and fluorescence emission must occur from vibrationally relaxed states for these conditions. For the purposes of this study we have carried out the experiments reported here at pressures for which reaction 3 is not rate determining.

Observe in Table I and in Figure 1 the marked deviation from the high pressure, near constant value of the biacetyl triplet lifetime for experiments in the pressure range below about 1 Torr. Parmenter and Poland[11] have reported a similar effect and attributed this to the increasing importance of biacetyl triplet deactivation on the cell wall as the pressure is lowered (reaction 12). This hypothesis fits the present data well. The parameters that control the low-pressure phenomenon can be identified by estimating the difference between the reciprocals of the observed lifetimes ($1/\tau_{obsd}$) at low pressures and the mean value of $1/\tau_M$ for the pressure range 1.4–31.4 Torr. Note in Figure 2 that this difference is within the experimental error a linear function of the reciprocal of the biacetyl pressure. Furthermore, the addition of cyclohexane (triangles in Figure 1) or SO_2

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(16) The (0,0) band occurs at 4373 Å in the pure crystal at 20°K: J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 77, 6461 (1955).

(squares) to biacetyl at low pressures causes a return of the observed lifetime to a value near that found for biacetyl alone at the pressure of the combined gases. These are the theoretically expected results if wall deactivation of triplets is important at low pressures; the rate of deactivation at the wall in reaction 12, $(1/\tau_{\mathrm{obsd}}) - (1/\tau_{\mathrm{M}})$, should be inversely proportional to the pressure of the gas through which the triplets must diffuse to react at the wall. With this model one expects that the onset of the effect will occur for our conditions somewhat below 1 Torr where the average distance which the triplet molecules can diffuse during their lifetime approaches the average distance from the cell wall at which the molecules are excited (about 1 cm in our system).[17] It can be shown that the average distance which a biacetyl triplet diffuses during its lifetime will be about 1.8 cm at 11.4 μ and 0.3 cm at 0.6 Torr. Since the onset of the effect is at pressures of about 1 Torr, these considerations support the hypothesis of the pressure effect below 1 Torr originating from wall destruction of the triplets. However, on the basis of this evidence alone one cannot exclude as a contributing factor to the observed loss of phosphorescence intensity some deficiency of triplet formation in reaction 4 at low pressures. Work which bears directly on this point has been obtained in this study and is presented in the next section.

All of the data in Table I for runs at pressures greater than about 1 Torr should have no significant contribution from the two pressure effects considered: deactivation of triplets at the wall (reaction 12) and the decomposition of vibrationally nonequilibrated excited singlet molecules (reaction 1). These data should provide a good test of the importance of collisional deactivation of triplet molecules (reaction 11), judged significant by Garabedian and Dows.[9] It can be seen from the lifetime data of Table I that the lifetime of biacetyl triplet is relatively insensitive to change in the exciting wavelength and the pressure for the relatively high pressure regions employed in runs at 3471, 3829, and 4365 Å. The average values of τ are: $(1.65 \pm 0.18) \times 10^{-3}$ sec[19] at 3471 Å; $(1.54 \pm 0.32) \times 10^{-3}$ sec at 3829 Å; $(1.49 \pm 0.20) \times 10^{-3}$ sec at 4365 Å. The average of all of the data for pressures which exclude diffusional effects and excited molecule decomposition gives $\tau = (1.52 \pm 0.17) \times 10^{-3}$ sec for experiments at 25°. These data check well with the published lifetime data for triplet biacetyl vapor excited using light of wavelengths near 4300 Å in experiments at pressures above a few Torr and near room temperature: $\tau = (1.65 \pm 0.2) \times 10^{-3}$ sec;[18] 1.40×10^{-3} sec;[20] 1.8×10^{-3} sec;[21] 1.7×10^{-3} sec;[8d] 1.8×10^{-3} sec.[11] Although no trend in lifetime with pressure is evident by inspection (for pressures above about 1 Torr), a statistical test of the data should be made to test the conclusions of Garabedian and Dows.[9] The least-squares treatment of the Stern-Volmer plot of the lifetime data from runs with pure biacetyl gives a small, theoretically impossible negative rate constant for reaction 11. Similarly the data from the 4365-Å runs with the pressure of biacetyl ≥ 1.07 and the pressure of cyclohexane = 0–85 Torr (Table I) show no detectable quenching of biacetyl triplets by cyclohexane. Assuming that biacetyl and cyclohexane have about equal quenching facilities, one can treat all the data from 4365-Å experiments above 1 Torr; this gives $k_{11} \cong 4 \times 10^3$ l./(mol sec). This is probably the best estimate of this quantity which we can derive from this work, and it is an order of magnitude smaller than the rate constants derived by Garabedian and Dows; they report with M = biacetyl, $k_{11} = 7.1 \times 10^4$; M = acetone, 4.3×10^4; M = propylene, 6.0×10^4; M = isopropyl alcohol, 4.5×10^4; and M = methyl chloride, 4.8×10^4 l./(mol sec). It is our opinion that the conclusions of Garabedian and Dows are in error; we conclude with most previous investigators that the quantum efficiency of biacetyl phosphorescence excited near 4300 Å is essentially independent of the pressure of biacetyl or of added, chemically inert gases with relatively high triplet energies ($E_{\mathrm{T}} \gg 57$ kcal/mol). Certainly one must not accept the suggestion of these workers to increase the quantum yield of phosphorescence emission from the value reported by Almy and Gillette,[3] $\phi_{\mathrm{p}} = 0.143 \pm 0.03$, to 0.17 in order to obtain the "true" value at zero pressure.

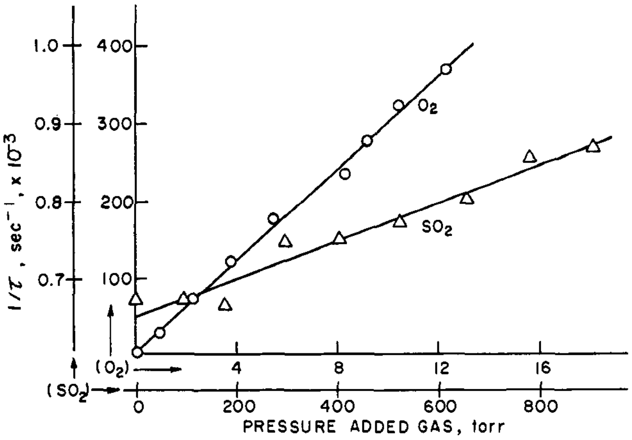

Figure 3. Stern–Volmer plots of the reciprocal of the biacetyl triplet lifetime *vs.* the pressure of added oxygen (circles, 0–16-Torr axis) and sulfur dioxide (triangles, 0–800-Torr axis) gases: excitation at 4365 Å; incident energy ≤ 50 ergs per laser pulse; temperature, 25°.

Quenching Reactions of Biacetyl Triplets with Sulfur Dioxide and Oxygen Gases. In view of the Garabedian and Dows findings, a determination of the extent of quenching of biacetyl triplets by SO_2 was deemed important in order to establish the accuracy of the SO_2 intersystem crossing ratios derived in the study of Rao, Collier, and Calvert.[12] A Stern–Volmer plot of the data of Table III is shown in Figure 3. The slope of the plot gives $k_{11} = (4.5 \pm 0.8) \times 10^3$ l./(mol sec) for M = SO_2. The smallness of this constant excludes the importance of this reaction for the conditions used in the previous SO_2-triplet energy transfer studies. It can be concluded that no significant error was introduced by the neglect of reaction 11 in the previous work.

Our results suggest that k_{11} is very small for M = SO_2, cyclohexane, or biacetyl [$k_{11} \cong 4 \times 10^3$ l. (mol sec)].

(17) The time in seconds for the triplet molecule to diffuse a distance x (centimeters) is given approximately by x^2/D, where D is the diffusion coefficient; $D = D_0$/pressure (Torr). See S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 446. For biacetyl triplets in biacetyl $D_0 = 3.2 \times 10^{-2}$ cm²/sec.[18]

(18) G. M. Almy and S. Anderson, *J. Chem. Phys.*, 8, 805 (1940).

(19) The error limits shown here and throughout this paper are the 95% confidence limits (2σ) derived from conventional statistical treatment of the result.

(20) R. D. Radcliffe, *Rev. Sci. Instrum.*, 13, 413 (1942).

(21) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, 18, 427 (1950).

The much higher results for k_{11} with M = biacetyl and a variety of compounds reported by Garabedian and Dows [$k_{11} \cong 4\text{–}7 \times 10^4$ l./(mol sec)][9] seems to be in error, perhaps as a result of the accidental introduction of a quenching impurity into the mixtures. Oxygen is the most likely of the common impurities to be present. In evaluating this possibility, we redetermined the k_{11} quenching rate constant for triplet biacetyl by oxygen. These data are given in Table III and in the Stern–Volmer plot shown in Figure 3. The least-squares treatment of these data gives $k_{11} = (5.5 \pm 0.2) \times 10^8$ l./(mol sec) for M = O_2. This estimate is in excellent agreement with the value determined by Kaskan and Duncan[21] who used a very much smaller range of oxygen pressures; they report $k_{11} = 5 \times 10^8$ l./(mol sec). It should be noted that as little as one molecule of oxygen impurity in 10^4 of added quencher molecule would lead to an apparent quenching rate constant of the magnitude observed by Garabedian and Dows. A possible alternative origin of the effect seen by these workers, the occurrence of reaction 10, is considered by Badcock, *et al.*[22]

Quantum Yield of Phosphorescence of Biacetyl as a Function of Pressure. It was evident to us that the relative intensity of phosphorescence as measured by the photomultiplier response (i_p) immediately after the laser pulse would be directly proportional to the concentration of triplets formed by intersystem crossing. Since under our experimental conditions the rate of removal of triplets by diffusion to the wall and subsequent deactivation is negligible compared to their rate of formation, no measureable decay can occur before our phosphorescence intensity observations start. Hence the effects of wall removal, so evident in lifetime data, cannot influence the magnitude of the intensity of phosphorescence extrapolated to zero time. The relative intensity of phosphorescence was determined in a series of experiments over a wide range of biacetyl pressures. Each set of emission data was extrapolated back to zero time by determining the least-squares intercept of the log i_p *vs.* time curve to obtain the quantity, i_p^0, which is proportional to the total number of triplets formed from the excited singlets produced in the laser pulse. These data are presented in Table IV. In each experiment the energy of the exciting laser beam transmitted through the cell was determined; this varied from experiment to experiment by as much as 10–20%. From the relative transmitted intensity, the measured extinction coefficient, and Beer's law, we estimated the relative energy of the absorbed light (I_a) within the monitored volume of the cell for each experiment. The ratio of i_p^0/I_a, given in the last column of Table IV, is proportional to the quantum yield of triplets formed from singlets following the laser pulse. Note that within the experimental error the i_p^0/I_a values are independent of the pressure of biacetyl over a 1000-fold variation in the pressure and down to the lowest pressure which we could determine accurately, 11.4 μ. On the average the excited singlet biacetyl molecule decays without an interaction for experiments below about 100 μ.[11] Thus these results prove convincingly the contention of Parmenter and Poland that the isolated excited singlet molecule of biacetyl undergoes a truly unimolecular intersystem crossing reaction with the same efficiency as in the collisionally perturbed system at high pressures. It is confirmed that the excited biacetyl molecule is in the "large molecule" limit discussed in the theories of radiationless transitions.[23–26] Parmenter and Poland have been able to rationalize this conclusion fairly well in terms of these theories.

Table IV. Biacetyl Phosphorescence Emission Intensity at Zero Time (i_p^0) and the Relative Phosphorescence Quantum Yield (i_p^0/I_a) Following a 4365-Å Laser Pulse[a]

Pressure of biacetyl, Torr	i_p^0 (arbitrary units)	i_p^0/I_a (arbitrary units)
0.0114	0.428	7.2
0.0280	1.01	6.9
0.0470	2.00	8.1
0.0858	4.25	9.4
0.144	6.80	9.0
0.241	12.9	10
0.815	50.8	12
1.07	57.1	10
1.37	56.0	7.8
2.29	115	9.6
5.06	259	9.8
12.5	845	7.6

[a] Incident energy ≤ 50 ergs/pulse; temperature, 25°.

Excited Singlet Lifetime of Biacetyl Vapor. The lifetime of the first-excited singlet state of biacetyl vapor was determined for the first time in this work using excitation at 3829 Å. These data are given in Table II. Note that the lifetime is independent of the pressure over the entire range of pressures which could be employed for these measurements (24–105 Torr). The average value of all the measurements gives $\tau = (2.35 \pm 0.43) \times 10^{-8}$ sec. This is in qualitative accord with the singlet lifetime of biacetyl measured by Turro and Engel for benzene solutions.[27] They found $\tau = 1 \times 10^{-8}$ sec. At the relatively high pressure employed, one anticipates that the excited-singlet species is vibrationally equilibrated, and the measured value of the lifetime should equal the rate constant function, $1/(k_4 + k_5 + k_6)$. This value and published quantum yield data can be used to derive an experimental estimate of k_5. Okabe and Noyes found $\phi_p/\phi_f = 58 \pm 8$ for biacetyl excited under conditions employed here. Taking $\phi_p = 0.149 \pm 0.009$,[4] we estimate $\phi_f = (2.6 \pm 0.4) \times 10^{-3}$. For similar conditions Collier, Slater, and Calvert[4] estimated $\phi_f = (1.9 \pm 0.6) \times 10^{-3}$. If we take the average of the two estimates, $\phi_f = k_5/(k_4 + k_5 + k_6) = (2.3 \pm 0.5) \times 10^{-3}$, and our lifetime estimate, we find $k_5 = (9.8 \pm 2.8) \times 10^4$ sec^{-1}. It is likely that intersystem crossing in biacetyl singlets is the dominant, if not the exclusive, relaxation mode other than fluorescence in the gas phase.[28] Therefore, the present lifetime and quantum yield data provide an estimate of the rate constant for intersystem crossing in excited biacetyl singlet: $k_4 \cong k_4 + k_6 = (4.25 \pm 0.78) \times 10^7$ sec^{-1}.

Since the natural radiative lifetime of the singlet, τ^0, is equal to $1/k_5$, we can estimate from these data,

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(22) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, B. R. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, **94**, 19 (1972).

(23) G. W. Robinson, *J. Chem. Phys.*, **47**, 1967 (1967).

(24) M. Bixon and J. Jortner, *ibid.*, **48**, 715 (1968).

(25) J. Jortner and R. S. Berry, *ibid.*, **48**, 2757 (1968).

(26) D. P. Chock, J. Jortner, and S. A. Rice, *ibid.*, **49**, 610 (1968).

(27) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **90**, 2989 (1968).

(28) For examples of this evidence, see (a) H. Ishakawa and W. A. Noyes, Jr., ref 7; (b) C. S. Parmenter and H. M. Poland, ref 11.

$\tau^0 = (1.0 \pm 0.3) \times 10^{-5}$ sec. An independent theoretical estimate of this quantity can be derived using absorption data for biacetyl[29] and the method of Strickler and Berg.[30] This procedure gives the "theoretical" estimate, $\tau^0 = 1.2 \times 10^{-5}$ sec. Using less refined, older methods of calculation and other absorption data, Almy and Anderson obtained the "theoretical" estimate of $\tau^0 = 0.85 \times 10^{-5}$ sec.[18] Obviously the experimental value reported here is in excellent accord with the theoretical values. Apparently the Strickler and Berg relation applies reasonably well to the weakly allowed transitions involving the carbonyl bond, although it is expected to apply rigorously for allowed transitions only.

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A Study of the Triplet–Triplet Annihilation Reaction in Biacetyl Vapor Excited at 4365 Å and 25°

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Abstract: A study has been made of the phosphorescence intensity–time curves for biacetyl triplets ($^3A_0$) generated with a 4365-Å laser pulse of varied intensity. The spatial distribution of the incident intensity in the laser beam and the total energy of the pulse have been determined. The rates of phosphorescence decay in runs at high intensity deviate markedly from the first-order rates observed at low intensities. The results are quantitatively explicable in terms of the importance of the biacetyl triplet–triplet annihilation reaction in the experiments at high light intensities. Two curve-matching techniques were employed to estimate the triplet annihilation rate constant. An assumed value of this constant was adjusted until the desired match of the data was found for either the initial slope of the decay curve or the intensity at some given time after the pulse. Account was taken of the nonhomogeneous triplet concentrations created by the laser pulse. The average rate constant for the reaction, $^3A_0 + {}^3A_0 \rightarrow A^* + A$ (10), at 25° was estimated to be $k_{10} = (4.2 \pm 1.7) \times 10^{11}$ l./(mol sec). The results of this study are compared with those derived from published product quantum yield data from experiments at 4358 Å. It seems probable that the excited molecule A* of reaction 10 is formed in a vibrationally rich, second excited singlet electronic state of biacetyl which is very similar to that formed on direct photolysis of biacetyl at 2800 Å.

In our previous studies of the photochemistry of sulfur dioxide, we have employed biacetyl both as a triplet energy acceptor and as a standard for phosphorescence quantum yield measurements.[1-3] In the evaluation of potential sources of error in this work, we recognized that the very long lifetime for the biacetyl triplet molecule, $\tau = (1.52 \pm 0.26) \times 10^{-3}$ sec,[4] could lead to some unusual complications in our experiments. Thus a significant lowering of biacetyl phosphorescence emission may result from the biacetyl triplet–triplet annihilation reaction, especially in runs at reasonably high intensities. However, no estimates of this rate constant have been reported, and we cannot now evaluate realistically the possible influence of this reaction on the accuracy of the previous sulfur dioxide studies.

Kaskan and Duncan[5] first observed that the biacetyl triplet lifetime was intensity dependent in flash excitation of biacetyl in the 4300-Å region. They speculated that a product of biacetyl decomposition may have been responsible for the effect. Subsequently, Noyes and his coworkers carried out several quantitative studies in which they have elucidated this phenomenon.[6-8] They found that for biacetyl excited at 4358 Å and room temperature, little or no decomposition of biacetyl occurred in experiments at low intensities. However, the quantum yield for the primary dissociation of biacetyl increased regularly with increased absorbed light intensity. The decomposition obviously did not arise from a simple unimolecular decomposition of the triplet species. The quantum energy at 4358 Å (66 kcal/mol)

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