

Transfer of Triplet State Energy in Fluid Solutions

II. Further Studies of the Quenching of Biacetyl Phosphorescence in Solution

KJELL SANDROS and HANS L. J. BÄCKSTRÖM

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

Rate constants for the quenching of biacetyl phosphorescence in benzene solution at 20°C are presented for 21 quenchers of the type for which the quenching mechanism is assumed to be a transfer of the triplet state excitation energy from the biacetyl molecule to a molecule of the quencher, as the result of coupled transitions in the two molecules. The results are discussed on the basis of triplet state energy data from the literature. It is concluded that the energy transfer takes place in molecular encounters, and that the probability of transfer increases with the extent of overlap of the phosphorescence spectrum of biacetyl with the singlet \rightarrow triplet absorption spectrum of the quencher, as well as with the oscillator strengths of the individual transitions involved in the process. A strong argument in favour of the assumed quenching mechanism is the fact that, at the temperature of the measurements, also substances with triplet state energies somewhat higher than that of biacetyl may act as quenchers, and that for these quenchers the energy transfer may be reversed. As a consequence, their quenching power decreases with increasing biacetyl concentration. As was to be expected, the same effect of the biacetyl concentration on the value of the quenching constant has been found also for quenchers with triplet levels somewhat lower than that of biacetyl.

A previous study¹ of the quenching effect of different types of compounds on biacetyl phosphorescence in benzene solution at 20°C led to the conclusion that the quenching action of certain aromatic compounds is due to a transfer of excitation energy, resulting in a triplet \rightarrow singlet ($T \rightarrow S$) transition in the biacetyl molecule and the reverse ($T \leftarrow S$) transition in the quencher molecule. This interpretation received additional support from experiments on sensitized biacetyl phosphorescence in solution². The present paper gives the results of further work on the relation between quenching power and triplet state energy for quenchers of this type.

EXPERIMENTAL

The method employed was to irradiate the oxygen-free biacetyl solution with a short light flash of moderate intensity and to measure the rate of decay of the phosphorescence with a photomultiplier tube and an oscilloscope. The experimental arrangements were the same as earlier¹. The solvent was benzene and the temperature 20°C. The concentration of biacetyl was generally about 3×10^{-3} M, one drop of biacetyl being used to 50 ml of solution.

Materials

2-Iodonaphthalene was prepared from 2-naphthylamine by the method of Schmidlin and Huber². It was purified by shaking the solution in methyl isobutyl ketone with dilute sulfuric acid, by treatment with active carbon, by recrystallization from aqueous ethanol, and finally by fractional distillation at 0.05 mm.

All other chemicals were of the highest purity obtainable commercially and were further purified as stated below.

The following substances were recrystallized several times using the solvents indicated. *2,2'-Dinaphthyl*, benzene; *1,2-benzanthracene*, methanol; *1-nitronaphthalene*, aqueous ethanol; *1,8-dinitronaphthalene*, acetone; *2-nitrofluorene*, first aqueous ethanol, then aqueous acetone. *Methyl β -naphthyl ketone* was treated three times with active carbon and then recrystallized from aqueous ethanol. *4,4'-Dinitrobiphenyl* and *1,5-dinitronaphthalene* were freed from basic impurities by shaking their solutions in methyl isobutyl ketone with dilute sulfuric acid. They were then recrystallized from acetone.

The following substances were fractionally distilled at the pressures stated, using an efficient column: *Nitrobenzene*, atmospheric pressure; *1-chloronaphthalene*, 20 mm; *1-bromonaphthalene*, 10 mm; *1-iodonaphthalene*, 0.02 mm. The latter had a refractive index agreeing with the value reported by Krollpfeiffer⁴, $n_D^{14} = 1.7054$.

Biacetyl and *benzene* were purified as described earlier¹.

Coronene from Rütgerswerke, Castrop-Rauxel, was used without purification. Its ultraviolet absorption spectrum agreed with that published by Clar⁵.

RESULTS OF SYSTEMATIC EXPERIMENTS WITH DIFFERENT QUENCHERS

Table 1 gives the experimental values of the quenching constant k , in $l \text{ mole}^{-1} \text{ sec}^{-1}$, for the different quenchers studied, as well as their triplet state energies E_T , in cm^{-1} , as obtained from the literature.

The k -values for phenanthrene, naphthalene, chrysene, anthracene, pyrene, *trans*-stilbene, and 3,4-benzpyrene, are taken from our previous paper¹. For nitrobenzene and 1,2-benzanthracene the use of purer preparations resulted in values of k appreciably different from those found earlier.

The results with coronene did not obey the Stern-Volmer quenching formula. The deviations were such that they might be accounted for on the assumption that a dimer was formed which had negligible quenching power. However, this assumption was not supported by light extinction measurements on coronene solutions of varying concentration. The k -value given in the table must be regarded as uncertain.

The E_T -values given represent the energy difference in cm^{-1} between the zero vibrational levels of the lowest triplet state and the singlet ground state of the molecule. Most of the values have been obtained from phosphorescence ($T \rightarrow S$ emission) spectra of solid solutions at liquid air temperature⁶⁻¹³. The values of Evans¹⁴, however, have been obtained from a study of the reverse process ($T \leftarrow S$ absorption) in liquid solution at ordinary temperature. For

Table 1. Quenching constants and triplet state energies (E_T) for different quenchers.

	k l mole ⁻¹ sec ⁻¹	E_T cm ⁻¹		
Phenanthrene	2.3×10^8	21 600 ⁷ ,	21 600 ¹⁴ ,	21 640 ¹⁰
Naphthalene	3.8×10^8	21 300 ⁶ ,	21 246 ⁸ ,	21 180 ¹⁴
Nitrobenzene	1.4×10^8		21 100 ⁶	
2-Iodonaphthalene	1.1×10^8		21 040 ⁶	
Methyl β -naphthyl ketone	8.3×10^8		20 700 ⁷	
1-Chloronaphthalene	5.9×10^8	20 700 ⁶ ,	20 645 ⁸ ,	20 700 ¹²
1-Bromonaphthalene	1.0×10^8	20 700 ⁶ ,	20 652 ⁸ ,	20 650 ¹⁴ ,
		20 650 ¹²		
2-Nitrofluorene	1.4×10^8		20 600 ⁶	
1-Iodonaphthalene	2.8×10^7		20 500 ¹⁸	
4,4'-Dinitrobiphenyl	3.6×10^8		20 200 ⁶	
1,8-Dinitronaphthalene	2.1×10^8		20 000 ⁶	
Chrysene	2.4×10^8	20 000 ⁶ ,	19 800 ⁷ ,	20 040 ¹⁰
1,5-Dinitronaphthalene	2.5×10^8		19 900 ⁶	
2,2'-Dinaphthyl	9.7×10^8		19 560 ¹⁰	
1-Nitronaphthalene	1.1×10^8		19 250 ¹²	
Coronene	2.0×10^8 *	19 100 ⁷ ,	19 040 ¹⁰	
<i>trans</i> -Stilbene	4.4×10^9		17 750 ¹⁴	
Pyrene	7.5×10^9	16 800 ⁷ ,	16 930 ¹⁴ ,	16 850 ¹⁰
1,2-Benzanthracene	7.0×10^9	16 500 ⁷ ,	16 520 ¹⁰	
Anthracene	8.1×10^9	14 700 ⁶ ,	14 927 ⁹ ,	14 870 ¹⁴
3,4-Benzpyrene	8.2×10^9	14 670 ¹⁴ ,	14 670 ¹¹	

* Extrapolated to zero quencher concentration.

most substances the $T \leftarrow S$ absorption is immeasurably weak under these conditions. As found by Evans, however, the absorption intensity increases in the presence of oxygen. A theoretical treatment of this phenomenon has recently been given by Tsubomura and Mulliken¹⁵. By saturating the solution with oxygen under pressure, the $T \leftarrow S$ absorption bands can often be obtained in sufficient intensity to be measured. The longest-wavelength band of a substance very nearly coincides with the shortest-wavelength band of its phosphorescence spectrum in solid solution at low temperature. Table 1 gives several instances of this agreement. It may be concluded that E_T -values in the table, obtained by the latter method, may be assumed to be valid with good approximation also under our experimental conditions.

In the case of biacetyl it has been possible to measure both $T \rightarrow S$ and $T \leftarrow S$ spectra in solution at ordinary temperature. This is connected with the short natural lifetime of its triplet state (*cf.* p. 964). In solvents like heptane and benzene, Forster¹⁶ found a very weak absorption band at $19\,800 \pm 100$ cm⁻¹, which is probably the 0-0 $T \leftarrow S$ absorption band. This sets an upper limit to the triplet state energy of biacetyl under these conditions. On the other hand, examination of the phosphorescence spectrum observed under the same conditions, which is shown in Fig. 1, seems to justify the conclusion that the true value of E_T cannot be much lower than that mentioned above, even though a certain amount of anti-Stokes radiation is to be expected at room temperature¹⁷. We conclude, therefore, that the true value of E_T under our conditions

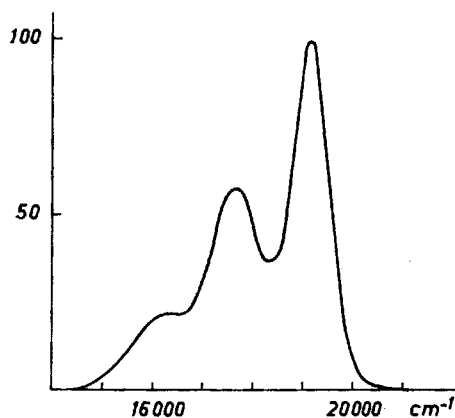


Fig. 1. Phosphorescence spectrum of biacetyl in benzene solution at 20°C, showing relative numbers of light quanta emitted vs. wave number in cm^{-1} . (From Ref.²).

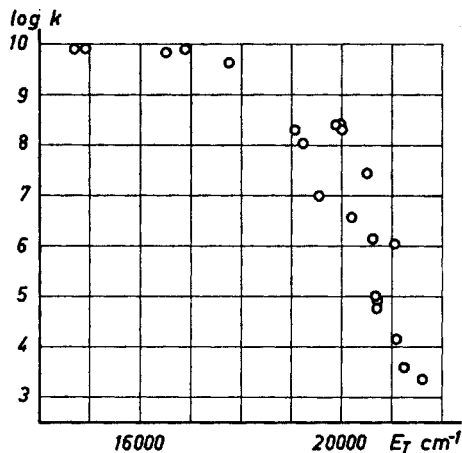


Fig. 2. Log k vs. triplet state energy (E_T) for the quenchers listed in Table 1. E_T in cm^{-1} , k in $\text{l mole}^{-1} \text{sec}^{-1}$.

is about $19\,700 \text{ cm}^{-1}$. This value is in general agreement also with the results of low-temperature phosphorescence studies^{6,18}. Fortunately, an exact knowledge of the value of E_T for biacetyl is not necessary for the present purpose.

DISCUSSION

The results are represented in graphical form in Fig. 2, where $\log k$ is plotted against E_T . From the diagram it is evident that the effectiveness of a quencher of the type studied is mainly determined by the position of its lowest triplet energy level. The results thus confirm our previous conclusion that for substances of this type, quenching is the result of a transfer of triplet state excitation energy from biacetyl to the quencher. In the following we shall discuss the mechanism of this energy transfer, on the basis of the experimental results.

The first thing to be noted is that the strongest quenchers (those with E_T -values below $17\,000 \text{ cm}^{-1}$) have practically the same value of k . This value is close to the limit which is set by the rate of diffusion, and which may be estimated by a formula given by Debye¹⁹. For a bimolecular process in benzene solution at 20°C the calculated limiting value is $1.0 \times 10^{10} \text{ l mole}^{-1} \text{ sec}^{-1}$. Similarly, a determination of k for anthracene in a somewhat more viscous solvent, methyl benzoate, gave a value of $2.80 \times 10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$ as against $3.15 \times 10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$ according to the formula of Debye.

The viscosity dependence of the quenching constant for strong quenchers shows that the transfer of excitation energy takes place only as a result of molecular encounters and not over larger distances. Experimental and theoretical investigations of sensitized fluorescence in solution have shown that,

under certain conditions, intermolecular transfer of the energy of electronic excitation between singlet states of both donor and acceptor can occur across distances much greater than kinetic-theory collision diameters, by a non-radiative process, generally called "inductive resonance". Transfer over distances of the order of 70 Å has been established in favourable cases. Work in this field has been reviewed in a recent paper by Förster²⁰, where also other cases of excitation transfer are discussed. As regards the case dealt with in the present paper, he concludes that excitation transfer between triplet states may only be expected to occur at short distances.

Intermolecular transfer of excitation energy between triplet states was first demonstrated by Terenin and Ermolaev²¹ as sensitized phosphorescence in solid solutions at low temperature. A closer study of this phenomenon led them to the conclusion¹² that excitation transfer in this case is due to exchange interaction resulting from beginning overlap of the electronic clouds of the two molecules. This would imply that energy transfer would be possible over distances somewhat larger than those of molecular contact. Our results do not exclude this possibility since, in fluid solution, a molecular encounter²² (involving repeated collisions) would nevertheless be necessary for the transfer to take place.

For quenchers with triplet levels higher than 17 000 cm⁻¹ the general trend is a lowering of the quenching constant with increasing triplet state energy, but there are considerable individual variations. This was to be expected. The radiationless transfer of the energy of electronic excitation from an excited donor molecule to an unexcited molecule of the acceptor is the result of coupled transitions in the two molecules. Fig. 3 represents a schematic energy level diagram for donor and acceptor, showing only vibrational levels belonging to the singlet ground states and the lowest triplet states of the two molecules. The temperature is assumed to be so low that both molecules are originally in so-called nonoscillating states. The transitions marked ν_0 are the pure electronic (0-0) transitions. Generally only a small fraction of the transitions actually occurring are of this kind. This is due to the difference between the nuclear equilibrium configurations of ground and of excited states which, in accordance with the Franck-Condon principle, favours transitions to different vibrational levels of the final state (see, *e.g.*, Förster²³). Two such transitions of equal energy in the two molecules, marked ν^D and ν^A , are shown in the diagram. If the two transitions occur simultaneously, due to quantum-mechanical resonance, the energy of excitation is transferred from donor to acceptor. The energy transferred corresponds to a frequency which is common to the phosphorescence spectrum of the donor and the T ← S absorption spectrum of the acceptor, *i.e.*, it belongs to the region of overlap of the two spectra. With increasing overlap the number of possible coupled transitions will increase, and consequently the possibilities for transfer.

In the present case the donor (biacetyl) is the same throughout. Its T → S emission spectrum at room temperature is shown in Fig. 1. It does not differ essentially from that observed at low temperature²⁴. The pure T ← S absorption spectra of the different acceptors (quenchers) are too weak to be measured, but they must extend from the positions of their 0-0 bands, known from phosphorescence spectra, toward higher wave numbers. The extent of spectral

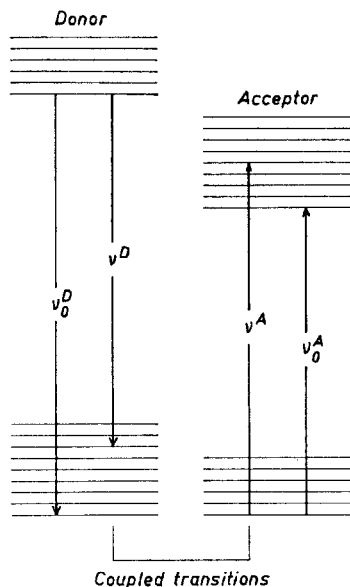


Fig. 3. Schematic energy level diagram illustrating transfer of the triplet state excitation energy from donor to acceptor through coupled transitions. For further explanations see text.

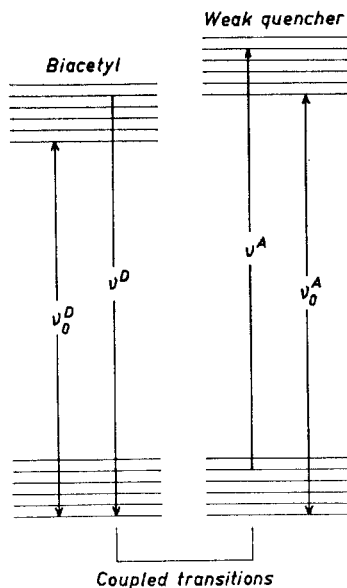


Fig. 4. Schematic energy level diagram illustrating transfer of the excitation energy from a biacetyl molecule in the triplet state to a molecule of a quencher with somewhat higher triplet state energy. For further explanations see text.

overlap must therefore increase with the difference between the triplet state energies of donor and acceptor. A general correlation between quenching constant and triplet state energy for the different quenchers may therefore be expected. However, the probability that coupled transitions will take place in donor and acceptor may be expected to depend also on the oscillator strengths of the individual transitions involved, in a similar way as in long-range excitation transfer according to the theory of Förster²³. In the present case this means that the intensities of the T←S absorption bands of a quencher as well as their positions should determine the value of its quenching constant. This we believe to be the main cause of the individual variations in the quenching constants observed. We shall return to this point in connection with the discussion of certain experimental results.

At low temperature, where the molecules are originally in vibrationless states, only transitions of the kind illustrated in Fig. 3 are possible. Under these circumstances, a transfer of the excitation energy from the biacetyl to a quencher is possible only if $\nu_o^A \leq \nu_o^D$. At higher temperatures this is no longer true. From Fig. 2 it is also quite evident that substances with triplet state energies higher than that of biacetyl may act as weak quenchers under our experimental conditions.

In the schematic energy level diagram shown in Fig. 4, the triplet state energy of the quencher is assumed to be somewhat higher than that of biacetyl ($\nu_0^A > \nu_0^D$). It is further assumed that the temperature is relatively high, so that transitions from higher vibrational levels may be expected. Two such transitions of equal energy, ν^D and ν^A , are indicated in the diagram. Their occurrence as coupled transitions would transfer the excitation energy from the biacetyl to the quencher. It should be noted in this connection that, as shown by a simple calculation, 1 molecule in 100 has a vibrational energy exceeding 900 cm^{-1} at 20°C .

However, in this case the transfer may evidently be reversed if, during its lifetime, the triplet state quencher molecule should encounter a biacetyl molecule in its ground state. Consequently, for quenchers with triplet levels above that of biacetyl, the quenching constant may be expected to decrease with increasing biacetyl concentration. This has been confirmed, which constitutes another strong argument in favour of the assumed quenching mechanism. As an illustration, results obtained with 1-iodonaphthalene as quencher will be presented in a separate section at the end of this paper. Experiments with other quenchers are in progress and will be reported later by one of us. However, it should be mentioned here that, as was to be expected, the same effect of the biacetyl concentration on the value of the quenching constant has been found also for quenchers with triplet levels somewhat lower than that of biacetyl.

Even though the k -values listed in Table 1 were obtained in experiments where the biacetyl concentration was low, there can be no doubt that many of them do not represent the true quenching constant, uninfluenced by excitation transfer in the reverse direction. In this sense they must be regarded as preliminary. Under these circumstances we prefer to postpone a discussion of the results for individual quenchers. However, an exception will be made for the 1-halogen derivatives of naphthalene. As has already been pointed out by Ermolaev and Terenin¹², these compounds are suitable for testing whether the rate of transfer of triplet state excitation energy depends on the oscillator strengths of the transitions involved in the process. Their phosphorescence spectra are similar as regards both position (*cf.* Table 1) and structure. From the approximate mirror symmetry between absorption and emission spectra^{17,23} it may be concluded that the same must be true of their $T \leftarrow S$ absorption spectra. On the other hand, the oscillator strengths (f -numbers) of their $T \leftarrow S$ transitions must vary markedly. This follows from the relation between the f -number for absorption and the natural mean lifetime, τ_0 , for emission²⁵. In the case under consideration, where the positions of the absorption bands may be expected to be nearly the same, the f -number should be inversely proportional to τ_0 . The mean lifetime of phosphorescence in solid solution at liquid air temperature was found by Ermolaev and Svitashv¹³ to be $2.0 \pm 0.2 \times 10^{-3}$ sec for 1-iodonaphthalene and 0.29 sec for 1-chloronaphthalene. Together with the authors' quantum yield determinations, these figures indicate a ratio of the oscillator strengths for these compounds of about 170.

The E_T -value of 1-iodonaphthalene is about 200 cm^{-1} lower than that of the chloro-derivative. As shown by Fig. 2, the general trend of our results is such

that a ratio of their quenching constants of about 4 would appear normal. The experimental value is 450. Our results with these compounds therefore must be said to confirm the expected dependence of the probability of excitation transfer on the oscillator strengths of the individual transitions involved*.

In similar experiments with solid solutions at liquid air temperature, Ermolaev and Terenin¹² obtained quite different results. Naphthalene and its 1-halogen derivatives were found to be equally effective, within limits of error, as quenchers of the phosphorescence of benzophenone. However, the triplet state energy of benzophenone⁶ is $24\,400\text{ cm}^{-1}$, *i.e.*, $> 3\,000\text{ cm}^{-1}$ higher than for naphthalene. There is reason to believe, therefore, that the condition of spectral overlap was in all cases so well fulfilled that some other factor governing the probability of excitation transfer was rate-determining. Obviously, this cannot have been the rate of diffusion, as for quenchers with triplet levels below $17\,000\text{ cm}^{-1}$ in the present work. Instead it must have been intermolecular distance. This interpretation fits in very well with the theory proposed by Terenin²⁶ to explain their results on the influence of the concentration of the acceptor on the quenching of the phosphorescence of benzophenone.

Besides the type of quenchers dealt with in the present paper, there are also quenchers of a different type, characterized by the presence in the molecule of a loosely bound hydrogen atom¹. For this class of compounds, the quenching mechanism has been assumed to be a photochemical reaction. Since the strongest quenchers in this class are aromatic compounds like hydroquinone and diphenylamine, it may be worth pointing out that their triplet state energies^{27,6} are so high ($> 23\,000\text{ cm}^{-1}$) that quenching by transfer of the excitation energy is excluded.

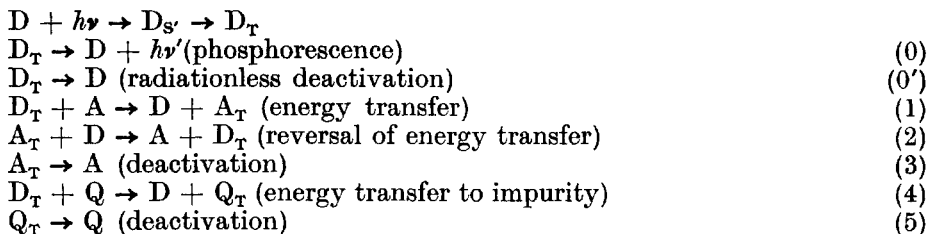
RESULTS WITH 1-IODONAPHTHALENE AS QUENCHER AND WITH VARYING BIACETYL CONCENTRATION

The results are given in Table 2. As seen from column 2, raising the biacetyl concentration caused a considerable increase in the phosphorescence mean life. In column 3 the values of τ have been corrected for the slight "self-quenching" of the biacetyl used**. In pure benzene solution τ decreased from 685 to 597 μsec when the biacetyl concentration was raised from 0.0069 to 0.1666 M.

In order to account for the results we have found it necessary to assume that the iodonaphthalene used contained a small fraction of a stronger quencher as an impurity. In the following reaction scheme D denotes biacetyl, A iodonaphthalene, and Q the quenching impurity, all in their ground states.

* *Note added in proof:* A redetermination of k for 1-chloronaphthalene, using a preparation of very high purity, gave a value of the quenching constant, corrected for energy transfer in the reverse direction, of $4.1 \times 10^3\text{ l mole}^{-1}\text{ sec}^{-1}$. With the corresponding value for 1-iodonaphthalene (p. 967) this gives a ratio of the corrected quenching constants = 8 400.

** *Cf. Ref.*¹, p. 827.



The first equation represents the formation of a triplet excited biacetyl molecule (D_T), *via* the singlet excited state ($D_{S'}$), as the result of the absorption of a light quantum (*cf.* Ref.²). As regards eqn. (0), the natural mean lifetime of biacetyl ($\tau_o = 1/k_o$) must be at least equal to 2.25×10^{-3} sec, the value found for the phosphorescence mean life in solid solution at 77°K⁷. However, the true lifetime under our experimental conditions extrapolated to zero biacetyl concentration, was only 689 μ sec, whence the sum of k_o and k_o' equalled $1.45 \times 10^3 \text{ sec}^{-1}$.

As regards the rate constant of reaction (3), the fact that 1-iodonaphthalene exhibits no detectable phosphorescence in solution at ordinary temperature shows that the triplet state lifetime under these conditions must be several orders of magnitude shorter than in solid solution at 77°K, 2×10^{-3} sec. In the present case, therefore, $k_3 \gg k_o + k_o'$.

On the above reaction scheme, the rate of phosphorescence decay after a light flash will be governed by the following differential equations, where symbols within brackets denote concentrations in mole/l.

$$\frac{d[D_T]}{dt} = -(k_o + k_o')[D_T] - k_1[A][D_T] + k_2[D][A_T] - k_4[Q][D_T] \quad (6)$$

$$\frac{d[A_T]}{dt} = k_1[A][D_T] - k_2[D][A_T] - k_3[A_T] \quad (7)$$

According to eqn. (7) the following relation would hold under steady-state conditions (constant illumination):

$$[A_T] = \frac{k_1[A][D_T]}{k_2[D] + k_3} \quad (8)$$

In the particular case under consideration ($k_3 \gg k_o + k_o'$) the same relation may be expected to hold with good approximation. This is confirmed by a study of the general solution of the equation system, which need not be given here. Under these conditions the following expression is obtained for $1/\tau_{\text{corr}}$:

$$\frac{1}{\tau_{\text{corr}}} = - \frac{d \ln [D_T]}{dt} = k_o + k_o' + k_4[Q] + \frac{k_1 k_3 [A]}{k_2 [D] + k_3} \quad (9)$$

In order to apply this equation to the experimental data it was transformed into

$$\varphi(\tau) = \frac{\tau_{\text{corr}}}{1-K \tau_{\text{corr}}} = \frac{1}{k_1[A]} + \frac{k_2[D]}{k_3} \quad (10)$$

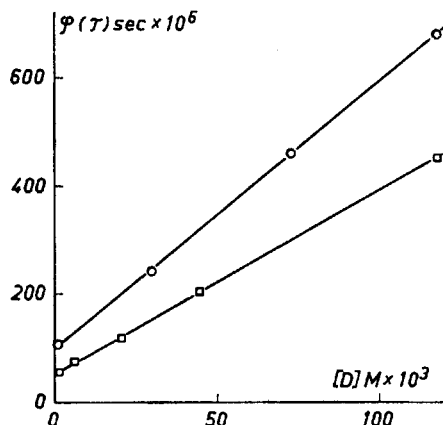


Fig. 5. $\varphi(\tau) = \tau_{\text{corr}}/(1 - K \tau_{\text{corr}})$ vs. biacetyl concentration $[D]$. Data from Table 2. \square Series 1, $K = 3280 \text{ sec}^{-1}$. \circ Series 2, $K = 2353 \text{ sec}^{-1}$. For further explanations see text.

where $K = k_0 + k_0' + k_4[Q]$. The value of K was varied until a plot of $\varphi(\tau)$ vs. $[D]$ gave as nearly as possible a straight line. The result is shown in Fig. 5. The equations of the lines are, with τ in sec

$$\text{Series 1: } \frac{\tau_{\text{corr}}}{1 - 3280 \tau_{\text{corr}}} = 49.9 + 10^{-6} + 3.41 \times 10^{-3} [D]$$

$$\text{Series 2: } \frac{\tau_{\text{corr}}}{1 - 2353 \tau_{\text{corr}}} = 97.8 \times 10^{-6} + 4.94 \times 10^{-3} [D]$$

Values of τ_{corr} calculated from these equations are given in Table 2, column 4.

The two series of measurements give closely agreeing results as regards the value of k_1 , 3.48 and $3.40 \times 10^7 \text{ l mole}^{-1} \text{ sec}^{-1}$. As regards the value of k_2/k_3 the agreement is less satisfactory, the calculated values being 68 and 51 l mole^{-1} , respectively.

Table 2. Influence of biacetyl concentration $[D]$ on the phosphorescence mean life τ at two concentrations of 1-iodonaphthalene $[A]$. For further explanations see text.

	$[D] \text{ M}$ $\times 10^3$	$\tau_{\text{obs}} \text{ sec}$ $\times 10^6$	$\tau_{\text{corr}} \text{ sec}$ $\times 10^6$	$\tau_{\text{calc}} \text{ sec}$ $\times 10^6$
Series 1. $[A] =$ $5.76 \times 10^{-4} \text{ M}$	1.5	46.0	46.0	46.6
	6.1	58.9	58.9	57.4
	20.8	84.9	85.1	86.5
	44.8	121.4	122.3	121.8
	118.0	177.0	182.1	182.1
Series 2. $[A] =$ $3.01 \times 10^{-4} \text{ M}$	1.2	84.5	84.5	83.4
	29.7	152.9	153.8	155.2
	72.9	216.2	220.9	220.4
	117.8	251.0	261.4	261.5

The assumption made, that the idonaphthalene contained a small fraction of a stronger quencher Q, requires that the term $k_4[Q]$ should be proportional to $[A]$. This was the case within limits of error. The ratio $k_4[Q]/[A]$, as obtained by subtracting $(k_o + k_o') = 1.45 \times 10^3$ from the above K -values, and dividing by the value of $[A]$, is 3.18×10^6 and 3.00×10^6 l mole⁻¹ sec⁻¹, respectively. This would correspond to the presence in the idonaphthalene of, e.g., 0.04 mole per cent of a quencher as strong as anthracene.

The value of k_1 obtained in these experiments differs relatively little from the corresponding value in Table 1. Results with other quenchers have shown that the difference may in certain cases be considerable.

REFERENCES

1. Bäckström, H. L. J. and Sandros, K. *Acta Chem. Scand.* **12** (1958) 823.
2. Bäckström, H. L. J. and Sandros, K. *Ibid.* **14** (1960) 48.
3. Schmidlin, J. and Huber, M. *Ber.* **43** (1910) 2829.
4. Krollpfeiffer, F. *Ann.* **430** (1923) 204.
5. Clar, E. *Aromatische Kohlenwasserstoffe. Polycyclische Systeme*, 2nd Ed., Springer, Berlin 1952.
6. Lewis, G. N. and Kasha, M. *J. Am. Chem. Soc.* **66** (1944) 2100.
7. McClure, D. S. *J. Chem. Phys.* **17** (1949) 905.
8. Ferguson, J., Iredale, T. and Taylor, J. A. *J. Chem. Soc.* **1954** 3160.
9. Padhye, M. R., McGlynn, S. P. and Kasha, M. *J. Chem. Phys.* **24** (1956) 588.
10. Clar, E. and Zander, M. *Chem. Ber.* **89** (1956) 749.
11. Muel, B. and Hubert-Habart, M. *J. Chim. Phys.* **55** (1958) 377.
12. Ermolaev, V. and Terenin, A. *J. Chim. Phys.* **55** (1958) 698.
13. Ermolaev, V. and Svitashv, K. *Optika i Spektroskopiya* **7** (1959) 664.
14. Evans, D. F. *J. Chem. Soc.* **1957** 1351.
15. Tsubomura, H. and Mulliken, R. S. *J. Am. Chem. Soc.* **82** (1960) 5966.
16. Forster, L. S. *J. Chem. Phys.* **26** (1957) 1761.
17. Pringsheim, P. *Fluorescence and Phosphorescence*, Interscience Publishers, New York 1949.
18. Sidman, J. W. and McClure, D. S. *J. Am. Chem. Soc.* **77** (1955) 6461.
19. Debye, P. *Trans. Electrochem. Soc.* **82** (1942) 265.
20. Förster, Th. *Discussions Faraday Soc.* **27** (1959) 7.
21. Terenin, A. and Ermolaev, V. *Trans. Faraday Soc.* **52** (1956) 1042.
22. Rabinowitch, E. *Trans. Faraday Soc.* **33** (1937) 1225.
23. Förster, Th. *Fluoreszenz organischer Verbindungen*, Vandenhoeck & Ruprecht, Göttingen 1951.
24. Lewis, G. N. and Kasha, M. *J. Am. Chem. Soc.* **67** (1945) 1001.
25. Kasha, M. *Radiation Research, Suppl.* **2** (1960) 251.
26. Terenin, A. N. *Discussions Faraday Soc.* **27** (1959) 97.
27. Zudin, A. A. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.* **23** (1959) 142.

Received December 4, 1961.