$\tau^0 = (1.0 \pm 0.3) \times 10^{-5}$ 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.

(29) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 422.

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

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.

I n 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)

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

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

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

(4) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, 94, 13 (1972).

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

(6) G. F. Sheats and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, 77, 1421 (1955).

(7) G. F. Sheats and W. A. Noyes, Jr., *ibid.*, 77, 4532 (1955).

(8) W. A. Noyes, Jr., W. A. Mulac, and M. S. Matheson, *J. Chem. Phys.*, 36, 880 (1962).
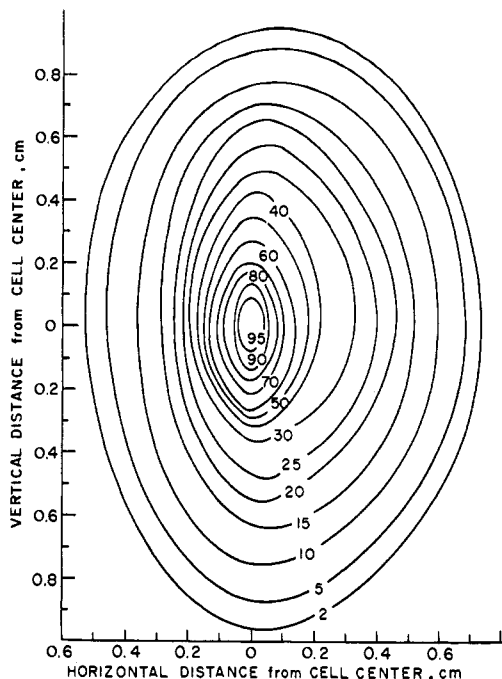
Figure 1. The distribution of the incident intensity in the cross section of the 4365-Å laser beam. Contours of equal intensity are shown in percentage of the maximum intensity at the cell center; the beam was essentially parallel along the cell axis.

is insufficient to dissociate biacetyl in the absence of considerable additional vibrational energy in the molecule; for ground-state biacetyl, a minimum of about 70 kcal/mol is necessary to disrupt the weakest bond in the molecule: $(CH_3CO)_2 \rightarrow 2CH_3CO$. Unimolecular decomposition of biacetyl triplets excited at 4358 Å becomes measurable only at higher temperatures where the unusual effect of intensity on the quantum yield for dissociation disappears.[8] The first-order dissociation of triplet biacetyl has an activation energy of about 15 kcal/mol.[8] Sheats and Noyes concluded that for runs at room temperature the rate-determining step was second order in some active species, possibly the long-lived triplet state of biacetyl formed in the photolysis.[6,7]

In definitive experiments employing the rotating sector technique, Noyes, Mulac, and Matheson[8] showed that the mean lifetime of the active species responsible for the unusual intensity effect ($\tau = 1.5 \times 10^{-3}$ sec) was equal within the experimental error to that observed for the triplet state of biacetyl. Hence, it seems reasonable to assume that for biacetyl excitation at 4358 Å in experiments at room temperature, the reaction between two triplet state molecules was responsible for the formation of dissociation products.

We report here a study designed to determine the rate constant for the biacetyl triplet–triplet annihilation reaction. The high concentration of biacetyl triplets desired to ensure the importance of the bimolecular triplet–triplet reaction was generated using a 4365-Å laser pulse of high intensity, short duration, and well-defined geometry. The measured decay of phosphorescence emission was used to establish the rate of the triplet removal processes.

Experimental Section

A 10-nsec pulse of 4365-Å laser light was used to excite the biacetyl. The details of the laser system and equipment for phosphorescence lifetime measurements have been given previously[4]
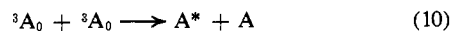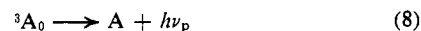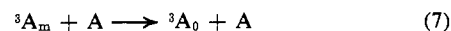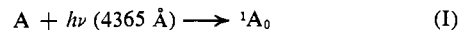
and need not be repeated here. A Kodak Wratten filter No. 4, placed in front of the photomultiplier for phosphorescence detection, restricted the monitored emission to those wavelengths greater than 4600 Å. Emission from the cell was measured at right angles to the excitation beam. The sides of the cell were blackened so that only a horizontal portion, 3.5 cm in length, and the full vertical height of the cell, 2.5 cm, was viewed by the detector.

The intensity of the laser beam was measured directly using a calibrated ITT FW 114 fast rise time phototube detector system (rise time, 0.3 nsec) placed at the rear of the cell. All the light emerging from the cell was passed through a calibrated uniform density filter and then focused to cover well the phototube surface. The output from the detector was displayed on a Tektronix 519 oscilloscope (rise time 0.3 nsec) fitted with a Polaroid camera. The photograph of the trace was integrated and corrected for phototube response and internal resistance of the oscilloscope, and the intensity of the beam was calculated from the calibration data. A correction was made for the attenuation of the intensity due to absorption by the biacetyl in estimating the incident energy at the midpoint of the cell from which emission data were observed. The beam intensity was varied over a factor of 5 by simply varying the pumping energy of the laser flash lamp. The incident energy of the 3765-Å beam at full flash lamp energy (I^0) was found to be 1.66×10^3 erg/pulse.

The cross-sectional area of the light beam in the cell at the position of measurement of emission was determined by photographing the suitably attenuated laser beam directly. Variation of the camera position along the length of the cell showed virtually no beam divergence. The densitometer tracings of several laser pulse intensity pictures were used to construct a contour map of the intensity of the cross-sectional area of the beam. See Figure 1. The cross section of the beam is seen to be elliptical in character, with the major axis vertically positioned in the cell. The distribution out from the center of the cell is somewhat Gaussian-like in character. The biacetyl was purified as previously described.[4] Pressure measurements were made using a spiral manometer as a null instrument.

Results and Discussion

The mechanism of the photolysis of biacetyl has been rather well established, largely through the studies of Noyes and his coworkers.[6-9] In this work we have attempted to derive the rate constant for the triplet–triplet annihilation reaction of excited biacetyl. We have drawn upon the published information and our own experience[4] to pick conditions for biacetyl photolysis which would maximize the triplet biacetyl concentration and minimize the number of competing first-order decay paths of the triplet molecule. We have determined the time dependence of the phosphorescence emission from biacetyl excited with a relatively high intensity laser pulse of 4365 Å in experiments at a temperature of 25° and at a pressure of biacetyl of 2.67 Torr. For these conditions the results should be explicable in terms of the following reaction mechanism.[10]

$$A + h\nu \ (4365 \ \text{Å}) \longrightarrow {}^1A_0 \qquad (I)$$

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

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

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

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

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

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

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

$$ A^* \longrightarrow \text{products} \qquad (13)$$

(9) For a few examples of the many definitive studies, see (a) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, Chem. Rev., 56, 49 (1956); (b) H. Okabe and W. A. Noyes, Jr., J. Amer. Chem. Soc., 79, 801 (1957); (c) H. Ishikawa and W. A. Noyes, Jr., J. Chem. Phys., 37, 583 (1962).

(10) The numbering of the reactions follows that for the more complete mechanism of biacetyl photolysis given in the previous paper.[4] The mechanism is largely that suggested by Noyes and coworkers.[6-9]

A represents a ground-state biacetyl molecule; $^1A_0$ and $^3A_0$ are the vibrationally equilibrated, first-excited singlet and triplet biacetyl molecules, respectively; ^3A_m is the triplet molecule which contains some excess vibrational energy; A^* may be a higher excited singlet state which, in any case, leads to decomposition products.

Estimation of the Rate Constant for the Biacetyl Triplet–Triplet Annihilation Reaction 10.

For the conditions which we have chosen, biacetyl excited singlet decay is so fast, $k_4 + k_5 + k_6 = (4.26 \pm 0.78) \times 10^7$ sec^{-1},[4] that the intensity of fluorescence emission will be negligible for times greater than about 100 nsec; only the phosphorescence emission will be observable on the time scale which we have employed here (0–300 μsec). On the other hand, triplet biacetyl decay is so very slow that no measureable decay of triplets can occur before our phosphorescence intensity observations start. At the pressures, wavelength, and temperature used in this work, wall deactivation of triplets and dissociation of vibrationally excited singlet molecules should be unimportant. However, the data suggest that the bimolecular triplet decay reaction 10 is an important decay mode for triplets under our conditions. Note in Figure 2 the results of a few of the typical phosphorescence decay rate data which we have obtained in experiments at several different laser beam intensities. In each experiment the observed decay of the phosphorescence emission (solid lines in Figure 2) deviates markedly from that expected if only the usual first-order decay reactions of biacetyl were important (dashed curves). Note that the extent of the divergence of the observed curve from the theoretical first-order decay curve becomes less as the incident intensity is lowered. Qualitatively these are the effects one would expect if the enhanced decay rate of biacetyl seen at high light intensities stems from the occurrence of the biacetyl triplet–triplet annihilation reaction.

In terms of the proposed mechanism, the decay of triplet biacetyl in the present work should be described by the relation A. For experiments at 4365 Å and for

$$-\frac{d[^3A_0]}{dt} = [^3A_0](k_8 + k_9) + [^3A_0]^2 2k_{10} \quad \text{(A)}$$

the pressure range employed here, we found $k_8 + k_9 = (6.72 \pm 0.91) \times 10^2$ sec^{-1}.[4] Then in principle, values of the desired rate constant k_{10} can be calculated from relation A using the measured rates of triplet decay and the known value of $k_8 + k_9$. However, here, as with most photochemical systems, there is a nonuniformity in the concentrations of triplets in the cell which complicates the seemingly obvious method of evaluation of k_{10}. A detailed description of the $[^3A_0]$ throughout the cell is necessary to proceed toward a meaningful estimate. In our case, the initial biacetyl triplet distribution is predictable from the measured incident light intensity variation with position in the cell (Figure 1), since each absorbed 4365-Å quantum of light generates a triplet biacetyl molecule with near perfect efficiency.[11] Furthermore, the diffusion of the excited triplet species is relatively unimportant in altering the
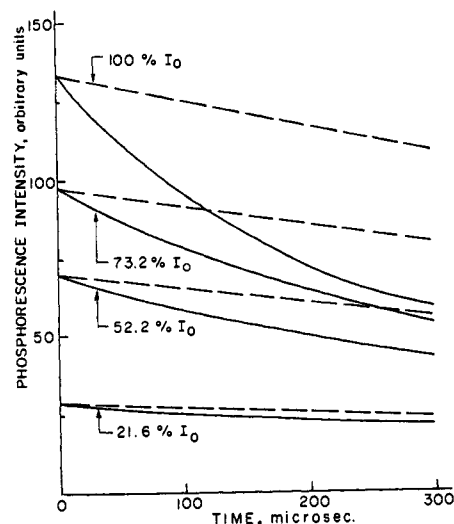

Figure 2. The relative intensity of biacetyl phosphorescence as a function of time following the excitation in a 4365-Å laser pulse for experiments at different incident intensities: $I^0 = 3.64 \times 10^{14}$ quanta/pulse; solid lines are the observed data, and the dashed lines represent the theoretical decay curves if only first-order decay of triplets occurred.

$[^3A_0]$ distribution for the time scale over which we observed phosphorescence. From the diffusion coefficient of triplet biacetyl in biacetyl vapor at room temperature derived by Almy and Anderson,[12] we can estimate that the average distance which a triplet molecule diffuses in biacetyl at 2.67 Torr during a period of 150 μsec is 0.026 cm. Although this type of diffusion calculation is never very precise, its applicability to our present experimental system is reasonable as shown in the previous paper.[4] Thus a reasonable yet approximate approach to the estimation of k_{10} can be had in defining a set of incremental volume elements within which the laser beam intensity and hence the $[^3A_0]$ are relatively uniform. Then a summation of the theoretically expected phosphorescence emission intensities from each of the volume increments can be matched to the observed emission intensity to estimate k_{10}. A reasonably accurate treatment of the present data can be had using 14 different volume elements, the cross sections of which are defined by the areas of the elliptical rings between adjacent lines of equal intensity in Figure 1 and whose lengths run parallel to the cell axis. With this procedure we have assigned the average relative incident light intensity, $\bar{i}_i$ (proportional to the number of quanta/cm^2 incident on the ith area), starting with the outermost area: 3.5, 7.5, 12.5, 17.5, 22.5, 27.5, 35, 45, 55, 65, 75, 85, 92.5, and 97.5 arbitrary units. The actual areas (cm^2), a_i, of the cross sections of the ith volume increments in the same order are 0.335, 0.397, 0.303, 0.204, 0.157, 0.141, 0.126, 0.057, 0.051, 0.043, 0.0210, 0.0211, 0.0133, and 0.0096.

For the conditions of weak absorption which apply here (fraction of the incident light absorbed per centimeter = 0.0058), the number of triplet molecules (N^0_i) which will be formed initially per centimeter of path in the ith volume increment is given by relation B,

$$N^0_i = \frac{a_i \bar{i}_i I^0 \epsilon [A] 2.303}{\Sigma(a_i \bar{i}_i)} \quad \text{(B)}$$

(11) For examples of the numerous studies which suggest $k_4/(k_4 + k_5 + k_6) \cong 1$, see (a) H. J. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); *ibid.*, **14**, 48 (1960); (b) H. Ishakawa and W. A. Noyes, Jr., ref 9c; (c) C. S. Parmenter and H. M. Poland, *J. Chem. Phys.*, **51**, 1551 (1969).

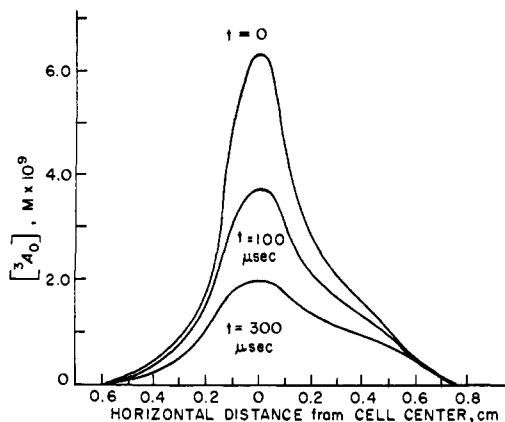(12) G. M. Almy and S. Anderson, *ibid.*, **8**, 805 (1940).

Figure 3. The theoretical spatial distribution of the biacetyl triplet concentration as a function of the horizontal distance from the cell center (perpendicular to the cell axis) and the time following the triplet excitation pulse: calculated for the case of incident light intensity $= 2.5 \times 10^{14}$ quanta/pulse; biacetyl pressure, 2.67 Torr; temperature, 25°.
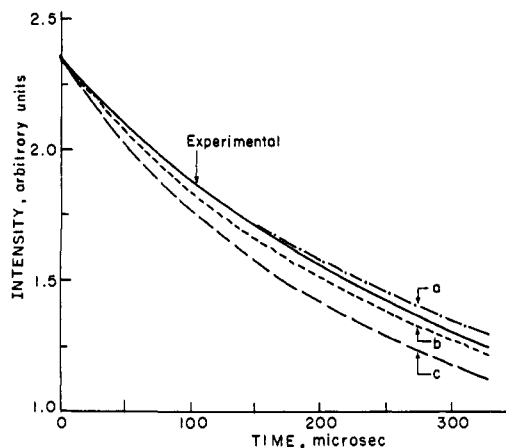

Figure 4. Comparison of the experimentally observed and theoretical phosphorescence decay curves of biacetyl triplets for various choices of the triplet–triplet annihilation reaction rate constant. Values chosen for k_{10} were (a) 3.5×10^{11}; (b) 4.2×10^{11}; and (c) 5.4×10^{11}. $k_{10} = 3.9 \times 10^{11}$ l./(mol sec) gave the best fit of the data at 150 μsec; data are from experiments with $I^0 = 2.7 \times 10^{14}$ quanta/pulse.

and the triplet concentration (moles/liter) in the ith volume element, $[^3A_0] = N^0_i/a_i$ (6.02 $\times$ 10^{20}). I^0 represents the total number of quanta in the laser pulse and was estimated for each run; it varied from 3.64 $\times$ 10^{14} to 0.786 $\times$ 10^{14} quanta/laser pulse; $\epsilon = 17.1$ l./(mol cm); [A] $= 1.44 \times 10^{-4}$ M for our experiments. Since the mixing of the triplets between the chosen volume elements will be relatively unimportant for the short time periods employed here, we can use the integrated form of relation A and calculate the time dependence of the triplet concentration in each of the volume elements.

$$[^3A_0]^t_i = \frac{[^3A_0]^0_i(k_8 + k_9)}{e^{t(k_8 + k_9)}[k_8 + k_9 + 2k_{10}[^3A_0]^0_i] - 2k_{10}[^3A_0]^0_i}$$
(C)

The curves of Figure 3 have been derived using this approach. The geometrical distribution of $[^3A_0]$ as a function of time is shown for a run at $I^0 = 2.5 \times 10^{14}$ quanta/pulse.

The phosphorescence emission which one observes at time t is proportional to the total number of biacetyl triplet molecules (N^t_{total}) which remain per centimeter of cell length at the observation time t, and $N^t_{total} = \Sigma N^t_i$. The number of triplets (N^t_i) which remain per centimeter of length in the ith volume element at time t is simply, $N^t_i = N^0_i[^3A_0]^t_i/[^3A_0]^0_i$. Then the theoretical value of the observed phosphorescence emission intensity (i^t_p) at time t is related to the initial intensity (i^0_p) by $i^t_p = i^0_p(N^t_{total}/N^0_{total})$.

In applying the method outlined, the value chosen for k_{10} was varied until reiterative computer calculations provided the desired match of the emission data. Two somewhat different methods of data fitting were used. In the first method, the value of k_{10} was selected which generated the best fit to the initial slopes of the phosphorescence intensity–time curves. The average value of k_{10} derived with this matching procedure is $k_{10} = (3.2 \pm 1.3) \times 10^{11}$ l./(mol sec). The second more accurate method of k_{10} estimation forced a perfect fit of the decay curve at some selected time interval following the pulse. The sensitivity of the fit on choice of k_{10} is illustrated in Figure 4 for an intensity of 2.5 $\times$ 10^{14} quanta/pulse. Curve a, derived assuming $k_{10} = 3.5 \times$

10^{11} l.(/mol sec), lies detectably above the observed phosphorescence curve and that calculated for the best fit, $k_{10} = 3.9 \times 10^{11}$. Choices of $k_{10} = 4.2 \times 10^{11}$ in b, and 5.4×10^{11} in c, force the theoretical decay curve significantly below the observed curve. A near fit of the calculated curve to the observed decay curve can be made over the entire 300-μsec observation time by the technique outlined. Estimates of the rate constant k_{10} obtained using this second calculation method are summarized in Table I for runs at various incident light in-

Table I. Summary of Rate Constants for the Biacetyl Triplet–Triplet Annihilation Reaction
$^3A_0 + {}^3A_0 \rightarrow A^* + A$ (10)[a]

Time at which perfect match was forced, μsec	Av k_1^0 $\times$ 10^{-11}, l./(mol sec)[b]	Incident laser intensity[a]	Av k_1^0 $\times$ 10^{-11}, l./(mol sec)[c]
25	4.2 ± 2.6	I^0	5.2 ± 1.1
50	4.0 ± 1.6	0.924 I^0	5.5 ± 0.7
75	4.3 ± 1.3	0.753 I^0	3.9 ± 0.7
100	4.0 ± 1.8	0.732 I^0	3.7 ± 0.6
125	4.4 ± 1.8	0.597 I^0	3.9 ± 0.8
150	4.1 ± 1.5	0.562 I^0	4.0 ± 1.0
175	4.3 ± 1.7	0.522 I^0	3.6 ± 0.5
200	4.1 ± 1.6	0.375 I^0	4.1 ± 1.1
225	4.3 ± 1.7	0.216 I^0	4.5 ± 1.6
250	4.1 ± 1.6		
275	4.4 ± 1.9		
300	4.4 ± 1.5		
Grand av $k_1^0 = (4.2 \pm 1.7) \times 10^{11}$ l./(mol sec)			

[a] Incident laser intensity, $I^0 = 2.64 \times 10^{14}$ quanta/pulse; wavelength, 4365 Å; pressure of biacetyl, 2.67 Torr; temperature, 25°. [b] Average value of k_{10} for runs at all intensities with forced fit at the particular time shown; error limits are twice the standard deviation, 95% confidence limits. [c] Average value of k_{10} for all times (25–300 μsec) in runs at the incident intensity shown.

tensities and times after the laser pulse. In the first half of Table I the values obtained from an average of the runs at the nine different initial intensities are shown; in

these cases a perfect match was forced at the specific times shown from 25 to 300 μsec. Note that the data are very consistent and reproducible even at the longest times employed where we would expect somewhat lower accuracy; for these conditions the theoretical concentration gradient could be altered somewhat from that predicted by our simple diffusion-free model. In the second half of Table I values of k_{10} are shown for experiments at specific incident light intensities and averaged over best fits at all times from 25 to 300 μsec. There is no trend of values with change in I^0, and the results are entirely consistent with those obtained by the first averaging procedure. The values of k_{10} obtained using the integrated rate law are somewhat higher than those obtained from initial slopes, but the differences are well within the error limits of the experimental data. Certainly less reliance should be placed on the results of the initial slope method, since they depend upon a least-squares fit of the rate data to a parabolic equation and extrapolation to zero time. The consistency of the rate data at all times and intensities suggests that further refinement of our model is unwarranted with the available accuracy of the present phosphorescence-time data. Probably the best estimate of k_{10} that can be derived from the present data is the grand average of all the data of Table I; $k_{10} = (4.2 \pm 1.7) \times 10^{11}$ l./(mol sec).[13]

Comparison of the Present Results with Those of Previous Biacetyl Studies. It is interesting to speculate on the detailed nature of the reaction 10 and compare our present findings with those of the earlier workers. Estimates of the primary quantum yield for molecular dissociation (ϕ_D) have been made by Sheats and Noyes[6] in experiments at 4358 Å and 27°. ϕ_D was relatively insensitive to pressure but increased linearly with absorbed light intensity. In view of the findings of Noyes, Mulac, and Matheson,[8] it is likely that the observed decomposition originated on interaction between two excited triplet biacetyl molecules. Spin conservation suggests that the most probable immediate products of the triplet–triplet annihilation in reaction 10 would be two singlet states; energy restrictions would favor formation of one product in an excited singlet state and the other in the ground state. The two singlet states cannot both be ground electronic states, since the equipartition of energy between the two molecules for this case would not lead to the observed decomposition; the lowest energy level above the ground state from which decomposition occurs is at about 72 kcal/mol.[6] Therefore one excited singlet and one ground state are the likely primary products of the reaction 10. The electronic energy of each of the two triplet states is 57 kcal/mol. Thus the combined electronic energy, 114 kcal/mol, is sufficient to excite the second excited singlet of biacetyl whose (0,0) band lies at about 90 kcal/mol above the ground state in the pure biacetyl crystal at 20°K.[14] If one assumes that on the average the excess electronic energy is about equally distributed as vibrational energy between the second excited singlet and the ground-state molecules formed in reaction 10, then the excited singlet will have about 12 kcal of excess vibrational energy in addition to

the 90 kcal/mol of electronic energy. From these very simple arguments one would expect that the product which we have labeled A* in reaction 10 would be similar in properties to the biacetyl molecule formed on absorption of a light quantum of wavelength near 2800 Å. Many years ago Noyes and coworkers[9a] pointed out the similarity of the primary process for decomposition at 4358 Å and room temperature to that at 2700 Å. In both cases the α, defined in the following primary dissociative step, is equal to about 0.5.

$$CH_3COCOCH_3 + h\nu \longrightarrow 2(1 - \alpha)CH_3CO + 2\alpha CH_3 + 2\alpha CO$$
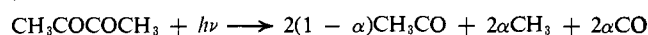
Values of k_{10} have not been estimated by previous workers. However, we may use the previously published data of Sheats and Noyes[6] and Noyes, Mulac, and Matheson[8] to test the hypothesis given as to the nature of A* formed in reaction 10. We can estimate values for k_{10} from their data as well, but the accuracy of the values is probably very low since the degree of homogeneity of the absorbed light is unknown, and several questionable assumptions must be made in the calculations.

Sheats and Noyes[6] have calculated the primary dissociative quantum yields at 4358 Å and room temperature for experiments at several light intensities. In terms of the mechanism outlined, the experimental estimate of ϕ_D/I_a should be given by the relation D.

$$(\phi_D/I_a) \cong \phi'_D k_{10}[k_4/(k_4 + k_5 + k_6)(k_8 + k_9)]^2 \quad (D)$$

ϕ_D and ϕ'_D are the primary quantum yields of biacetyl molecule dissociation for experiments at 4358 and at 2800 Å, respectively. Bell and Blacet[15] photolyzed biacetyl at 2804 Å, [A] = 1.3×10^{13} M, and found ϕ_D = 0.27; this is in reasonable agreement with ϕ_D = 0.31 measured at 2700 Å by Sheats and Noyes.[6] A value of $\phi_D/I_a = 5.1 \times 10^{-17}$ (cc sec)/molecule can be obtained from the data of Sheats and Noyes for runs at room temperature, 4358 Å, and [A] = 1.5×10^{-3} M. Taking $k_4/(k_4 + k_5 + k_6) = 1$, $k_8 + k_9 = 6.7 \times 10^2/$ sec^{-1}, we estimate $k_{10} \cong 5.1 \times 10^{10}$ l./(mol sec).

In a similar fashion, an estimate of k_{10} can be made from the published data of Noyes, Mulac, and Matheson. They report for the photolysis of biacetyl at 4358 Å and 25°, the rate ratio $(dP/dt)(1/I_a)^2 = 4.8 \times 10^{-16}$ (cc sec)/molecule. (dP/dt) is the rate of formation of gaseous products which are noncondensable at liquid nitrogen temperature, and I_a is the absorbed light intensity. Most of the measured product was carbon monoxide, so we can assume $(dP/dt) \cong (d[CO]/dt)$. In terms of the presently accepted mechanism for biacetyl photolysis at 4358 Å and 25°, we expect relation E to hold approximately. We assume $\alpha = 0.5$,[9a] and

$$(d[CO]/dt)(1/I_a)^2 \cong k_{10}(2\alpha)\phi'_D \times$$
$$\{k_4/(k_4 + k_5 + k_6)[1/(k_8 + k_9)]\}^2 \quad (E)$$

the values of the other terms on the right side of relation E are as before; this procedure gives $k_{10} \cong 4.8 \times 10^{11}$ l./(mol sec). The agreement between the estimates of k_{10} based on product quantum yield data and the value of k_{10} which we estimate from our phosphorescence decay measurements is certainly as good as one could anticipate in view of the probable inhomogeneity of the absorbed light intensity and uncertainties in the inter-

(13) The error limits shown are the 95% confidence limits (2σ) calculated assuming that random errors only contribute to the variations between estimates.
(14) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 77, 6461 (1955).
(15) W. E. Bell and F. E. Blacet, *ibid.*, 76, 5332 (1954).

pretation of the previous results. It lends credence to the hypothesis that one of the products of reaction 10 is a dissociative second-excited singlet state of biacetyl which is similar to that formed on direct photolysis at 2800 Å.

We are aware of only a very few published measurements of the rate constants for triplet–triplet annihilation reactions for other compounds in the gas phase. By flash spectroscopy Porter and West[16] estimate the rate constants for the bimolecular triplet–triplet annihilation reaction of naphthalene triplets at 90°, $k \geq$ $(6.3 \pm 0.8) \times 10^{10}$ l./(mol sec), and for anthracene triplets at 140°, $k = (1.4 \pm 0.4) \times 10^{11}$ l./(mol sec). The extinction coefficients for the gaseous triplets were assumed to be equal to those determined in liquid-phase experiments. Finger, Zamani-Khamiri, Olmsted, and Zahlan[17] also estimated the rate constants for the anthracene triplet–triplet annihilation reaction in the vapor phase, $k = 3.8 \times 10^{11}$ at 160° and 4.3×10^{11} l./(mol sec) at 280°.

In every case reported for triplet–triplet annihilation reactions in the gas phase, the apparent interaction distance at which the energy transfer occurs is rather large, somewhat greater than or equal to the collision number. Our data for biacetyl triplets suggest that reaction 10 occurs when the average distance between molecular centers (assuming spherical molecules) is about 11 Å.

Possible Importance of the Triplet–Triplet Annihilation Reaction in Biacetyl Photolyses with Steady Illumination. Using the k_{10} estimated in this work, we can determine now the conditions for which reaction 10 is anticipated to be significant in photochemical experiments with steady illumination. For experiments at room temperature, about 1% of the triplets decay by this reaction when the $[^3A_0] = 8.0 \times 10^{-12}$ M. Of course a greater proportion of triplet removal by (10) results at higher triplet concentrations. For runs at the wavelength 4365 Å and the pressure of biacetyl employed here, 2.67 Torr, the triplet concentration reaches a steady state value of 8.0×10^{-12} M for a light intensity of 5.7×10^{14} quanta/(sec cm²) incident on the cell face. At the highest pressures of biacetyl which can be employed at room temperature, about 40 Torr, an incident intensity of about 3.9×10^{13} quanta/(sec cm²) will generate this triplet concentration. Obviously the extent of participation of reaction 10 can be significant for condition commonly employed experimentally, although its occurrence appears not to have been considered in some previous work. For example, Garabedian and Dows[18] observed a small decrease in the relative ratio of the intensity of the biacetyl triplet phosphorescence to the absorbed light intensity as the pressure of biacetyl was increased in

(16) G. Porter and P. West, *Proc. Roy. Soc., Ser. A*, 279, 302 (1964).

(17) G. Finger, O. Zamani-Khamiri, J. Olmsted, III, and A. B. Zahlan, "The Triplet State," Cambridge University Press, New York, N. Y., 1967, p 455.

(18) M. E. Garabedian and D. A. Dows, *J. Amer. Chem. Soc.*, 90, 2468 (1968).

experiments at room temperature and 4000 ± 150 Å. This effect could have originated entirely from the participation of reaction 10, rather than the quenching reaction 11 which they suggest as the origin of the effect.

$$^3A_0 + A \longrightarrow 2A \qquad (11)$$
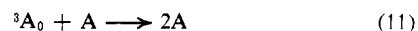
At experiments at constant incident light intensity, the effects of the occurrence of 10 and 11 are indistinguishable kinetically for their conditions. The light which they employed was largely of wavelengths 4045–4078 Å for which they found $\epsilon = 10.2$ l./(mol cm) for biacetyl. From this value and the present data, it can be shown easily that the apparent quenching rate constant which they report, $k_{11} = 7.1 \times 10^4$ l./(mol sec), could be an artifact resulting from the occurrence of reaction 10 if the incident light intensity in their experiments was about 1.5×10^{15} quanta/(sec cm²) at the cell face. They did not determine the absolute intensity of the light which they employed, but it well could have been about 10^{15} quanta/(sec cm²) since this is the usual magnitude of the incident intensity which one achieves using the type of lamp and filter assembly employed by Garabedian and Dows. If reaction 10 is the origin of the effect which these authors report, then the apparent quenching rate constant which they derive would be proportional to the incident light intensity. No test of this hypothesis is possible from their data which were determined at essentially constant incident light intensity. Our recent studies[4] indicate that k_{11} is far less than the value suggested by Garabedian and Dows, and we favor the occurrence of (10) and/or impurity quenching[4] in the explanation of their results.

At the very low intensities of the spectrophosphorimeter employed in the SO_2–biacetyl systems studied previously by our research group,[1,2] reaction 10 must be unimportant, and no significant error was introduced by neglecting it in that work. In the study of Sidebottom, et al.,[3] the quantum yield of phosphorescence emission from triplet sulfur dioxide excited using a 3829-Å laser pulse was estimated; the quantum yield of biacetyl emission excited under similar conditions at 3829 Å was accepted as the standard. The present rate data suggest that only a few per cent of the biacetyl triplets decayed by (10) for the conditions employed. This conclusion is in accord with the $^3A_0$ lifetimes observed in that work. These were independent of the biacetyl pressure in experiments from 0 to 0.2 Torr, and within the experimental error they were equal to $1/(k_8 + k_9)$ estimated in our later work.[4] No correction to the values of ϕ_p for SO_2 reported in that work is necessary within the accuracy of the measurements.