

## Transfer of Triplet State Energy in Fluid Solutions

### I. Sensitized Phosphorescence and Its Application to the Determination of Triplet State Lifetimes

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The photo-luminescence spectra of biacetyl, benzil, and anisil, in oxygen-free benzene solutions at room temperature have been determined, using the mercury line at  $366\text{ m}\mu$  as exciting light. All three substances show mainly phosphorescence, with a mean lifetime exceeding  $5 \times 10^{-8}$  sec, but also measurable fluorescence. Addition of an efficient phosphorescence quencher makes it possible to study the fluorescence spectra separately.

Measurements on solutions containing both benzophenone and one of the three substances mentioned have shown that the latter may be excited to luminescence also by light primarily absorbed by benzophenone. The spectrum of this sensitized luminescence shows it to be pure phosphorescence. This proves that the sensitization takes place by a transfer of triplet state energy from sensitizer to acceptor.

The triplet energy level of benzophenone lies  $4\,000\text{ cm}^{-1}$  above that of biacetyl. This difference is sufficiently large to justify the assumption that the transfer of triplet state energy is a diffusion controlled process. On this basis the mean life of benzophenone in its triplet state may be calculated from measurements of the intensity of sensitized biacetyl phosphorescence as a function of the concentration of biacetyl. The following values were obtained: in benzene solution at  $20^\circ\text{C}$ ,  $1.9 \times 10^{-6}$  sec, in isopropanol solution,  $5.7 \times 10^{-6}$  sec at  $20^\circ\text{C}$ , and  $4.6 \times 10^{-6}$  sec at  $25^\circ\text{C}$ . The latter figure is in satisfactory agreement with a previous value calculated from the kinetics of a photochemical reaction involving triplet state benzophenone.

Comparative intensity measurements of sensitized and unsensitized biacetyl phosphorescence indicated that the internal conversion from the excited singlet state to the triplet state is virtually complete in fluid solution. It is suggested that the low phosphorescence yield in biacetyl vapour is due to radiationless transitions to the ground state from higher vibrational levels of the triplet state.

In a previous paper<sup>1</sup> we presented the results of a study of the quenching effect of different types of compounds on the long-lived fluorescence of biacetyl in solution. As shown by Lewis and Kasha<sup>2</sup>, this luminescence accompanies the spin-forbidden transition of an excited biacetyl molecule

from its lowest triplet state to the singlet ground level. In the nomenclature proposed by these authors<sup>3</sup> it should therefore be termed phosphorescence to distinguish it from normal fluorescence, which is a spin-allowed transition (generally singlet  $\rightarrow$  singlet). In the present paper we have adopted this nomenclature.

One result of our study<sup>1</sup> was the discovery of a class of quenchers, consisting of unsaturated and aromatic compounds, that were assumed to act by a transfer of excitation energy resulting in a triplet  $\rightarrow$  singlet transition in the biacetyl molecule and the reverse transition in the quencher. This type of energy transfer has been shown by Terenin and Ermolaev<sup>4</sup> to explain the phenomenon of sensitized phosphorescence observed in solid solutions at liquid air temperature. Broadly speaking, the necessary condition for the transfer to be possible is that the triplet energy level of the sensitizer (donor) must lie above that of the acceptor. As pointed out in our previous paper, the same process of energy transfer may be expected to take place in fluid solutions at ordinary temperatures. Substances with triplet levels lying below that of biacetyl should therefore act as quenchers of biacetyl phosphorescence. This interpretation of our results receives strong support from further work on phosphorescence quenching, to be published shortly.

On the other hand, substances with triplet levels lying *above* that of biacetyl, should be able to function as sensitizers of biacetyl phosphorescence in solution. The present paper gives the results of experiments designed to test this conclusion. The experiments were extended to two other substances showing phosphorescence in solution, namely benzil and anisil.

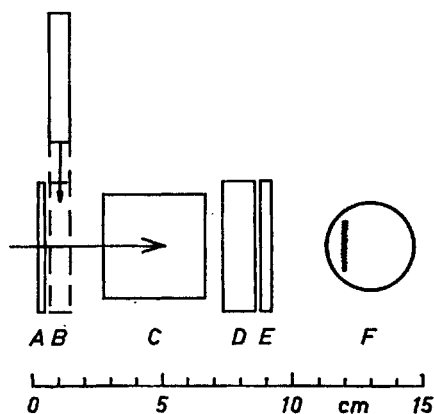
## EXPERIMENTAL

### Apparatus

For measuring *luminescence spectra* the optical system of a Beckman DU spectrophotometer was used. The cell compartment mounting block, containing the entrance mirror, was replaced by a similar metal block into which a sealed Pyrex tube (outer diameter 8 mm), containing the degassed solution to be studied, could be introduced from below directly in front of the entrance slit. An opening in the metal block permitted the tube to be illuminated from the side. Light from a water-cooled 80-watt A.C. mercury lamp, Hanau S 81, was filtered through a 2 mm Schott UG 2 glass and focused on the tube with a lense. The exciting light was therefore mainly of wavelength  $366 \mu$ . A Sorensen voltage regulator was used to keep the lamp voltage constant.

From the exit slit of the instrument the light beam passed through a hole (diameter 12.5 mm) in the metal block and struck the photocathode of a multiplier phototube of the head-on type. The latter was enclosed in a light-tight housing screwed on to the back of the metal block. Two different multiplier tubes were used, RCA 5819 and RCA 6217. The latter tube has a spectral sensitivity curve extending farther into the red wavelength region, but also a less favourable signal to noise ratio. The tube was connected to a stabilized adjustable voltage supply and the current was read on a sensitive light-spot galvanometer (Norma Model 251 J). The voltage was chosen so as to give satisfactory results with a low slit width. For biacetyl luminescence a slit width of 0.2 mm was used, corresponding to a half-intensity band width of  $4 \mu$  at the wavelength  $500 \mu$ . For benzil and anisil the slit width had to be increased to 0.3 mm owing to the lower luminescence yield.

In determining a spectrum, readings were taken at different settings of the wavelength selector. Repeated readings at the wavelength corresponding to the maximum in the luminescence curve served as a check on the constancy of the exciting light. Using the



*Fig. 1.* Schematic diagram of experimental arrangement for measuring relative luminescence intensities. (A) Light filter (Schott UG2, 2 mm). (B) Uranyl glass. (C) Cylindrical glass cell,  $4 \times 4$  cm. (D) Quartz cell with 0.5 M sodium nitrite solution. (E) Light filter (Chance OY3, 4 mm). (F) Multiplier phototube, RCA 931 A. — A light-tight box with an opening for the exciting beam enclosed parts C–F. The measurements were made in a darkened room.

spectral sensitivity curves of the multiplier phototubes, as given by the manufacturers, and the dispersion data for the Beckman spectrophotometer, relative intensity values at different wavelengths were calculated. No correction was made for the variation of reflexion losses with wavelength. The curve thus obtained was finally recalculated to give relative numbers of light quanta emitted at different wave-numbers.

For all three substances studied luminescence curves were determined with both photomultiplier tubes, covering the range from the onset of luminescence at about  $470 \text{ m}\mu$  to the limit (about  $610 \text{ m}\mu$ ) where the normal sensitivity of tube 5819 has dropped to 10 % of its maximum value. The results with the two tubes showed no systematic deviations. The curves shown in Figs. 4–6 are based on measurements made with tube 6217 for wavelengths above  $600 \text{ m}\mu$  and with tube 5819 for shorter wavelengths.

The experimental arrangement for measuring *relative luminescence intensities* is shown schematically in Fig. 1. The degassed solution was contained in the cylindrical glass cell C (shown in more detail in Ref.<sup>1</sup>, Fig. 2). It was excited to luminescence by a light beam of wavelength  $366 \text{ m}\mu$  from the exit slit of a Bausch and Lomb grating monochromator (1 200 grooves per mm, focal length 500 mm). The light source was an A.C. mercury lamp. Fluctuations in line voltage were eliminated with a Sorensen voltage regulator. The luminescence light reaching the cathode of the photomultiplier tube (F) was limited by the filter combination D + E to wavelengths  $>$  approximately  $510 \text{ m}\mu$ . The stabilized voltage applied to the multiplier tube was adjusted to give a current of suitable magnitude within one of the two lowest measuring ranges of a certified high-resistance light-spot galvanometer (Norma Model 251 J). The sensitivity in these ranges was  $1.975 \times 10^{-8}$  and  $1.975 \times 10^{-7}$  A per scale division, respectively.

The fluorescent uranyl glass (B) was used to obtain a measure of the intensity of the exciting light. With C removed and B in the path of the light beam, in an accurately fixed position, the photocurrent produced by the fluorescence light was determined. This current was in the third measuring range of the galvanometer ( $1.975 \times 10^{-7}$  A per scale division). Determinations made before and after a luminescence measurement showed that the intensity of the exciting light was constant to better than 1 % during an experiment.

In order to minimize photochemical changes in the solutions they were exposed to light as little as possible.

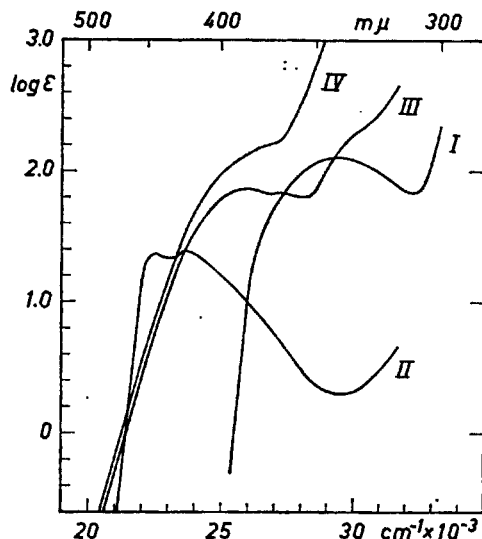


Fig. 2. Absorption spectra in benzene solution,  $\log \epsilon$  vs. wave number in  $\text{cm}^{-1}$ . (I) Benzophenone. (II) Biacetyl. (III) Benzil. (IV) Anisil.

### Materials

*Anisil* (*p,p'*-dimethoxybenzil) was prepared from anisoin according to the directions of Biltz and Arnd<sup>2</sup>. It was recrystallized three times from ethanol.

All other chemicals were of the highest purity obtainable commercially. *Biacetyl* was further purified and stored as described earlier<sup>1</sup>. *Benzil* was recrystallized three times from ethanol. *Benzophenone* was recrystallized twice from an ethanol-water mixture and once from a methanol-water mixture. *Benzene* and *isopropanol* were fractionally distilled using a column corresponding to 15 theoretical plates.

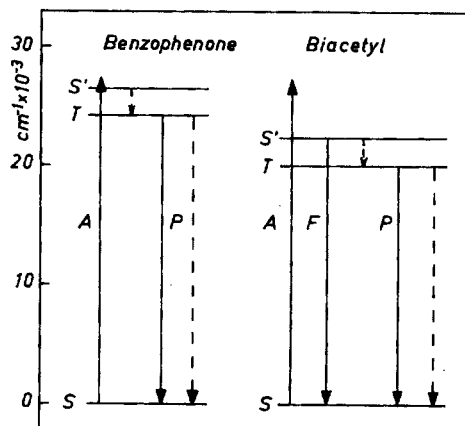
All solutions were degassed as described earlier<sup>1</sup>. The phosphorescence lifetime for biacetyl in dilute benzene solution at 20°C was generally found to be only about 700  $\mu\text{sec}$  as against 1 000  $\mu\text{sec}$  in our earlier work<sup>1</sup>. This shows that we did not succeed in obtaining the benzene as pure as earlier although the raw-material was from the same source and the method of purification was the same.

### RESULTS AND DISCUSSION

#### Luminescence spectra

The substance used as sensitizer was benzophenone. Its long-wave absorption band in benzene solution at room temperature is shown in Fig. 2, together with the corresponding spectra of the acceptors studied. The molar decadic extinction coefficients at 366  $m\mu$  were found to have the following values: benzophenone 67, biacetyl 4.5, benzil 68, anisil 180.

Energy level diagrams for benzophenone and biacetyl are shown in Fig. 3. Only the lowest excited levels are included as being the only ones of interest in the present connection. Since liquid solutions of benzophenone do not show



*Fig. 3.* Electronic energy level diagrams for benzophenone and biacetyl, showing the energy above the ground level (S), expressed in wave numbers, of the first excited singlet level (S') and the lowest triplet level (T). Solid arrows represent transitions involving radiation: (A) absorption of light of wavelength  $366\text{ m}\mu$ , (F) fluorescence, (P) phosphorescence. Dashed arrows represent radiationless transitions.

measurable phosphorescence, the position of its lowest triplet level is known only from its phosphorescence spectrum in solid solutions at liquid air temperature. For this reason the diagrams are based entirely on absorption and luminescence measurements made under those conditions<sup>4,6-8</sup>. The spectral changes produced by changing the temperature or the solvent are small enough to be unimportant in the present discussion.

Only the zero-point vibrational levels are shown, in order not to complicate the diagrams\*. It will be noted that no radiative  $S' \rightarrow S$  transition is indicated in the case of benzophenone. Benzophenone shows no fluorescence, only phosphorescence, which proves<sup>10</sup> that the radiationless transition to the slightly lower lying triplet level is essentially complete. This means that the lifetime of benzophenone in its excited singlet state must be so short that transfer of energy to the acceptor from benzophenone molecules in this state may be ruled out as a possibility. This is one of the advantages of using benzophenone as a sensitizer in the present case.

The value reported<sup>7</sup> for the quantum efficiency of phosphorescence in solid solution at  $77^\circ\text{K}$ ,  $0.84 \pm 10\%$ , shows that under these conditions radiationless transition to the ground state must be of minor importance. The rate of decay of phosphorescence under the same conditions<sup>7</sup> corresponds to a mean life of the triplet state of 0.008 sec. In liquid solution at ordinary temperature, collisional deactivation or chemical reaction with the solvent reduces the lifetime to a small fraction of this value (See p. 59).

\* In accordance with the Franck-Condon principle, molecular spectra are largely determined by the higher vibrational levels. See, e.g., Förster<sup>9</sup>. The absorption and luminescence spectra of benzophenone have recently been discussed by Dörr<sup>6</sup>.

Biacetyl shows fluorescence as well as phosphorescence, and the same is true of the other two substances studied as acceptors in the present work. As found by Groh<sup>11</sup>, irradiation of biacetyl vapour with light of wavelength 366  $m\mu$  leads to the emission of a "fast" fluorescence of low intensity and with a spectrum lying mostly between 400 and 500  $m\mu$ , in addition to the previously known slow fluorescence (phosphorescence) whose spectrum lies mostly at wavelengths  $> 500 m\mu$ . Similarly, Sidman and McClure<sup>8</sup> found that the photoluminescence of biacetyl crystals at low temperatures contains a weak blue component. An analysis of its band spectrum showed it to be true fluorescence.

For the purpose of the present investigation, the most important difference between benzophenone and biacetyl is that the latter compound shows strong phosphorescence even in liquid solution in a suitable solvent. No measurements of quantum efficiency either in solid or in liquid solution have been made, but already the existence of fluorescence shows that the internal conversion  $S' \rightarrow T$  cannot be complete. However, molecules that have reached the triplet state exhibit remarkable stability toward deactivating influences. This is shown by the fact that the triplet state lifetime in benzene solution at 20°C may amount to<sup>1</sup> as much as  $1.0 \times 10^{-3}$  sec, which is 45 % of the value found in solid solution at liquid air temperature.

As regards the relative positions of the energy levels of the two substances, Fig. 3 shows that the  $S'$  level of benzophenone lies above that of biacetyl. From this point of view an energy transfer:  $D_{S'} + A_S = D_S + A_{S'}$  ( $D$  donor,  $A$  acceptor) would be possible. For the reason mentioned above this possibility may, however, be excluded. That this is not the mechanism of the sensitized luminescence observed is confirmed by the experimental results. As shown below, the sensitized luminescence is pure phosphorescence, whereas raising the acceptor to the  $S'$  level by direct light absorption produces both fluores-

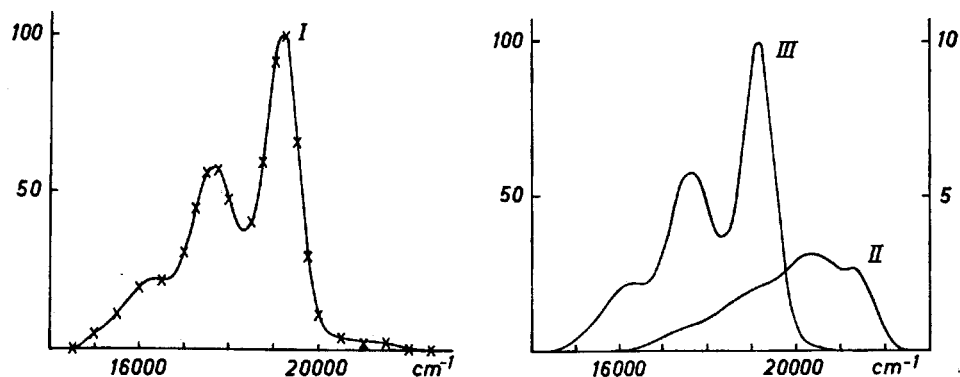


Fig. 4, a and b. Luminescence spectra of biacetyl in benzene solution, showing relative numbers of light quanta emitted *vs.* wave number in  $cm^{-1}$ . (I) Unsensitized luminescence. Biacetyl 0.222 M, observed values. (X) Calculated values. (II) Fluorescence (scale to the right). Biacetyl 0.222 M, pyrene  $4.4 \times 10^{-4}$  M. (III) Sensitized luminescence (scale to the left). Benzophenone  $2.64 \times 10^{-2}$  M, biacetyl  $7.0 \times 10^{-3}$  M.

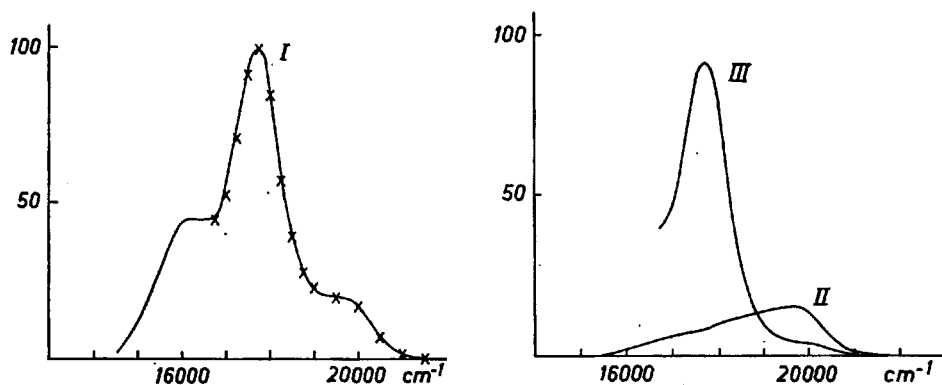


Fig. 5, a and b. Luminescence spectra of benzil. (I) Unsensitized luminescence. Benzil  $2.14 \times 10^{-3}$  M, observed values. (X) Calculated values. (II) Fluorescence. Benzil  $2.75 \times 10^{-3}$  M, pyrene  $2.7 \times 10^{-4}$  M. (III) Sensitized luminescence. Benzophenone  $3.43 \times 10^{-3}$  M, benzil  $1.49 \times 10^{-3}$  M. — The measurements represented by curve III met with difficulties and were only pursued as far as shown. Apparently a photochemical reaction took place, leading to a change in the spectrum.

cence and phosphorescence. There can be no doubt, therefore, that the sensitization takes place by a process:  $D_T + A_S = D_S + A_T$ . That this process is energetically possible is shown by the relative position of the triplet levels.

The results obtained with the three acceptors studied are given in graphical form in Figs. 4–6, the relative number of light quanta emitted being plotted in arbitrary units against the wave-number in  $\text{cm}^{-1}$ . In each case, curve I represents the spectrum obtained on irradiating a pure solution of the acceptor in benzene with light of wavelength  $366 \text{ m}\mu$ . This spectrum is partly fluorescence, partly phosphorescence. The curves marked II represent the pure fluorescence spectrum as obtained by eliminating the phosphorescence by the addition of a small quantity of pyrene, which is a strong phosphorescence quencher<sup>1</sup>. The fact that pyrene itself shows fluorescence made it necessary to apply a slight correction. The fluorescence of pyrene in very dilute solutions<sup>1a</sup> lies mainly in the ultraviolet but extends into the visible with decreasing intensity. The magnitude of the correction was obtained from the observed fluorescence in the region  $23\,000\text{--}25\,000 \text{ cm}^{-1}$  where the acceptors themselves show no luminescence, as is evident from curves I.

The curves marked III represent the luminescence spectra of solutions containing both benzophenone and a low concentration of acceptor. The concentrations were such that only a small fraction (2–7 %) of the absorbed light went to the acceptor, the rest being absorbed by the benzophenone. Nevertheless, visual comparison showed that the luminescence intensity was much higher than that obtained when the acceptor was present alone in the same low concentration. This was confirmed by quantitative intensity measurements of biacetyl luminescence that will be presented in a later section (p. 60).

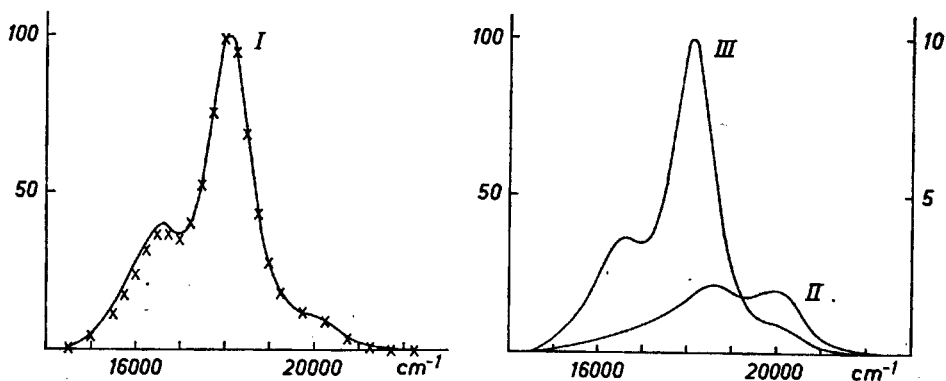


Fig. 6, a and b. Luminescence spectra of anisil. (I) Unsensitized luminescence. Anisil  $6.9 \times 10^{-2}$  M, observed values. (X) Calculated values. (II) Fluorescence (scale to the right). Anisil  $1.27 \times 10^{-2}$  M, pyrene  $2.7 \times 10^{-4}$  M. (III) Sensitized luminescence (scale to the left). Benzophenone  $2.64 \times 10^{-3}$  M, anisil  $7.8 \times 10^{-4}$  M.

There is thus no doubt that radiation absorbed by benzophenone gives rise to a sensitized luminescence of the acceptor. The spectrum of this luminescence differs from that obtained on direct excitation of the acceptor. Curve I for benzil shows a hump which coincides with the maximum in the fluorescence spectrum (curve II) and which is absent in curve III. Similarly curve I for biacetyl extends to higher wave-numbers than curve III. In the case of anisil the difference is less apparent which can be connected with the position and low intensity of its fluorescence. The conclusion seems inevitable that fluorescence is absent from the sensitized luminescence, which therefore represents pure phosphorescence. In agreement with this it is found that by multiplying the experimental intensity values for sensitized luminescence and for fluorescence by suitably chosen factors, one for each kind of luminescence, curves are obtained that, when added together, reproduce the directly excited luminescence (curve I) of the acceptor in question. In the figures, curves II and III have been drawn in this manner, and the result of the addition is represented by the crosses in Figs. 4a, 5a and 6a. By determining the areas under the curves it is found that the ratio between the quantum efficiencies of phosphorescence and of fluorescence under our experimental conditions was 20:1 for biacetyl, 4.0:1 for benzil, and 25:1 for anisil.

Obviously, very different values may be expected under other conditions. Thus it has been reported by Ermolaev<sup>13</sup>, who studied the luminescence of different carbonyl compounds, including benzil, in solid solutions at  $-195^\circ\text{C}$ , that their luminescence, within an error of 2–3 %, consisted entirely of long-lived radiation. For benzil he found a mean life of this radiation of  $4.4 \times 10^{-3}$  sec. Under our conditions it was only  $7 \times 10^{-5}$  sec, which shows that the phosphorescence yield had been reduced in the ratio of 60:1. The fluorescence yield, on the other hand, probably changes relatively little with temperature. Our results are therefore not incompatible with those of Ermolaev.



Table 1. Intensity of sensitized biacetyl phosphorescence in benzene solution at 20°C as a function of biacetyl concentration. Sensitizer: benzophenone,  $1.65 \times 10^{-3}$  mole/l.

[A] mole/l	I, scale divisions	$\tau_A$ $\mu\text{sec}$	$\tau_A/I$ observed	$\tau_A/I$ calculated
$2.76 \times 10^{-3}$	90.5	489	5.40	5.35
$2.73 \times 10^{-4}$	71.5	445	6.22	6.28
$5.07 \times 10^{-5}$	39.5	440	11.1	10.8
$2.39 \times 10^{-5}$	31.0	528	17.0	17.0
$1.64 \times 10^{-5}$	21.1	440	20.9	22.4

For benzil and anisil, phosphorescence in fluid solution has not been reported previously. The following values of the phosphorescence mean life were determined as described earlier<sup>1</sup>: Benzil in benzene,  $5.9 \times 10^{-3}$  M,  $\tau = 71 \mu\text{sec}$ , benzil in carbon tetrachloride,  $4.7 \times 10^{-3}$  M,  $\tau = 141 \mu\text{sec}$ , anisil in benzene,  $1.4 \times 10^{-3}$  M,  $\tau = 60 \mu\text{sec}$ .

The intensity of sensitized phosphorescence as a function of the acceptor concentration. The triplet state lifetime of the sensitizer

With benzophenone as sensitizer and biacetyl as acceptor, the intensity of the sensitized phosphorescence was studied as a function of the acceptor concentration, using the method described above. In one series of measurements the solvent was benzene, in two others, *isopropanol*. In each series the voltage applied to the photomultiplier tube was adjusted so that the fluorescence of the uranyl glass always gave the same photocurrent. The phosphorescence photocurrents observed were therefore directly comparable. Before a measurement the solution was brought to the desired temperature. For every solution the phosphorescence mean life was determined at 20°C.

The results for benzene solutions at 20°C are given in Table 1, those for *isopropanol* solutions at 20 and 25°C in Fig. 7. They can be accounted for on the following reaction scheme. In addition to the processes indicated in the energy level diagram, Fig. 2, the scheme includes possible chemical reactions with the solvent (L) (steps 3 and 7).



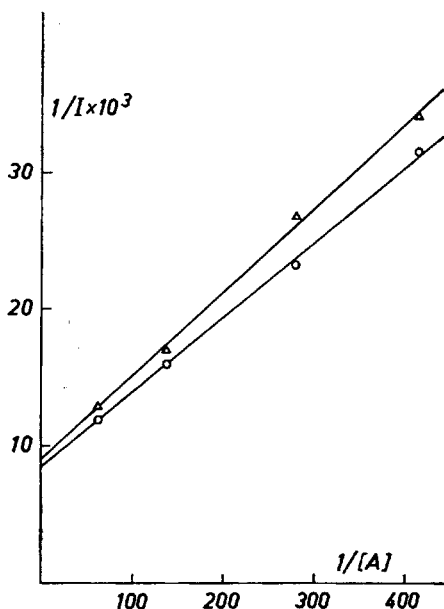


Fig. 7. Sensitized phosphorescence of biacetyl in isopropanol solution,  $1/I$  vs.  $1/[A]$ .  $I$  = phosphorescence intensity in scale divisions,  $[A]$  = biacetyl concentration in mole/l. Sensitizer benzophenone,  $3.74 \times 10^{-2}$  M.  $\odot$  20°C,  $\Delta$  25°C.

The assumption that, in the case of benzophenone, step (1) has a quantum efficiency = 1, seems to be supported by all known facts\*. Triplet state acceptor molecules will then be formed with the quantum efficiency

$$\varphi_4 = \frac{k_4[A_S]}{k_2 + k_3[L] + k_4[A_S]}$$

The probability for radiative transition of  $A_T$  to the ground state is equal to

$$\frac{k_5}{k_5 + k_6 + k_7[L]}$$

The quantum efficiency of phosphorescence therefore becomes

$$\varphi_5 = \frac{k_4[A_S]}{k_2 + k_3[L] + k_4[A_S]} \cdot \frac{k_5}{k_5 + k_6 + k_7[L]}$$

The natural mean lifetime of the acceptor in its triplet state,  $\tau_A^N$ , its mean lifetime in the solution,  $\tau_A$ , and the triplet state lifetime of the donor in the absence of acceptor,  $\tau_D^0$ , are given by:

$$\tau_A^N = \frac{1}{k_5}; \quad \tau_A = \frac{1}{k_5 + k_6 + k_7[L]}; \quad \tau_D^0 = \frac{1}{k_2 + k_3[L]}$$

$$\text{Hence: } \frac{1}{\varphi_5} = \frac{\tau_A^N}{\tau_A} \left( 1 + \frac{1}{k_4[A]\tau_D^0} \right) \quad (8)$$

where  $[A]$  denotes the concentration of the acceptor.

\* For a discussion of this point, see Bäckström, H. L. J., Steneryr, A. and Perlmann, P. *This Journal* 12 (1958) 8.

Provided that the experimental conditions are such that the photocurrent ( $I$ ) may be assumed to be proportional to  $\varphi_s$ , the following relations should hold:  $I = a\varphi_s$ , where  $a$  is a constant, and

$$\frac{\tau_A}{I} = K \left( 1 + \frac{1}{k_4[A]\tau_D^0} \right), \text{ where } K = \frac{\tau_A^N}{a}$$

The values of  $\tau_A/I$  given in the last column of Table 1 were calculated from a formula of this type, namely,

$$\frac{\tau_A}{I} = 5.25 \left( 1 + \frac{1}{1.87 \times 10^4[A]} \right)$$

The high value of the mean lifetime of triplet state biacetyl in benzene solutions makes it very susceptible to deactivation by impurities accidentally present. This is probably the explanation of the variations in  $\tau_A$  in Table 1. It may easily be shown that eqn (8) should be valid also if a deactivation of this kind is included in the reaction scheme. The necessary condition is only that the impurity should not change the value of  $\tau_D^0$ . However, the much shorter lifetime of benzophenone in its triplet state makes it much less susceptible to deactivating influences.

In isopropanol solutions the lifetime of biacetyl in its triplet state is considerably reduced by reaction with the solvent (step 7). Within limits of error the same value of  $\tau_A$  was found in all cases (21  $\mu$ sec at 20°C). The results of the intensity measurements are given in graphical form in Fig. 7,  $1/I$  being plotted against  $1/[A]$ . The straight lines correspond to the formulas

$$\frac{1}{I} = 8.43 \times 10^{-3} \left( 1 + \frac{1}{153[A]} \right) \text{ at } 20^\circ\text{C, and}$$

$$\frac{1}{I} = 9.02 \times 10^{-3} \left( 1 + \frac{1}{147[A]} \right) \text{ at } 25^\circ\text{C.}$$

The reaction scheme rests on the assumption that the light is absorbed exclusively by the sensitizer. This was very nearly the case in the benzene experiments, but less so in the isopropanol experiments where the lower value of  $\tau_D^0$  made it necessary to use higher biacetyl concentrations. However, the fraction of the light absorbed by the biacetyl never exceeded 5%.

Step 4 is a transfer of triplet state energy. The triplet level of biacetyl is 4 000  $\text{cm}^{-1}$  lower than that of benzophenone, corresponding to an energy difference of  $> 11$  kcal/mole. The results on phosphorescence quenching given in Ref.<sup>1</sup>, Table 2, indicate that this energy difference is sufficient to make the process diffusion controlled, and this is confirmed by later results. The rate constant may therefore be estimated by a formula derived by Debye<sup>14</sup> on the assumption that the molecules may be regarded as spheres. If the molecular diameters of the reacting species are assumed equal the result is:

$$k = \frac{8RT}{3\,000\eta} \text{ l mole}^{-1} \text{ sec}^{-1}$$

where  $\eta$  is the viscosity in dyne-sec/cm<sup>2</sup> and  $R = 8.31 \times 10^7$  erg/°K. This simplified form of the equation is the one generally used. However, if the diameters ( $d_1$  and  $d_2$ ) are not equal the result should be multiplied by a factor

$$\frac{1}{4} \left( 2 + \frac{d_1}{d_2} + \frac{d_2}{d_1} \right)$$

For benzene solutions at 20°C the simplified formula gives  $1.0 \times 10^{10}$  l mole<sup>-1</sup> sec<sup>-1</sup>. Our results in this solvent thus indicate a mean life of benzophenone in its triplet state of about  $1.9 \times 10^{-6}$  sec. The results of the low-temperature work of Gilmore, Gibson, and McClure<sup>7</sup>, mentioned on p. 52, show that the natural lifetime is about 0.01 sec. Accordingly the phosphorescence yield under our experimental conditions must have been about 0.02 %. A weak blue luminescence could be seen when an oxygen-free solution of benzophenone in benzene was irradiated with light of wavelength 366 m $\mu$ . As was to be expected<sup>15</sup>, saturation of the solution with air caused a marked reduction in luminescence intensity.

As regards the measurements in *isopropanol* solution, some results of Forster<sup>16</sup> point to a possible source of error. In a study of the visible absorption spectrum of biacetyl he found that the extinction coefficients of solutions in certain alcohols decrease with time and approach an equilibrium value while the spectral shape is unchanged. This indicates a reaction with the solvent, leading to the formation of a colourless reaction product. In agreement with this we found that the extinctions of a solution of biacetyl in *isopropanol* at wavelengths in the visible and near ultraviolet decreased with time whereas their ratio remained unchanged. At the same time the extinctions at shorter wavelengths (<330 m $\mu$ ) increased. However, the reaction was so slow that the decrease in concentration of unchanged biacetyl during the time required for a measurement of the intensity of sensitized phosphorescence (about 2 h) was of the order of 1 %.

For solutions in *isopropanol*, the rate constant given by the simplified Debye formula is  $2.7 \times 10^9$  l mole<sup>-1</sup> sec<sup>-1</sup> at 20°C and  $3.2 \times 10^9$  l mole<sup>-1</sup> sec<sup>-1</sup> at 25°C. With these values for  $k_4$  the experimental results at the two temperatures give  $5.7 \times 10^{-8}$  sec and  $4.6 \times 10^{-8}$  sec, respectively, for the triplet state lifetime ( $\tau_D^\circ$ ) of benzophenone in *isopropanol* solution. An independent value of the same quantity at 25°C has previously been obtained by an entirely different method<sup>15</sup>. A study of the retarding effect of nitric oxide on the photochemical reaction between nitric oxide and *isopropanol*, sensitized by benzophenone, yielded a value of 252 for the product  $k \times \tau^\circ$ , where  $k$  is the rate constant for the deactivation of excited benzophenone molecules in their triplet state by nitric oxide. There is reason to believe that this is also a diffusion controlled process<sup>15</sup>. Assuming  $k = 3.2 \times 10^9$  l mole<sup>-1</sup> sec<sup>-1</sup>,  $\tau^\circ$  becomes  $7.9 \times 10^{-8}$  sec. However, this is a case where the molecules taking part in the diffusion controlled process are very different in size. According to the complete Debye formula this leads to an increase in the rate constant and a corresponding decrease in the calculated value of  $\tau^\circ$ . Since the molecules are far from spherical it is not possible to calculate the magnitude of this effect. The conclusion seems justified, however, that the results of the two determinations of  $\tau^\circ$  agree within the probable limits of error. This agreement furnishes a very

direct proof that the biradical state of benzophenone appearing as an intermediate in its photochemical reactions is identical with the triplet state responsible for its phosphorescence at low temperatures<sup>15</sup>.

Comparison of the values of  $\tau_D^0$  in benzene and in *isopropanol* shows that the latter value is determined almost entirely by the reaction with the solvent (step 3). The same is true of  $\tau_A$  in *isopropanol* (21  $\mu$ sec). Hence  $k_3/k_7 \sim 350$ , *i.e.*, biacetyl in the triplet state reacts much more slowly with *isopropanol* than does benzophenone.

#### Intensity measurements on sensitized and unsensitized phosphorescence

The following experiments were made in order to demonstrate the existence of sensitized phosphorescence by intensity measurements, and to compare the quantum efficiencies of sensitized and unsensitized phosphorescence in the case of biacetyl. The sensitizer was benzophenone, the solvent benzene. The experimental arrangements were the same as in the previous section.

1. A  $3.07 \times 10^{-3}$  M solution of biacetyl, with a calculated light absorption at 366  $m\mu$  of 12.0 %, gave a galvanometer deflection of 11.5 scale divisions. The phosphorescence decay rate corresponded to a triplet state lifetime of 796  $\mu$ sec.

2.  $3.46 \times 10^{-3}$  M biacetyl +  $7.74 \times 10^{-3}$  M benzophenone. Calculated total light absorption 99.3 %, 2.9 % absorbed by biacetyl and the rest by benzophenone. Galvanometer deflection 98.0 scale divisions,  $\tau = 756 \mu$ sec.

Obviously most of the luminescence in this case must be sensitized phosphorescence.

3. A 0.1226 M solution of biacetyl gave an extinction at 366  $m\mu$  of 0.515, corresponding to a light absorption of 99.1 % in a layer thickness of 4 cm. It gave a galvanometer deflection of 21.0 scale divisions, and  $\tau = 154 \mu$ sec. The low value of  $\tau$  is due to the high concentration ("self-quenching")<sup>1</sup>.

In experiments 2 and 3, the solutions had very nearly the same extinctions. The galvanometer deflections observed may therefore be assumed to be strictly proportional to the phosphorescence yields.

As will appear from the following, no appreciable error is introduced if the phosphorescence observed in experiment 2 is assumed to be entirely sensitized. Its quantum yield ( $\varphi_2$ ) will then be given by eqn (8). As regards the quantum yield in experiment 3 ( $\varphi_3$ ), it follows from the reaction scheme that

$$\varphi_3 = \frac{(\tau_A)_3}{\tau_A^N} \cdot P$$

where  $P$  denotes the probability under our experimental conditions for the internal conversion of singlet excited biacetyl to the triplet state (*Cf.* Fig. 3). With the value of  $k_4\tau_D^0$  found above in benzene solution,  $1.87 \times 10^4$  l mole<sup>-1</sup>, and with  $[A] = 3.46 \times 10^{-3}$  mole/l, the factor within parentheses in eqn (8) becomes 1.015. Hence

$$P = \frac{756}{154} \times \frac{21.0}{98.0} \times \frac{1}{1.015} = 1.04$$

Experiments 2 and 3 were repeated under almost identical conditions but with a fresh sample of biacetyl. The resulting value of  $P$  was 1.10.

These results indicate that when biacetyl is excited by light absorption in solution, the internal conversion to the triplet state is practically complete. The fraction of the singlet excited biacetyl molecules returning to the ground state with the emission of fluorescence may be estimated at about 0.22 %. This figure is based on the ratio between phosphorescence and fluorescence found above (p. 55) for a 0.222 M solution, an estimate of the triplet state lifetime in that solution ( $100 \pm 10 \mu\text{sec}$ ), and assuming the natural lifetime to be equal to the phosphorescence lifetime,  $2.25 \times 10^{-3}$  sec, in a solid solution at 77°K<sup>17</sup>.

The phosphorescence quantum yield of biacetyl in the vapour state at 27°C has been determined by Almy and Gillette<sup>18</sup>. When the wavelength of the exciting light is 366 m $\mu$  the phosphorescence yield rises with pressure, apparently from zero at zero pressure, and seems to approach a value almost as great as that obtained when the mercury lines at 405 or 436 m $\mu$  are used as exciting light. This value,  $0.145 \pm 0.030$ , is nearly constant in the pressure range investigated (2–45 mm).

Under the same conditions the integrated intensity ratio of phosphorescence to fluorescence has been found by Okabe and Noyes<sup>19</sup> to be  $58.4 \pm 2.5:1$ , independent of pressure and incident wavelength. Recalculated to relative numbers of quanta the ratio becomes 64:1, giving a fluorescence quantum yield of  $0.145/64 = 0.23 \%$ , *i.e.* within limits of error the same value as in solution. This indicates that the yield of fluorescence from the low lying vibrational levels of the excited singlet state is determined entirely by the relative rates of light emission and of internal conversion to the triplet state, and that the latter rate is not affected by the presence of the solvent. (*Cf.* Ref.<sup>17</sup>, p. 906).

On this basis the efficiency of the internal conversion to the triplet state from the low lying vibrational levels of the excited singlet state should be 99.8 % both in the vapour and in solution. Since the phosphorescence lifetime of biacetyl in the vapour state at 25°C has been found<sup>20</sup> to be  $1.80 \times 10^{-3}$  sec, whereas the natural lifetime may be assumed<sup>17</sup> to be about  $2.25 \times 10^{-3}$  sec, the phosphorescence yield observed by Almy and Gillette corresponds to a conversion efficiency of only about 20 %. This must be due to a radiationless process which originates in the higher vibrational levels of the triplet state and which will therefore be suppressed in solution, where the excess vibrational energy is rapidly removed by collisions with solvent molecules. On the other hand, the process must be sufficiently rapid to compete with collisional deactivation in a gas at low pressures. Dissociation may be excluded as a possibility both on the basis of the photochemical data<sup>21</sup> and because the available energy, 64 kcal/mole, is too low. Probably, therefore, the explanation of the discrepancy is the occurrence of radiationless transitions to the ground state. The theoretical treatment of such processes<sup>22</sup> has shown that they are possible only if the two electronic states differ in some essential way, for instance in multiplicity, as in the present case. Furthermore they may be expected to be favoured by atomic oscillations that cause the molecule to become distorted.

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