Transfer of Triplet State Energy in Fluid Solutions

IV. Determination of Triplet Yields by the Measurement of Sensitized Biacetyl Phosphorescence

KJELL SANDROS

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, S-402 20 Göteborg 5, Sweden

Triplet yields have been determined for twelve aromatic compounds in cyclohexane solution from measurements of the intensity and lifetime of sensitized biacetyl phosphorescence at varying biacetyl concentration. Complementary spectrofluorometric measurements were performed for sensitizers having a triplet to singlet lifetime ratio not great enough to permit direct separation of triplet and singlet energy transfer. For benzene and toluene the sum of the fluorescence and the triplet formation quantum yields is less than unity, indicating a considerable radiationless deactivation of the singlet excited state in addition to the intersystem crossing process. The measurements also gave the ratios between the rate constants for decay and energy transfer from both the singlet and the triplet excited states. Assuming an energy transfer rate constant of 5×10^9 M^{-1} sec^{-1} the triplet lifetimes of benzene and toluene are estimated at 2×10^{-6} and 3×10^{-6} sec, respectively.
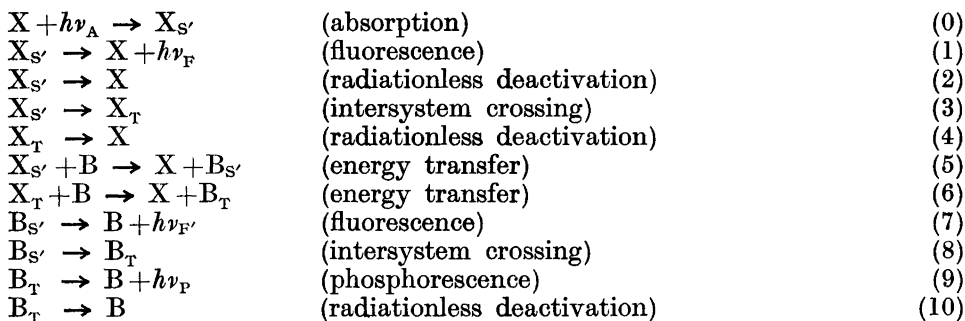
As pointed out by Parker and Joyce[1] there has been little quantitative information available on triplet yields (Φ_T), in spite of their great importance in organic photochemistry. Recently, however, some papers on this subject have been published. Flash absorption spectroscopy has been applied by Bowers and Porter.[2] This technique, combined with fluorescence efficiency measurements, has been used by Medinger and Wilkinson.[3] Lamola and Hammond[4] have devised a method in which the compound to be studied acts as a photosensitizer for reactions known to involve a triplet state of the substrate. Parker and Joyce[1] measured relative intensities and lifetimes of the *P*-type delayed perylene fluorescence sensitized by the compound in question and by anthracene, the triplet yield of the latter taken to be 0.70.

Some years ago the triplet yield of biacetyl was estimated in this laboratory to be close to unity.[5] The estimation was based on a comparison between the unsensitized and the benzophenone sensitized phosphorescence of biacetyl, with the value of Φ_T for benzophenone taken to be 1.00. Although the measure-

ment of sensitized biacetyl phosphorescence has been used to determine triplet yields in the vapour state (see, *e.g.*, Noyes and Unger [6]), this method does not seem to have been applied to solutions. The purpose of the present work is to show how measurements of relative intensity and lifetime of sensitized biacetyl phosphorescence at varying biacetyl concentration permit the calculation of the triplet yield of the sensitizer. The requirement on the triplet energy of the sensitizer is more restrictive in the present method than in that of Parker and Joyce since the triplet energy of biacetyl (19 700 cm^{-1}) is higher than that of perylene (12 500 cm^{-1}). The low extinction coefficients of biacetyl at wavelengths >230 nm, on the other hand, facilitate the study of some compounds. Thus benzene and some substituted benzenes, the triplet yields and triplet lifetimes of which have been a matter of discussion, can be studied using biacetyl as the energy acceptor. For such donor compounds the use of aromatic acceptors meets with difficulties. In addition, the reference value $\Phi_T = 1.00$ for biacetyl used here seems to be better established than the reference value $\Phi_T = 0.70$ for anthracene.

PRINCIPLE OF THE METHOD

In a degassed solution containing a sensitizer (X) and biacetyl (B), which is irradiated by light absorbed mainly by X, the following processes may be assumed to be of importance:

$X + h\nu_A \rightarrow X_{S'}$	(absorption)	(0)
$X_{S'} \rightarrow X + h\nu_F$	(fluorescence)	(1)
$X_{S'} \rightarrow X$	(radiationless deactivation)	(2)
$X_{S'} \rightarrow X_T$	(intersystem crossing)	(3)
$X_T \rightarrow X$	(radiationless deactivation)	(4)
$X_{S'} + B \rightarrow X + B_{S'}$	(energy transfer)	(5)
$X_T + B \rightarrow X + B_T$	(energy transfer)	(6)
$B_{S'} \rightarrow B + h\nu_{F'}$	(fluorescence)	(7)
$B_{S'} \rightarrow B_T$	(intersystem crossing)	(8)
$B_T \rightarrow B + h\nu_P$	(phosphorescence)	(9)
$B_T \rightarrow B$	(radiationless deactivation)	(10)

The processes (2), (4), and (10) are meant to include bimolecular reactions with the solvent and with impurities in the samples of B and X. These impurities have been discussed in an earlier paper.[7] The statements made there imply that k_2 and k_4 are unaffected by the impurities in the biacetyl sample and will have constant values at constant sensitizer concentration. Both the singlet energy transfer (5) and the triplet energy transfer (6) are known to be diffusion controlled in solutions of not too low viscosity, provided the energy of $X_{S'}$ and of X_T is sufficiently higher than the energy of $B_{S'}$ and of B_T, respectively.[8,7,9] The biacetyl fluorescence quantum yield [10] is very small and almost 100 % of the singlet excited biacetyl molecules cross over to a triplet state (8). Contrary to most other substances biacetyl phosphoresces with an appreciable quantum yield in an inert, degassed, fluid solvent (9).

Steady state treatment can be applied to $[X_{S'}]$, $[X_T]$, and $[B_T]$, if the rate of light absorption (I_A) is constant. Since $k_8(k_7+k_8)^{-1}$ can be approximated by unity it follows that:

$$\frac{d[X_{S'}]}{dt} = I_A - [X_{S'}](k_1+k_2+k_3+k_5[B]) = 0 \qquad (I)$$

$$\frac{d[X_T]}{dt} = k_3[X_{S'}] - [X_T](k_4+k_6[B]) = 0 \qquad (II)$$

$$\frac{d[B_T]}{dt} = [B](k_5[X_{S'}]+k_6[X_T]) - [B_T](k_9+k_{10}) = 0 \qquad (III)$$

Denoting $k_1+k_2+k_3$ by k_s one obtains:

$$[B_T] = \frac{I_A[B]}{(k_s+k_5[B])(k_9+k_{10})}\left(k_5 + \frac{k_3k_6}{k_4+k_6[B]}\right) \qquad (IV)$$

The biacetyl phosphorescence intensity (I), as registered by a photo-multiplier-galvanometer device, is equal to $\alpha k_9[B_T]$, where the value of α depends on the experimental conditions. Denoting the natural lifetime (k_9^{-1}) by τ_N and the measured phosphorescence lifetime $([k_9+k_{10}]^{-1})$ by τ the following equation is obtained:

$$\frac{I}{\tau} = K\frac{[B]}{k_s+k_5[B]}\left(k_5 + \frac{k_3k_6}{k_4+k_6[B]}\right) \qquad (V)$$

where $K=\alpha I_A\tau_N^{-1}$ is a constant, provided αI_A is kept constant by an appropriate arrangement (cf. p. 2820). As seen from eqn. (V) the limiting value of I/τ at infinite biacetyl concentration is K. Eqn. (V) can be converted into a form more suitable for graphical representation of the experimental data. Two cases may be distinguished: 1. $k_s \gg k_4$ and 2. $k_s \ggg k_4$.

1. If $k_s \gg k_4$ and if Φ_T is sufficiently large also to ensure $k_3 \gg k_4$ it is possible to choose a biacetyl concentration range where the singlet energy transfer from $X_{S'}$ can be ignored compared with the triplet energy transfer from X_T. When [B] is small enough to make $k_5[B] \approx k_6[B] \ll k_3$ and when the inequalities given above are valid eqn. (V) can be approximated to:

$$\left(\frac{I}{\tau}\right)_T = K\frac{k_3k_6[B]}{k_s(k_4+k_6[B])} \qquad (VI)$$

where the subscript T indicates that the phosphorescence is sensitized by the triplet state of the donor.

Inversion of eqn. (VI) gives:

$$\left(\frac{\tau}{I}\right)_T = \frac{k_s}{Kk_3}\left(1 + \frac{k_4}{k_6[B]}\right) \qquad (VII)$$

A plot of τ/I vs. $1/[B]$ should give a straight line with intercept k_s/Kk_3. The value of $k_3/k_s = \Phi_T$, i.e. the triplet yield of the donor, can be calculated if the value of K is known. Slope and intercept give k_4/k_6.

In the case that the biacetyl concentration is chosen so high that the energy transfer from X_T is virtually complete, i.e. $k_6[B]/(k_4+k_6[B]) \approx 1$, the following relationship should be approximately valid:

$$\frac{I}{\tau} = \frac{K}{k_{\mathrm{s}}+k_5[\mathrm{B}]}\ (k_5[\mathrm{B}]+k_3) = \frac{K}{1+k_5[\mathrm{B}]/k_{\mathrm{s}}}\left(\frac{k_5[\mathrm{B}]}{k_{\mathrm{s}}}+\frac{k_3}{k_{\mathrm{s}}}\right) \quad \text{(VIII)}$$

Knowing the value of k_3/k_{s} from determinations at lower biacetyl concentrations, the value of $k_5[\mathrm{B}]/k_{\mathrm{s}}$ can be calculated. In eqn. (VIII) the term $Kk_5[\mathrm{B}]/(k_{\mathrm{s}}+k_5[\mathrm{B}])$ represents the contribution to I/τ from the singlet energy transfer $(I/\tau)_{\mathrm{S}}$. Thus we have:

$$\left(\frac{\tau}{I}\right)_{\mathrm{S}} = \frac{1}{K}\left(1+\frac{k_{\mathrm{s}}}{k_5[\mathrm{B}]}\right) \quad \text{(IX)}$$

i.e. a linear relationship with intercept $1/K$ and slope k_{s}/Kk_5.

2. For sensitizers with $k_{\mathrm{s}} \gg k_4$ it is not possible to separate triplet energy transfer from singlet energy transfer directly. The following transformation of eqn. (V) is appropriate in this case:

$$\left[\frac{I\{1+k_{\mathrm{s}}/(k_5[\mathrm{B}])\}}{\tau K}-1\right]^{-1} = \frac{k_5 k_4}{k_3 k_6}+\frac{k_5}{k_3}\ [\mathrm{B}] = F \quad \text{(X)}$$

The value of k_{s}/k_5 must then be chosen to give the best linearity of the left member of eqn. (X) as a function of [B].

Handling the data in this manner, however, leads to rather uncertain results. A more satisfactory method is to combine the intensity-lifetime measurements with fluorometric determinations, similar to those performed by Dubois and Wilkinson.[11] Degassed solutions containing X and B are irradiated in a spectrophotofluorometer first with light absorbed almost exclusively by X (265 nm) and then with light absorbed only by B (436 nm). The biacetyl luminescence intensities at the phosphorescence maximum (520 nm) and at the fluorescence maximum (460 nm) upon irradiation with 265 nm light and with 436 nm light are measured. After correction for the small fluorescence contribution to the 520 nm intensities, $(I_{520}/I_{460})_{265} \times (I_{520}/I_{460})_{436}^{-1}$ is calculated. This expression is a simple function of relevant parameters as seen from the following:

436 nm excitation: Steady state treatment of $[\mathrm{B_T}]$ gives:

$$\mathrm{d}[\mathrm{B_T}]/\mathrm{d}t = k_8[\mathrm{B_{S'}}]-(k_9+k_{10})[\mathrm{B_T}] = 0 \quad \text{(XI)}$$

Thus:

$$\left(\frac{I_{520}}{I_{460}}\right)_{436} = \frac{\beta k_9}{\gamma k_7}\left(\frac{[\mathrm{B_T}]}{[\mathrm{B_{S'}}]}\right)_{436} = \frac{\beta k_9 k_8}{\gamma k_7(k_9+k_{10})} \quad \text{(XII)}$$

where β and γ are apparatus constants.

265 nm excitation: Steady state treatment of $[\mathrm{B_{S'}}]$ gives:

$$\mathrm{d}[\mathrm{B_{S'}}]/\mathrm{d}t = k_5[\mathrm{X_{S'}}][\mathrm{B}]-(k_7+k_8)[\mathrm{B_{S'}}] = 0 \quad \text{(XIII)}$$

Using eqn. (I), eqn. (IV) can be written:

$$[\mathrm{B_T}] = \frac{[\mathrm{X_{S'}}][\mathrm{B}]}{k_9+k_{10}}\left(k_5+\frac{k_3 k_6}{k_4+k_6[\mathrm{B}]}\right) \quad \text{(XIV)}$$

It then follows that:

$$\left(\frac{I_{520}}{I_{460}}\right)_{265} = \frac{\beta k_9}{\gamma k_7}\left(\frac{[B_T]}{[B_{S'}]}\right)_{265} = \frac{\beta k_9(k_7+k_8)}{\gamma k_7(k_9+k_{10})}\left[1+\frac{k_3 k_6}{k_5(k_4+k_6[B])}\right] \quad (XV)$$

Since $k_7+k_8 \approx k_8$ eqns. (XII) and (XV) give:

$$\left(\frac{I_{520}}{I_{460}}\right)_{265}\left(\frac{I_{520}}{I_{460}}\right)_{436}^{-1} \approx 1+\frac{k_3 k_6}{k_5(k_4+k_6[B])} \quad (XVI)$$

Eqn. (XVI) can be transformed into

$$\left[\left(\frac{I_{520}}{I_{460}}\right)_{265}\left(\frac{I_{520}}{I_{460}}\right)_{436}^{-1}-1\right]^{-1} = \frac{k_5 k_4}{k_3 k_6}+\frac{k_5}{k_3}[B] \equiv F \quad (XVII)$$

Thus fluorometric measurements give the function F. The values of F for the solutions used in the intensity-lifetime measurements can be calculated and the k_S/k_5 values are then obtained from eqn. (X). The mean of the k_S/k_5 values, together with the value of the slope of F vs. [B], gives the triplet yield of X.

EXPERIMENTAL

The equipment used to measure *relative phosphorescence intensities* was similar to an arrangement described earlier.[5] It is schematically shown in Fig. 1. In order that the
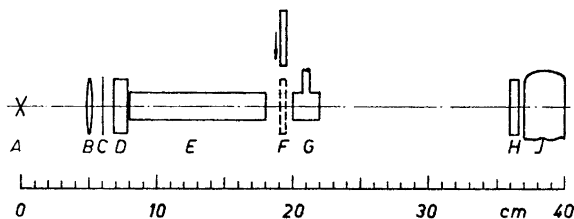

Fig. 1. Schematic diagram of the experimental arrangement for measuring relative phosphorescence intensities. (A) Low pressure Hg-lamp (Thermal Type T/M5/534C) surrounded by a water cooled mantle. (B) Quartz lens. (C) Shutter. (D) 0.1 mM 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate solution.[12] (E) Solution of NiSO$_4$, 15 %, +CoSO$_4$, 12.5 %.[13] (F) Uranyl glass. (G) Cylindrical quartz cell, 20×20 mm. (H) Glass filter (Chance OY3, 4 mm) transmitting only wavelengths >510 nm. (J) Multiplier phototube (RCA 1P21). ——— A light-tight box with an opening for the exciting beam enclosed parts D−J. The measurements were made in a darkened room.

direct excitation of biacetyl compared with that of the aromatic sensitizers could be disregarded, the mercury line at 253.7 nm was chosen as the exciting light. This line is dominant in the emission from the lamp (A). With the "in line arrangement" chosen the exciting light had to be carefully freed from light transmitted by the filter (H). A 10 cm long filtercell (E) was therefore used. This filter also reduced the intensity of the exciting light to a level which was sufficiently low to make negligible disturbing photo-chemical reactions in the solution during the measurement. The quartz lens (B) gave an image of the mercury arc in the center of the cell (G). The photomultiplier (J) was fed from a stabilized, adjustable, high voltage power supply (Oltronix Type L S 524 R) and the photocurrent was read on a light-spot galvanometer (Norma Model 251 J).

The experimental procedure follows: A stock solution of the sensitizer was prepared using cyclohexane, which has no absorption at 253.7 nm, as the solvent. A small amount of a cyclohexane solution of biacetyl was weighed in a volumetric flask and the flask was filled to the mark with the stock solution. The sensitizer-biacetyl solution was transferred to the degassing vessel shown in Fig. 2. The ground glass joints and the
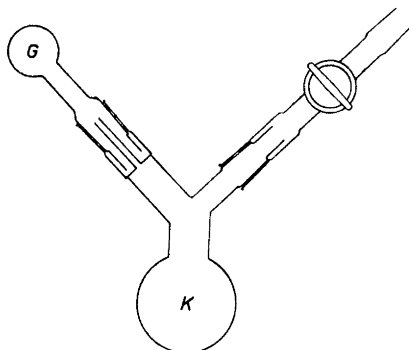

Fig. 2. Cylindrical luminescence quartz cell (G) with arrangements for degassing the solution. All parts except (G) with ground joint are made of Pyrex glass. The degassing procedure is performed with the solution in the bulb (K).

stopcock were greased with Apiezon L and the solution was degassed by freezing-pumping-thawing cycles as previously described.[14] The temperature of the solution was then raised to 20°C. The voltage applied to the multiplier was adjusted to give a galvanometer deflection of 100 divisions with the uranyl glass (F) placed in the exciting beam. The degassing vessel was tilted to transfer the solution into the measuring cell, which was then placed in the cell holder. The uranyl glass was withdrawn and the galvanometer deflection upon opening the shutter (C) was read. The *phosphorescence lifetime* was then immediately determined in a flash apparatus described earlier.[14] Finally, air was admitted into the vessel and the galvanometer deflection upon irradiation of the aerated solution was read. This small "blank" value was subtracted from that of the deaerated solution.

The *fluorometric measurements* were performed with an Aminco Bowman spectrophotofluorometer, fitted with a UV-absorbing filter in the emission light path to remove scattered excitation light. Lipsky [15] pointed out that upon irradiation of a cyclohexane solution of benzene and biacetyl with 255 nm light, the biacetyl phosphorescence intensity decays with time. This was attributed to a sensitized decomposition of the 3.9 eV state of biacetyl, assuming that the decomposition products quench triplet benzene. In the present work an intensity decay was also found with the benzene derivatives studied, the decay rate increasing with decreasing biacetyl concentration. To avoid excessive irradiation of the sample a shutter was mounted in the path of the exciting light. With the recorder used, it took about 0.5 sec to record an emission intensity. During this short irradiation time the biacetyl phosphorescence intensity decreased by less than 2 %, as found from separate experiments with oscilloscope recording.

The following procedure was used. A solution of biacetyl and the sensitizer was degassed in the vessel mentioned above, now fitted with a rectangular quartz luminescence cell. The cell was placed in the temperature-controlled cell holder. With the excitation monochromator set at 436 nm and the emission monochromator at 460 nm the shutter was opened and the emission intensity recorded. The emission intensity at 520 nm was then recorded with the sensitivity of the measuring device reduced by a factor of ten. A "blank" emission spectrum was recorded with a solution containing only the sensitizer in an identical cell. All measuring operations were repeated with the excitation wavelength 265 nm. To correct for the fluorescence contribution to the intensity at 520 nm, the emission spectrum of an aerated biacetyl solution was recorded. This spectrum showed that the recorded biacetyl fluorescence intensity at 520 nm was 25 % of that at 460 nm with the same sensitivity control setting at both wavelengths. Consequently, 2.5 % of the I_{460} values had to be subtracted from the recorded I_{520} values.

Materials. *Cyclohexane* (Fisher, Spectroquality) was fractionally distilled since the original product exhibited fluorescence upon excitation at 265 nm. *Biacetyl* was fractionally distilled and stored in the dark. *Benzophenone* and *fluorene* were crystallized twice from a methanol-water mixture and from ethanol, respectively. p-*Phenylbenzophenone* was sublimed *in vacuo*. *Phenanthrene* was freed from anthracene by repeated treatment with maleic anhydride in toluene and was then recrystallized from ethanol. *Naphthalene, biphenyl, triphenylene,* and *acenaphthene* were zone melted. *Benzene, fluorobenzene, toluene,* and p-*xylene* were fractionally distilled.

RESULTS

The results of the measurements made to determine the value of the constant K (*cf.* p. 2817) under the prevailing experimental conditions are presented in Fig. 3. The biacetyl phosphorescence intensity (I galvanometer
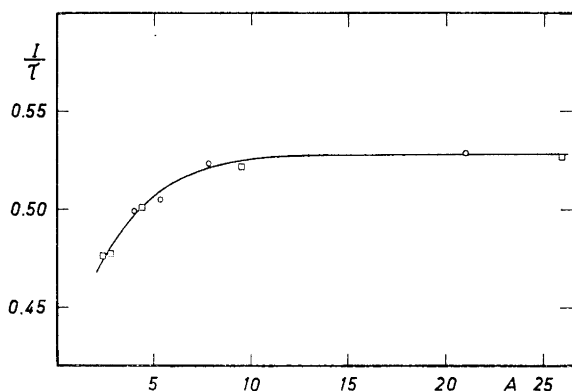

Fig. 3. I/τ *vs.* total absorbance (A) in 20 mm at 253.7 nm of benzophenone-biacetyl solutions (□) and of phenanthrene-biacetyl solutions (○). The biacetyl concentration was 0.12 M in the benzophenone and 0.05 M in the phenanthrene solutions.

scale divisions) and the phosphorescence lifetime (τ μsec) were determined in solutions with a sufficiently high biacetyl concentration for the energy transfer from the sensitizer, benzophenone or phenanthrene, to proceed with more than 99 % efficiency. The absorbance of the solutions (A) was varied by varying the sensitizer concentration. The absorbances all corresponded to virtually complete absorption of the exciting light. The variation of K with the absorbance is probably due, therefore, to changes in the luminescence geometry. K-values read from the smoothed curve in the figure were used in all calculations. The results of the measurements at high biacetyl concentrations in solutions of the different sensitizers studied seem to justify this procedure, which implies unchanged measuring conditions.

The data from experiments with *sensitizers having a great triplet to singlet lifetime ratio* have been treated to give linear relationships in accordance

with eqns. (VII) and (IX).* Fig. 4 gives a representative example of the results thus obtained. The lines drawn have been calculated by the method of least squares.
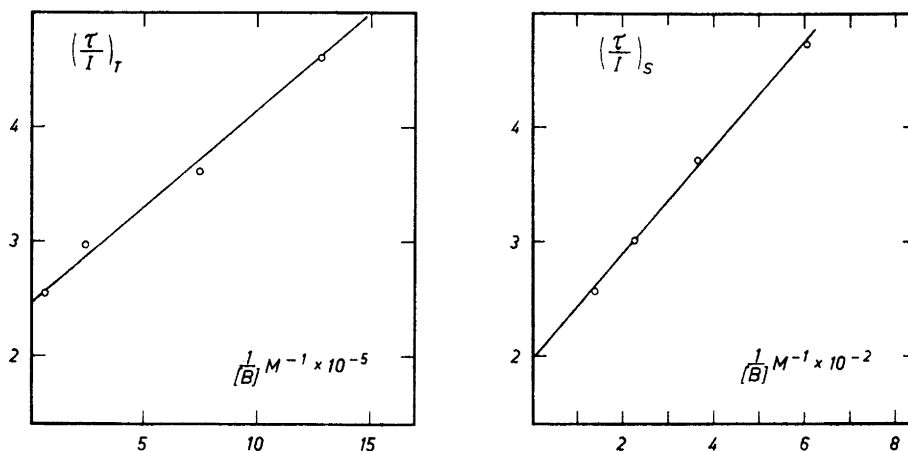

Fig. 4. Biacetyl phosphorescence sensitized by triplet energy transfer (*a*) and by singlet energy transfer (*b*). Sensitizer: 3.6×10^{-5} M phenanthrene. $A = 4.2$. For further explanations, see text.

Phenanthrene: The equations for the straight lines drawn in Fig. 4 are:

$$(\tau/I)_T = 2.45 + 1.70 \times 10^{-6} \ [B]^{-1} \quad \text{and} \quad (\tau/I)_S = 1.97 \pm 4.62 \times 10^{-3} \ [B]^{-1}.$$

The K-value read from Fig. 3 at $A = 4.2$ is 0.500. The intercept of the first line gives $k_S/Kk_3 = 2.45$ and thus $\Phi_T = k_3/k_S = 0.816$. From slope and intercept $k_4/k_6 = 6.9 \times 10^{-7}$ M. The intercept of the second line, 1.97, corresponds to a K-value of 0.508 in good agreement with the value 0.500 used in the calculations. Slope and intercept give $k_S/k_5 = 2.35 \times 10^{-3}$ M.

Naphthalene, 5.6×10^{-4} M, gave $A = 3.1$ and thus $K = 0.484$. From the linear relationships obtained,

$$(\tau/I)_T = 3.05 + 4.58 \times 10^{-7} \ [B]^{-1} \quad \text{and} \quad [\tau/I]_S = 2.05 + 1.59 \times 10^{-3} \ [B]^{-1}$$

it follows that $\Phi_T = 0.678$, $k_4/k_6 = 1.5 \times 10^{-7}$ M and $k_S/k_5 = 0.78 \times 10^{-3}$ M.

Biphenyl, 1.4×10^{-4} M, gave $A = 4.2$ and thus $K = 0.500$. From the linear relationships obtained,

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* Since these sensitizers have long triplet lifetimes in deaerated cyclohexane solutions, a very low biacetyl concentration is sufficient to give an appreciable triplet energy transfer. A biacetyl concentration of 10^{-8} M gives an energy transfer efficiency of about 5 % if the triplet lifetime is 10^{-3} sec. Thus uncontrolled introduction of biacetyl to the solution (*e.g.* from vapour present in the air) had to be carefully avoided. Observations in the present work give cause for a re-interpretation of some emission results presented in Table 4 in Ref. 7. The emission from solutions of naphthalene and some of its derivatives was stated there to be the phosphorescence from these substances. It now seems more likely that the emission was a sensitized biacetyl phosphorescence. Fortunately, this does not invalidate the results given for the triplet lifetimes of the sensitizers.

$$(\tau/I)_{\mathrm{T}} = 2.48 + 7.27 \times 10^{-6} \text{ [B]}^{-1} \text{ and } (\tau/I)_{\mathrm{S}} = 2.03 + 1.38 \times 10^{-2} \text{ [B]}^{-1}$$

it follows that $\Phi_{\mathrm{T}} = 0.806$, $k_4/k_6 = 2.9 \times 10^{-6}$ M and $k_{\mathrm{S}}/k_5 = 6.8 \times 10^{-3}$ M.

Fluorene, 1.7×10^{-4} M, gave $A = 5.5$ and thus $K = 0.510$. From the linear relationship obtained,

$$(\tau/I)_{\mathrm{T}} = 6.23 + 5.50 \times 10^{-6} \text{ [B]}^{-1} \text{ and } (\tau/I)_{\mathrm{S}} = 1.96 + 1.67 \times 10^{-2} \text{ [B]}^{-1}$$

it follows that $\Phi_{\mathrm{T}} = 0.315$, $k_4/k_6 = 8.8 \times 10^{-7}$ M and $k_{\mathrm{S}}/k_5 = 8.5 \times 10^{-3}$ M.

Triphenylene, 3.7×10^{-5} M, gave $A = 5.4$ and thus $K = 0.510$. From the linear relationships obtained,

$$(\tau/I)_{\mathrm{T}} = 2.28 + 2.28 \times 10^{-6} \text{ [B]}^{-1} \text{ and } (\tau/I)_{\mathrm{S}} = 1.95 + 4.00 \times 10^{-3} \text{ [B]}^{-1}$$

it follows that $\Phi_{\mathrm{T}} = 0.860$, $k_4/k_6 = 1.00 \times 10^{-6}$ M and $k_{\mathrm{S}}/k_5 = 2.05 \times 10^{-3}$ M.

Acenaphthene. For the sensitizers hitherto presented the reversed triplet energy transfer

$$B_{\mathrm{T}} + X \rightarrow B + X_{\mathrm{T}} \text{ (energy transfer)} \tag{11}$$
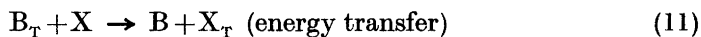
has been neglected. If this process is taken into account the following relationship should hold in a biacetyl concentration range where singlet energy transfer is negligible:

$$\left[\frac{1}{I(k_9 + k_{10})} \right]_{\mathrm{T}} = \frac{k_{\mathrm{S}}}{Kk_3} \left[1 + \frac{k_4 + k_4 k_{11}(k_9 + k_{10})^{-1}[X]}{k_6[B]} \right] \tag{XVIII}$$

The biacetyl phosphorescence decay after a flash absorbed only by biacetyl is exponential if process (11) can be disregarded. Otherwise the decay is exponential only when $k_6[B] \gg k_{11}[X]$. The phosphorescence lifetime then obtained is equal to $(k_9 + k_{10})^{-1}$, just as in the absence of process (11).

A comparison of eqn. (XVIII) with the corresponding eqn. (VII) shows that reversed energy transfer can be neglected if $k_{11}(k_9 + k_{10})^{-1}[X] \ll 1$. A rough estimate of k_{11} values can be made from Fig. 1 in Ref. 7 if the triplet energy of the sensitizer is known. This figure is based on measurements in benzene solutions and the corresponding rate constants in the more viscous cyclohexane solutions are expected to be somewhat lower. The triplet energy of acenaphthene, estimated from a phosphorescence spectrum in EPA at 77° K, is about 20 800 cm^{-1} and the expected value of k_{11} is about 2×10^7 sec^{-1} M^{-1}. Such a value of k_{11} indicates that for a concentration of acenaphthene giving a sufficient aborbance, $k_{11}(k_9 + k_{10})^{-1}[X] \ll 1$. Two series with different acenaphthene concentrations were therefore run. For solutions having a biacetyl concentration so low that the inequality $k_6[B] \gg k_{11}[X]$ was badly fulfilled the value of $k_9 + k_{10}$ could not be experimentally determined. It was therefore tentatively assumed that the values of $k_9 + k_{10}$ were equal to those obtained in solutions with higher biacetyl concentration. Linear relationships were obtained between $[1/I(k_9 + k_{10})]_{\mathrm{T}}$ and $1/[B]$, indicating that the value of $k_9 + k_{10}$ was fairly constant within each series.

Series 1: $[X] = 2.40 \times 10^{-3}$ M gave $A = 6.1$ and thus $K = 0.513$. The value of $(k_9 + k_{10})^{-1}$ was 214 μsec. The linear relationship,

$$[1/I(k_9 + k_{10})]_{\mathrm{T}} = 4.20 + 2.17 \times 10^{-5} \text{ [B]}^{-1}, \text{ gives } \Phi_{\mathrm{T}} = 0.464.$$

Series 2: $[X]=7.89 \times 10^{-4}$ M gave $A=2.0$ and thus $K=0.465$. The value of $(k_9+k_{10})^{-1}$ was 165 μsec. The linear relationship,

$[1/I(k_9+k_{10})]_T=4.75+7.58 \times 10^{-6}$ $[B]^{-1}$, gives $\Phi_T=0.453$.

From the two linear relationships, the corresponding values of $(k_9+k_{10})^{-1}$, and the concentrations of acenaphthene, a value for $k_{11}=2.4 \times 10^7$ sec^{-1} M^{-1} and for $k_4/k_6=3.9 \times 10^{-7}$ M can be calculated.

An inspection of the pertinent data for the other sensitizers presented above shows that reversed triplet energy transfer may have been of importance only in the case of naphthalene. The value of $k_{11}(k_9+k_{10})^{-1}[X]$ in these experiments can be roughly estimated at 0.4. The value of k_4/k_6 given for naphthalene is therefore probably somewhat high.

Benzophenone, 1.6×10^{-4} M, gave $A=5.4$ and thus $K=0.510$. From the linear relationship obtained, $(\tau/I)_T=1.97+2.23 \times 10^{-3}$ $[B]^{-1}$, it follows that: $\Phi_T=0.995$ and $k_4/k_6=1.13 \times 10^{-3}$ M. The small deviation from unity in the Φ_T value is, of course, within the limits of experimental error. The fact that no sensitized fluorescence could be detected in the benzophenone sensitized luminescence from a 0.222 M biacetyl solution [5] seems to be conclusive proof that the biacetyl luminescence was sensitized by the triplet state of benzophenone.

p-*Phenylbenzophenone*, 2.4×10^{-4} M, gave $A=6.5$ and thus $K=0.516$. From the linear relationship, $(\tau/I)_T=1.90+1.12 \times 10^{-6}$ $[B]^{-1}$, it follows that $\Phi_T=1.02$ and $k_4/k_6=5.9 \times 10^{-7}$ M.

The data from the fluorometric measurements with *sensitizers having a moderate triplet to singlet lifetime ratio* (not great enough to permit direct separation of triplet energy transfer from singlet energy transfer) have been treated to give linear relationships in accordance with eqn. (XVII). Fig. 5
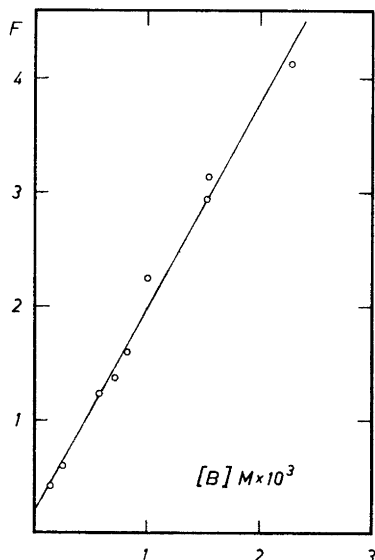

Fig. 5. $F = \left[\left(\dfrac{I_{520}}{I_{460}}\right)_{265} \left(\dfrac{I_{520}}{I_{460}}\right)_{436}^{-1} - 1 \right]^{-1}$ *vs.* biacetyl concentration, [B], from fluorometric measurements on solutions containing 1.9×10^{-2} M benzene. For further explanations, see text.

Table 1. Biacetyl phosphorescence sensitized by singlet and triplet energy transfer. Sensitizer: 2.9×10^{-2} M benzene. $A = 5.1$, $K = 0.508$. For further explanations, see text.

[B] M $\times 10^3$	$\dfrac{I}{\tau}$	F	k_s/k_5 M $\times 10^3$
0.582	0.1905	1.24	2.22
1.08	0.2444	2.14	2.21
2.28	0.3220	4.32	2.15
2.38	0.3224	4.50	2.20
13.0	0.4531	23.72	2.19
			Mean: 2.19

Table 2. Sensitizer: 3.0×10^{-2} M toluene. $A = 10.0$, $K = 0.526$.

[B] M $\times 10^3$	$\dfrac{I}{\tau}$	F	k_s/k_5 M $\times 10^3$
0.530	0.3164	0.58	1.87
1.18	0.3582	1.21	1.98
1.82	0.3835	1.84	2.03
2.63	0.4261	2.63	1.85
3.44	0.4354	3.42	1.93
9.42	0.4851	9.27	1.90
			Mean: 1.93

Table 3. Sensitizer: 1.8×10^{-2} M *p*-xylene. $A = 7.0$, $K = 0.518$.

[B] M $\times 10^3$	$\dfrac{I}{\tau}$	F	k_s/k_5 M $\times 10^3$
0.978	0.3818	0.75	2.12
2.05	0.4239	1.55	2.07
3.24	0.4402	2.43	2.14
3.26	0.4384	2.45	2.16
5.27	0.4587	3.94	2.19
			Mean: 2.14

Table 4. Sensitizer: 5.8×10^{-3} M fluorobenzene. $A = 7.3$, $K = 0.520$.

[B] M $\times 10^3$	$\dfrac{I}{\tau}$	F	k_s/k_5 M $\times 10^3$
1.63	0.3762	0.38	6.55
2.17	0.3806	0.49	6.84
2.47	0.4042	0.54	6.59
4.79	0.4347	0.98	6.78
5.80	0.4434	1.16	6.87
8.38	0.4690	1.65	6.54
			Mean: 6.70

gives an example of the results obtained. Tables 1—4 give the results from the intensity-lifetime measurements, the F-values as obtained from the corresponding linear relationships, and the values of k_s/k_5 calculated from eqn. (X).

Benzene. The equation for the straight line drawn in Fig. 5 is $F = 0.19 + 1.81 \times 10^3[B]$. According to eqn. (XVII) the slope is equal to k_5/k_3 while the intercept to slope ratio equals k_4/k_6. Table 1 gives $k_S/k_5 = 2.19 \times 10^{-3}$ M. Thus $\Phi_T = k_3/k_S = 0.252$ and $k_4/k_6 = 1.0 \times 10^{-4}$ M.

Toluene. The fluorometric measurements on 1.1×10^{-2} M solutions gave: $F = 0.06 + 9.78 \times 10^2[B]$. The value of k_S/k_5 from Table 2 is 1.93×10^{-3} M. Thus $\Phi_T = 0.530$ and $k_4/k_6 = 6 \times 10^{-5}$ M.

p-*Xylene.* The fluorometric measurements on 4.0×10^{-3} M solutions gave: $F = 0.02 + 7.44 \times 10^2[B]$. The value of k_S/k_5 from Table 3 is 2.14×10^{-3} M. Thus $\Phi_T = 0.628$ and $k_4/k_6 = 3 \times 10^{-5}$ M.

Fluorobenzene. The fluorometric measurements on 2.3×10^{-3} M solutions gave: $F = 0.08 + 1.87 \times 10^2[B]$. The value of k_S/k_5 from Table 4 is 6.70×10^{-3} M. Thus $\Phi_T = 0.798$ and $k_4/k_6 = 4 \times 10^{-4}$ M.

DISCUSSION

The triplet yields obtained in this work have been collected in Table 5 together with data from the literature. As regards the triplet yields, the results obtained from measurements using different solvents and different methods

Table 5. Summary of results from this work and from the literature. The last column gives results from measurements carried out in ethanol [1] or benzene [4] solutions. The other results have been obtained from cyclohexane solutions.

Sensitizer	Φ_T	Φ_F^{16}	$\Phi_T + \Phi_F$	Φ_T	
Phenanthrene	0.82			0.80,[1]	0.76 [4]
Naphthalene	0.68	0.23	0.91	0.71,[1]	0.40 [4]
Biphenyl	0.81	0.18	0.99		
Fluorene	0.32	0.80	1.12		0.31 [4]
Triphenylene	0.86	0.08	0.94	0.89,[1]	0.95 [4]
Acenaphthene	0.46	0.60	1.06	0.45,[1]	0.47 [4]
Benzophenone	1.00				1.00 [4]
p-Phenylbenzophenone	1.02				
Benzene	0.25	0.07	0.32		
Toluene	0.53	0.17	0.70		
p-Xylene	0.63	0.40	1.03		
Fluorobenzene	0.80	0.13	0.93		

agree remarkably well. The only exception is naphthalene where the value obtained by Lamola and Hammond differs significantly from the other two. The fluorescence quantum yields (Φ_F) given are values reported by Berlman [16] from measurements with cyclohexane as the solvent. For most substances

the sum $\Phi_T + \Phi_F$ is equal to unity within 10 %.* The latter figure is a reasonable error of $\Phi_T + \Phi_F$, though the accuracy of the Φ_T values is probably better than 5 %. For benzene and toluene, however, it seems justifiable to claim that $\Phi_T + \Phi_F$ is less than unity. It is of interest to compare the data for benzene in cyclohexane solution with the corresponding values obtained in the vapour phase[17] upon excitation with light of the same wavelength. The vapour-phase values are $\Phi_F = 0.18$ and $\Phi_T = 0.63$. Thus both Φ_F and Φ_T are increased by a factor of 2.5 in going from cyclohexane solution to the vapour phase, indicating that k_1/k_3 has the same value in the two media. The nature of the considerable radiationless depopulation of the singlet excited state of benzene in cyclohexane solution in addition to the intersystem crossing process is an open question. Valence isomerization[18] seems to account for only a part of the quantum yield deficit.

Since Berlman[16] has also measured fluorescence decay times (k_S^{-1}) it is possible to calculate values of the singlet energy transfer rate constant (k_5) from the k_S/k_5 values obtained. These data are shown in Table 6 together with the values of k_4/k_6 and very rough estimates of the values of k_4 assuming $k_6 = 5 \times 10^9$ sec^{-1} M^{-1}. The uncertain estimate of the k_6 value is based on earlier determinations[7] with benzene as the solvent, the somewhat higher viscosity of cyclohexane having been taken into account.

Table 6. Rate constants. For further explanations, see text.

Sensitizer	k_s/k_5 M $\times 10^3$	k_S sec^{-1} $\times 10^{-7}$	k_5 M^{-1}sec^{-1} $\times 10^{-10}$	k_4/k_6 M $\times 10^4$	k_4 sec^{-1} $\times 10^{-6}$
Phenanthrene	2.4			0.0069	0.003
Naphthalene	0.78	1.04	1.3	0.0015	0.001
Biphenyl	6.8	6.3	0.9	0.029	0.01
Fluorene	8.5	10.0	1.2	0.0088	0.004
Triphenylene	2.1	2.7	1.3	0.010	0.005
Acenaphthene				0.0039	0.002
Benzophenone				11	6
p-Phenylbenzophenone				0.0059	0.003
Benzene	2.19	3.4	1.6	1.0	0.5
Toluene	1.93	2.9	1.5	0.6	0.3
p-Xylene	2.14	3.3	1.5	0.3	0.2
Fluorobenzene	6.70	12.5	1.8	4	2

Since the singlet energy transfer is assumed to be a diffusion controlled process, it is of interest to compare the experimental values of k_5 obtained with the theoretically calculated value of the rate constant (k_{dif}) for such a process. Lacking pertinent data for diffusion coefficients and collision radii, the best that can be done is to accept the validity of the Stokes-Einstein

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* The value of Φ_F for fluorene given by Berlman is remarkably high compared with other values from the literature. Lamola and Hammond[4] conclude that the Φ_F value of fluorene is about 0.54 and is not much dependent on the medium.

equation and apply the Debye equation [19] in the slightly modified form used by Osborne and Porter:[20]

$$k_{\text{dif}} = 8RT/2000 \; \eta \qquad\qquad\qquad (XIX)$$

where η is the viscosity of the solvent. For a cyclohexane solution at 20°C this formula gives $k_{\text{dif}} = 1.0 \times 10^{10}$ sec^{-1} M^{-1}. Most of the k_5 values obtained are somewhat higher than this calculated value.* It should be noted that if one of the reactants has a sufficiently short lifetime (τ') the theory [21,22] predicts that k_{dif} is dependent on the value of τ'. The formula given above has then to be modified as follows:[9]

$$k_{\text{dif}} = \frac{8 \; RT}{2000 \; \eta} \left[1 + \frac{\sigma}{(D\tau')^{\frac{1}{2}}} \right] \qquad\qquad (XX)$$

where σ and D are the sums of the collision radii and the diffusion coefficients, respectively. If process (5) is diffusion controlled and if the last term of eqn. (XX) is of importance in the systems studied, k_5 must depend on [B] since the lifetime of the singlet excited state of the sensitizer τ' is equal to $(k_S + k_5[B])^{-1}$. Thus the plots of F vs. [B] from the fluorometric measurements should not have given straight lines as can be seen from eqn. (XVII). No deviation from linearity was observed, not even in the plots for fluorobenzene, the sensitizer which has the highest k_S value. A less sensitive test is the linearity in the plots of $(\tau/I)_S$ vs. [B]$^{-1}$.

It must be pointed out that the k_4 values are mainly determined by bimolecular quenching processes and are therefore only valid under the prevailing experimental conditions. Within each series the relevant conditions seem to have been constant since linear relationships were obtained between (τ/I) and [B]$^{-1}$ even for sensitizers for which the value of k_4 is small. Since only qualitative conclusions can be drawn from the k_4 values, the uncertainty in the k_6 value used to calculate k_4 is not a serious drawback. The k_4 values obtained for all sensitizers known to have a lowest triplet state of the $\pi^*\pi$ type, with the exception of benzene and its derivatives, are in the range $10^3 - 10^4$ sec^{-1}. p-Phenylbenzophenone belongs to this group [23] while benzophenone has a lowest π^*n triplet state. The k_4 value of benzophenone is higher than the corresponding value in benzene solution [5] by a factor of about ten. This is probably caused mainly by the reduction of the triplet benzophenone in cyclohexane solution.[23]

Benzene and its derivatives form perhaps the most interesting group of sensitizers studied. The lifetime of the triplet state of benzene and toluene in fluid solution has been a matter of discussion. From fluorometric studies similar to the present one, Dubois and Wilkinson [11,24] conclude that the triplet state lifetime of benzene and toluene in deaerated hexane solutions is equal to or shorter than the corresponding singlet lifetime. On the other hand Lipsky [15] estimates the lower limit of the benzene triplet lifetime at 10^{-6} sec in cyclohexane solution. His estimate is based on fluorometric determinations of the ratio between benzene fluorescence and biacetyl phos-

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* If only intensity-lifetime measurements are made, it is inherent in the method that the uncertainty of the k_3/k_5 values increases with increasing values of Φ_T.

phorescence. The k_4 value of benzene obtained in this work, corresponding to a lifetime of 2×10^{-6} sec, is compatible with Lipsky's estimate. Since it seems improbable that the undisturbed triplet lifetime of benzene in hexane solution is shorter than that in cyclohexane solution by a factor of about 100, there may be reason for seeking an explanation of the short lifetimes obtained by Dubois and Wilkinson. These authors recorded complete sensitized biacetyl emission spectra. The solutions were thus exposed to the exciting light during much longer periods of time than with the present technique. It can not be excluded that the triplet benzene was strongly quenched by the decomposition products proposed by Lipsky. This suggestion seems to be confirmed by a recent study [25] of biacetyl luminescence sensitized by benzene and toluene in hexane solutions. The results obtained indicate that the triplet lifetimes of these sensitizers are longer than the singlet ones also in hexane solutions.

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