

## Transfer of Triplet State Energy in Fluid Solutions

### III. Reversible Energy Transfer

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Rate constants for transfer of triplet state energy in benzene solution at 20°C are given for 11 systems, all including biacetyl as one of the reactants. For those systems in which the other reactant has a triplet state lifetime in liquid solution comparable to that of biacetyl, the rate constants of energy transfer in both directions have been determined. The results are discussed on the basis of triplet state energy data from the literature. It is shown that the ratio between the rate constants for energy transfer in the upward and in the downward direction is equal to  $\exp(-\Delta E_T/kT)$ , where  $\Delta E_T$  is the difference between the triplet state energies of the reactants. A possible mechanism is suggested as an interpretation of the results. An earlier conclusion<sup>1</sup> of a rate constant for energy transfer increasing with increasing oscillator strengths of the individual transitions involved has been found to be based on an erroneous assumption. The new results given here show no such dependence.

In a previous study<sup>1</sup> of the quenching of biacetyl phosphorescence in solution at room temperature by an energy transfer process, it was pointed out that a reverse transfer of energy from the quencher to the biacetyl is possible if the quencher, during its lifetime in the triplet state, comes in contact with a biacetyl molecule in its ground state, provided that the electronic excitation energy of the quencher in its triplet state is not much lower than that of biacetyl.\* Consequently, the quenching constant for such quenchers can be expected to decrease with increasing biacetyl concentration. This was confirmed in experiments with 1-iodonaphthalene as the quencher. In the present paper the results of additional experiments are presented using other donor-acceptor combinations for which reversible energy transfer has been shown to take place. In most cases biacetyl acted as the primary donor, but in systems containing naphthalene, 1-chloronaphthalene, and 1-bromonaphthalene, these molecules were the primarily excited ones.

\* In Ref.<sup>1</sup> eqn. (10) on p. 966 should read:

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

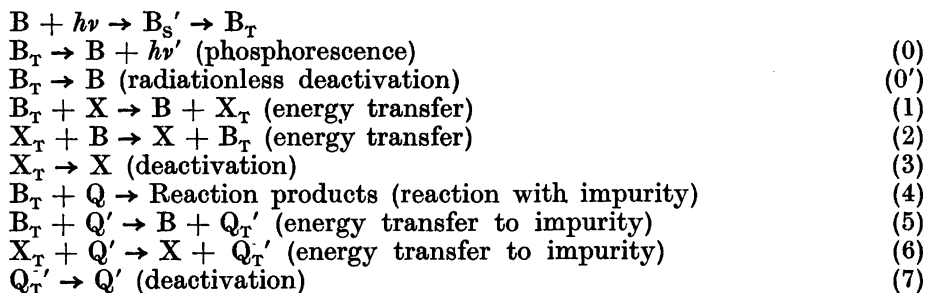
## EXPERIMENTAL

The method employed was to irradiate the oxygen-free solution with a short light flash of moderate intensity and to measure the rate of decay of the phosphorescence by a photomultiplier tube and an oscilloscope. The solvent was benzene, and the temperature  $20.0 \pm 0.1^\circ\text{C}$ . The experimental equipment and the method of degassing have been described earlier.<sup>2</sup> In this work the freezing-pumping-thawing cycle was repeated five times, the last two pumpings being performed with a mercury diffusion pump. The degassing efficiency was further improved by increasing the gas/liquid volume ratio to about 15. The longest emission lifetimes measured ( $> 10^{-2}$  sec) indicate an oxygen content of the degassed solution less than  $10^{-8}$  M.<sup>2,3</sup>

The light used for the excitation of biacetyl was limited to the wave-length range 3800–5000 Å by means of a filter combination consisting of a 4 mm Chance glass OB1 and 1 cm of an 0.5 M sodium nitrite solution. In order to excite molecules not absorbing at these wave-lengths, the incident light was confined to the wave-length range 3000–4000 Å by means of a 2 mm Schott glass UG2. In the study of phosphorescence from biacetyl, 2,2'-dinaphthyl and the naphthalenes mentioned, a 4 mm Chance glass OY3, which removed all wave-lengths below 5000 Å, was placed in front of the photomultiplier tube. Delayed fluorescence from fluoranthene, 1,2-benzopyrene, and pyrene was studied with a 4 mm Chance glass OB1 (transmitting in the wave-length range 3600–5000 Å) in front of the photomultiplier tube. The chemicals used were of the highest commercially obtainable purity and were further purified as described earlier.<sup>1,2</sup> Naphthalene and 2,2'-dinaphthyl were finally purified by zone melting. 1,2-Benzopyrene was used without any additional purification.

## RESULTS FROM EXPERIMENTS WITH BIACETYL AND SUBSTANCES HAVING SHORT LIFETIMES IN THE TRIPLET STATE COMPARED TO THAT OF BIACETYL

Substances with lifetimes in the (lowest) triplet state in solution at room temperature that are short compared with the corresponding lifetime of biacetyl were studied as quenchers of the phosphorescence of biacetyl at some different biacetyl concentrations. In order to interpret the results, the following reaction scheme is assumed:



B denotes biacetyl, X the phosphorescence quencher, Q and Q' impurities in the samples of B and X.\*

The principal features of the reaction scheme have been discussed earlier<sup>1</sup> in connection with similar experiments with the system biacetyl — 1-iodonaphthalene. Q is assumed to consist of molecules containing loosely bound

\* Since biacetyl acts as primary acceptor in some systems discussed in this study, the previously used symbols D(onor) and A(ceptor) for biacetyl and its reaction partner, respectively, now seem unsuitable.

hydrogen atoms whose reaction with  $X_T$  can be neglected, provided that  $X_T$  is in a  $^3(\pi^*\pi)$  state (see p. 2362). Measurements of the rate of phosphorescence decay in solutions containing unpurified biacetyl and acceptors having a long lifetime in the triplet state confirm this assumption.  $Q'$  is assumed to be a substance with low triplet state energy. Therefore  $k_5$  and  $k_6$  can be expected to be diffusion-controlled and approximately equal. If the mole fractions of the impurities in the samples of B and X are  $\alpha$  and  $\beta$ , respectively, then the rate of phosphorescence decay after a light flash in solutions containing B and X is determined by the following differential equations:

$$\frac{d[B_T]}{dt} = -(k_0 + k_0' + k_4\alpha[B] + k_5\beta[X]) [B_T] - k_1[X][B_T] + k_2[B][X_T] \quad (I)$$

$$\frac{d[X_T]}{dt} = -(k_3 + k_6\beta[X]) [X_T] + k_1[X][B_T] - k_2[B][X_T] \quad (II)$$

If  $k_0 + k_0' + k_4\alpha[B] + k_5\beta[X]$  is denoted by  $k_B$  and  $k_3 + k_6\beta[X]$  by  $k_X$ , the general solution of the system (I)–(II) may be written:\*

$$[B_T] = C_1 \exp[-(a-b)t] + C_2 \exp[-(a+b)t] \quad (III)$$

$$[X_T] = \frac{C_1}{k_2[B]} (-a + b + k_B + k_1[X]) \exp[-(a-b)t] + \frac{C_2}{k_2[B]} (-a - b + k_B + k_1[X]) \exp[-(a+b)t] \quad (IV)$$

where  $a = \frac{1}{2}(k_B + k_1[X] + k_2[B] + k_X)$  and  $b = \frac{1}{2}[(k_B + k_1[X] + k_2[B] + k_X)^2 - 4(k_B k_2[B] + k_B k_X + k_1 k_X [X])]^{\frac{1}{2}}$

The phosphorescence decay curves, recorded with a delay after the flash, were strictly exponential indicating that terms containing  $\exp[-(a+b)t]$  were negligible compared to terms containing  $\exp[-(a-b)t]$ . In the present case  $k_X \gg k_B$ , and with suitable values of  $[B]$  and  $[X]$ , the inequality  $k_X + k_2[B] \gg k_B + k_1[X]$  also holds. Then, neglecting small terms squared, one obtains

$$[B_T] \simeq C_1 \exp\left[-\left(k_B + \frac{k_X k_1 [X]}{k_X + k_2 [B]}\right)t\right] \quad (V)$$

Consequently, the rate of phosphorescence decay is given by the equation:

$$\frac{1}{\tau} = -\frac{1}{[B_T]} \frac{d[B_T]}{dt} = k_B + \frac{k_X k_1 [X]}{k_X + k_2 [B]} \quad (VI)$$

Tables 1–3 give the results of series of experiments where  $[X]$  and consequently  $k_X$  were kept constant within every series. In order to apply eqn. (VI) to the experimental data the observed phosphorescence lifetime ( $\tau$ ) was corrected for the quenching caused by impurities in the biacetyl sample. Measurements of the phosphorescence lifetime in biacetyl solutions at a few different concentrations gave the value of  $k_4\alpha$ . The values of  $\tau_{\text{corr}} =$

\* See, e.g., Martin, W. T. and Reissner, E. *Elementary Differential Equations*, Addison-Wesley Publishing Co. Reading, Mass., U.S.A. — London, England 1961, p. 180.

Table 1. Influence of biacetyl concentration [B] on the phosphorescence mean life  $\tau$  at two concentrations of 1,5-dinitronaphthalene [X]. For further explanation see text.

[X] M $\times 10^6$	[B] M $\times 10^4$	$\tau$ sec $\times 10^6$	$\tau_{\text{corr}}$ sec $\times 10^6$	$\tau_{\text{calc}}$ sec $\times 10^6$	$k_1$ sec $^{-1}$ M $^{-1}$ $\times 10^{-9}$	$k_2/k_X$ M $^{-1}$ $\times 10^{-3}$	$K$ sec $^{-1}$ $\times 10^{-3}$
3.36	3.60	152	152	150	2.45	1.22	0.96
	25.0	328	329	335			
	45.5	452	454	452			
	87.0	598	606	601			
	141	690	707	710			
7.35	8.30	103	103	104	2.20	1.05	0.98
	21.7	173	173	169			
	42.7	249	250	255			
	92.5	400	404	402			
	190	555	570	571			

Table 2. Influence of biacetyl concentration [B] on the phosphorescence mean life  $\tau$  at two concentrations of 1,8-dinitronaphthalene [X]. For further explanation see text.

[X] M $\times 10^6$	[B] M $\times 10^4$	$\tau$ sec $\times 10^6$	$\tau_{\text{corr}}$ sec $\times 10^6$	$\tau_{\text{calc}}$ sec $\times 10^6$	$k_1$ sec $^{-1}$ M $^{-1}$ $\times 10^{-9}$	$k_2/k_X$ M $^{-1}$ $\times 10^{-3}$	$K$ sec $^{-1}$ $\times 10^{-3}$
2.64	0.30	128	128	130	2.63	0.95	0.97
	21.0	309	310	305			
	47.6	447	449	451			
	95.0	592	600	604			
	151	690	708	705			
11.1	4.30	53.5	53.5	51.2	2.55	1.19	0.89
	45.1	179	179	188			
	69.0	259	260	254			
	98.0	323	326	322			
	144	402	408	411			

Table 3. Influence of biacetyl concentration [B] on the phosphorescence mean life  $\tau$  at two concentrations of 2-iodonaphthalene [X]. For further explanation see text.

[X] M $\times 10^8$	[B] M $\times 10^4$	$\tau$ sec $\times 10^6$	$\tau_{\text{corr}}$ sec $\times 10^6$	$\tau_{\text{calc}}$ sec $\times 10^6$	$k_1$ sec $^{-1}$ M $^{-1}$ $\times 10^{-6}$	$k_2/k_X$ M $^{-1}$ $\times 10^{-3}$	$K$ sec $^{-1}$ $\times 10^{-3}$
3.18	6.40	79.8	79.8	75.7	6.14	0.97	1.17
	23.6	133	133	141			
	82.2	304	306	299			
	139	397	404	397			
	158	406	414	422			
9.74	7.10	25.9	25.9	27.6	5.55	0.75	1.20
	78.0	115	115	111			
	220	227	231	235			
	341	303	313	311			
	532	374	399	399			

$\tau/1 - \tau k_4 \alpha [B]$  are presented in column 4 of the tables. Eqn. (VI) was transformed into

$$\varphi(\tau) = \frac{\tau_{\text{corr}}}{1 - K\tau_{\text{corr}}} = \frac{1}{k_1[X]} + \frac{k_2[B]}{k_x k_1[X]} \quad (\text{VII})$$

where  $K = k_0 + k_0' + k_5\beta[X]$ . The value of  $K$  was varied until the best linear relation between  $\varphi(\tau)$  and  $[B]$  was obtained. Calculated values of  $\tau_{\text{corr}}$  ( $\tau_{\text{calc}}$ ),  $k_1$ , and  $k_2/k_x$  from these relations are given in the tables together with the values of  $K$  used. The adopted values of  $K$  do not differ much from the values of  $k_0 + k_0'$  obtained by measuring the phosphorescence lifetimes in pure biacetyl solutions, which shows that the contributions to the  $K$ -values from the impurities in the samples used were small. The mean of the  $k_1$ -values for 1,5-dinitronaphthalene, 1,8-dinitronaphthalene, and 2-iodonaphthalene are  $2.33 \times 10^9$ ,  $2.59 \times 10^9$ , and  $5.85 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$ , respectively. The values of  $k_2/k_x$  differ very little for the three systems. If the  $k_2$ -values in these systems are assumed to be mainly determined by diffusion and to lie in the range  $(3-10) \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  (see p. 2372), then  $k_x$  for the three substances may be estimated to lie in the range  $(2.5-13) \times 10^6 \text{ sec}^{-1}$ .

#### RESULTS FROM EXPERIMENTS WITH BIACETYL AND SUBSTANCES HAVING LIFETIMES IN THE TRIPLET STATE COMPARABLE TO THAT OF BIACETYL

Solutions of a number of aromatic hydrocarbons, with or without the addition of the sensitizer benzophenone,<sup>4</sup> exhibited emission with a lifetime in the range  $10^{-2}$ – $10^{-3}$  sec after excitation by a light flash. This emission was assumed to be either phosphorescence or delayed fluorescence. As shown by Parker (key reference<sup>5</sup>), a number of aromatic hydrocarbons exhibit delayed fluorescence in solution at room temperature. Parker suggested a bimolecular reaction between molecules of these aromatics in their triplet states with the formation of an excited dimer in a singlet state. This dimer may either fluoresce or dissociate, giving rise to a fluorescing singlet excited monomer.

In order to elucidate the nature of the long-lived emission from aromatic hydrocarbons observed in the present work, its spectral distribution and the dependence of the emission intensity on the intensity of the exciting light flash were investigated.

To determine the spectral distribution of the emission, the solutions were excited by a light flash having passed an UG2-filter. The intensities of emitted light recorded with an OB1-filter and with an OY3-filter in front of the photomultiplier tube were compared.

With that filter inserted for which the photomultiplier tube gave the highest photocurrent, the emission intensities with and without a gauze filter inserted in front of the entrance slit were compared. The gauze filter reduced the intensity of the exciting flash by one half.

The results of these experiments are presented in Table 4. For fluoranthene, 1,2-benzpyrene, and pyrene, the emission was mainly in the range 3600–5000 Å, whereas phosphorescence from these substances lies in the range  $>5000$  Å. The dependence of the emission intensity on the excitation intensity also

Table 4. Characteristics of the long-lived emission from  $4 \times 10^{-5}$  M solutions of some aromatic hydrocarbons X upon excitation by a flash of moderate intensity, using benzophenone ( $3 \times 10^{-3}$  M) as a sensitizer. Filter OB1 transmits in the region 3600–5000 Å and OY3 transmits wave-lengths  $> 5000$  Å.

X	0–0 band of phosphorescence of X Å	Filter transmitting the main part of emission	Emission intensity dependence on flash intensity I	Main type of emission
Fluoranthene	5400	OB1	$\propto I^2$	Delayed fluorescence
1,2-Benzopyrene	5400	OB1	$\propto I^2$	»
Pyrene	5900	OB1	$\propto I^2$	»
2,2'-Dinaphthyl	5100	OY3	$\propto I$	Phosphorescence
Naphthalene	4700	OY3	$\propto I$	»
1-Chloronaphthalene	4800	OY3	$\propto I$	»
1-Bromonaphthalene	4800	OY3	$\propto I$	»

indicates that the long-lived emission from these substances consists mainly of delayed fluorescence. The nature of the emission from 2,2'-dinaphthyl and the naphthalenes, on the other hand, indicates that it is chiefly phosphorescence.

A study of the rate of decay of the emission from the pyrene solution used at varying excitation light intensity gave support to the assumption of a triplet-triplet reaction. When the solution was excited by an exceptionally high flash intensity, the decay of the emission was not strictly exponential, and the earliest measurable emission "lifetime" in this case was less than half of that obtained from the exponential decay curve for the emission after a flash of low intensity. In the final experiments, excitation resulting in a high concentration of molecules in the triplet state was avoided for substances that exhibit delayed fluorescence.

The different donor-acceptor systems are presented individually, since the experimental treatment of the systems had to be varied with respect to the relative triplet state energies of donor and acceptor.

*Biacetyl-fluoranthene.* In order to take into account the delayed fluorescence shown by fluoranthene, the following equation<sup>5</sup> has to be added to the reaction scheme presented above:



where  $X_2^*$ ,  $X_2^{**}$ , and  $X^*$  denote singlet excited states. On the basis of the experiments presented in the previous section, it is not possible to decide whether the emission arises from  $X_2^{**}$ ,  $X^*$ , or both. However, for the purpose of the present investigation it is sufficient that a study of the decay rate of the delayed fluorescence enables one to calculate the rate of decay of  $[X_T]$ . After the excitation of a fluoranthene solution, eqn. (VIII) applies:

$$\frac{d[X_T]}{dt} = -(k_3 + k_6\beta[X] + k_8[X_T])[X_T] \quad (VIII)$$

Experimental conditions can be chosen so as to make  $k_8[X_T]$  negligible in relation to  $k_3 + k_6\beta[X]$ .

Since  $X_2^{**}$  has a short lifetime compared to that of  $X_T$ , eqn. (IX) is a good approximation:

$$[X_2^{**}] = \text{constant } [X_T]^2 \quad (\text{IX})$$

Thus, for the lifetime,  $\tau$ , of the delayed fluorescence eqn. (X) applies:

$$\frac{1}{\tau} = - \frac{1}{[X_2^{**}]} \frac{d[X_2^{**}]}{dt} = 2(k_3 + k_6\beta[X]) \quad (\text{X})$$

The ratio of the decay constants for delayed fluorescence to those for  $[X_T]$  should therefore be 2. Measurements of the delayed fluorescence and the phosphorescence of pyrene performed by Stevens and Walker<sup>17</sup> gave  $1.7 \pm 0.3$  for this ratio.

After excitation of a solution containing biacetyl and fluoranthene, relations (I) and (II) apply if the bimolecular reaction between the fluoranthene molecules in the triplet state is neglected. If after a light flash the emission from such a solution is passed through an OY3-filter, the contribution from the delayed fluorescence of the fluoranthene can be neglected in relation to the biacetyl phosphorescence, and, when sufficient time has elapsed after the flash, the rate of phosphorescence decay will be given by:

$$\frac{1}{\tau} = k = - \frac{1}{[B_T]} \frac{d[B_T]}{dt} = a - b \quad (\text{XI})$$

Substitution of the expressions for  $a$  and  $b$  gives:

$$k_2[B] = \frac{k(k_B + k_1[X]) + k_X - k - k_X(k_B + k_1[X])}{k_B - k} \quad (\text{XII})$$

The values of  $k_B$  and  $k_X$  can be calculated after determining the lifetimes of the phosphorescence and the delayed fluorescence of pure solutions of biacetyl and fluoranthene of varying concentrations and assuming that  $k_5 = k_6$ . As the term  $k_5\beta[X]$  makes a slight contribution to  $k_B$ , this assumption, although only approximately valid, is not critical.

A determination of  $k_2$  requires that  $k_1$  can be determined separately. Such a determination is possible for this system. If a biacetyl-fluoranthene solution is excited by a light flash which has passed through an OB1-filter + 1 cm of 0.5 M  $\text{NaNO}_2$  solution, and which is therefore not absorbed by the fluoranthene, then immediately after the excitation  $[X_T]$  may be put equal to zero. If a sufficiently low concentration of  $[B]$  is chosen, the return of energy from  $X_T$  to B can be neglected during an initial period of time and for "the first measurable phosphorescence lifetime",  $\tau_*$ , eqn. (XIII) applies:

$$\frac{1}{\tau_*} = k_* = k_B + k_1[X] \quad (\text{XIII})$$

Measurements of emission lifetimes in biacetyl and fluoranthene solutions gave  $k_0 + k_0' = 1.00 \times 10^3 \text{ sec}^{-1}$ ,  $k_4\alpha = 7.6 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$ ,  $k_3 = 55 \text{ sec}^{-1}$ , and  $k_6\beta = 1.55 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$ . Measurements of "the first phosphorescence

Table 5. Determination of  $k_1$  from the "first observable phosphorescence lifetime"  $\tau_*$  of biacetyl ( $1.5 \times 10^{-5}$  M) in solutions of fluoranthene in varying concentration [X].

[X] M $\times 10^5$	$1/\tau_* = k_*$ sec <sup>-1</sup>	$k_B$ sec <sup>-1</sup>	$k_1 \text{ sec}^{-1} \text{ M}^{-1}$ $\times 10^{-9}$
—	1 030	1030	—
2.06	11 900	1033	5.28
3.09	17 510	1035	5.33
3.42	18 940	1035	5.24
4.48	24 510	1037	5.24
			Av. 5.27

Table 6. Determination of  $k_2$  from the biacetyl phosphorescence lifetime  $\tau$  in solutions of biacetyl B and fluoranthene X. In calculating  $k_2[B]$  the value of  $k_1 = 5.27 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$  has been used.

[B] M $\times 10^3$	[X] M $\times 10^5$	$1/\tau = k$ sec <sup>-1</sup>	$k_B$ sec <sup>-1</sup>	$k_X$ sec <sup>-1</sup>	$k_2[B] \text{ sec}^{-1}$ $\times 10^{-4}$	$k_2 \text{ sec}^{-1} \text{ M}^{-1}$ $\times 10^{-7}$
1.08	0.177	730	1011	58	2.30	2.13
1.07	0.480	483	1015	62	2.04	1.91
2.04	0.620	601	1026	65	4.17	2.04
1.87	1.77	364	1041	82	3.91	2.09
5.60	1.46	707	1066	78	13.5	2.42
6.00	3.07	545	1094	103	13.1	2.18
12.2	3.27	720	1144	106	25.0	2.05
						Av. 2.12

lifetime" in biacetyl-fluoranthene solutions are presented in Table 5. The mean value of  $k_1$  calculated from these experiments is  $5.27 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$ .

Measurements of the rate of decay of phosphorescence in biacetyl-fluoranthene solutions, performed with a delay after the light flash, are given in Table 6. These experiments gave  $k_2 = 2.12 \times 10^7 \text{ sec}^{-1} \text{ M}^{-1}$ .

The uncertainty in the determination of  $k_2$  is rather large due to the fact that the system is sensitive to disturbances caused by oxygen and impurities in the solvent, since the values of  $k_0 + k_0'$  and  $k_3$  are small. By adding a substance which reacts with biacetyl but not with fluoranthene in their triplet states, the accuracy of the determination can be improved. Molecules with a loosely bound hydrogen atom react with molecules in a  $^3(\pi^*n)$  state with a rate constant which is much greater than that for reaction with molecules in a  $^3(\pi^*\pi)$  state (see *e.g.* Ref.<sup>6</sup>). Therefore, diphenylamine was expected to react with fluoranthene triplets much more slowly than with biacetyl triplets.

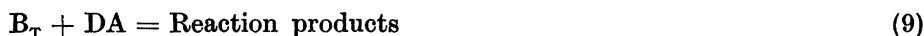
The lifetime of the delayed fluorescence from a solution of  $3.4 \times 10^{-5}$  M fluoranthene containing  $5.5 \times 10^{-3}$  M diphenylamine was 330  $\mu\text{sec}$ . Thus, the rate constant of the reaction between triplet fluoranthene and diphenylamine can be calculated at  $2.6 \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$ . The possibility that quenching of the delayed fluoranthene fluorescence is caused partly by impurities in the diphenylamine preparation should not be excluded. The rate constant of the



Table 7. Determination of  $k_2$  from the biacetyl phosphorescence lifetime  $\tau$  in solutions of biacetyl B, fluoranthene X and diphenylamine ( $2.70 \times 10^{-6}$  M). In calculating  $k_2[B]$  the value of  $k_1 = 5.27 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$  has been used.

[B] M $\times 10^3$	[X] M $\times 10^5$	$1/\tau = k$ sec <sup>-1</sup>	$k_B$ sec <sup>-1</sup>	$k_X$ sec <sup>-1</sup>	$k_2[B]$ sec <sup>-1</sup> $\times 10^{-3}$	$k_2 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-7}$
5.00	—	19 010	19 010	—	—	—
—	2.28	190	—	95	—	—
0.379	2.28	1 131	19 010	95	8.41	2.22
1.12	2.28	2 904	19 016	95	23.8	2.13
2.16	2.28	4 785	19 023	95	44.3	2.05
4.40	2.28	7 866	19 040	95	91.3	2.08
16.8	2.28	14 220	19 135	95	359	2.14
						Av. 2.12

reaction between biacetyl in the triplet state and diphenylamine has previously<sup>2</sup> been determined at  $6.8 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ . In the presence of diphenylamine the reaction scheme (0)–(8) must therefore be supplemented by:



where DA denotes diphenylamine.

Results from measurements of phosphorescence lifetimes of biacetyl-fluoranthene solutions containing  $2.70 \times 10^{-6}$  M diphenylamine are presented in Table 7. In this case  $k_9$  [DA] and  $k_{10}$  [DA] are included in the values of  $k_B$  and  $k_X$ , respectively. The value of  $k_2 = 2.12 \times 10^7 \text{ sec}^{-1}\text{M}^{-1}$  obtained from this series agrees with the value given above. As expected, the  $k_2$ -values from this series were less scattered than those from experiments without diphenylamine.

*Biacetyl-1,2-benzpyrene.* The triplet state energy of 1,2-benzpyrene is very close to that of fluoranthene. The same reaction scheme as for the system biacetyl-fluoranthene explains the results.

From measurements of lifetimes of the delayed fluorescence from 1,2-benzpyrene solutions the values  $k_3 = 57 \text{ sec}^{-1}$  and  $k_6\beta = 3.25 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$  were obtained. The value of  $k_{10}$  was found to be  $2.0 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ .

Table 8. Determination of  $k_1$  from the "first observable phosphorescence lifetime"  $\tau_*$  of biacetyl ( $1.0 \times 10^{-6}$  M) in solutions of 1,2-benzpyrene in varying concentration [X].

[X] M $\times 10^6$	$1/\tau_* = k_*$ sec <sup>-1</sup>	$k_B$ sec <sup>-1</sup>	$k_1 \text{ sec}^{-1} \text{M}^{-1}$ $\times 10^{-3}$
—	1 050	1050	—
2.46	15 820	1058	6.00
3.15	18 940	1060	5.68
3.55	21 650	1062	5.80
4.20	25 710	1064	5.87
			Av. 5.84

Table 9. Determination of  $k_2$  from the biacetyl phosphorescence lifetime  $\tau$  in solutions of biacetyl B, 1,2-benzpyrene X and diphenylamine ( $1.33 \times 10^{-6}$  M). In calculating  $k_2[B]$  the value of  $k_1 = 5.84 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$  has been used.

[B] M $\times 10^3$	[X] M $\times 10^5$	$1/\tau = k$ sec $^{-1}$	$k_B$ sec $^{-1}$	$k_X$ sec $^{-1}$	$k_2[B]$ sec $^{-1}$ $\times 10^{-4}$	$k_2 \text{ sec}^{-1} \text{ M}^{-1}$ $\times 10^{-7}$
1.02	—	9970	9 970	—	—	—
—	1.00	180	—	90	—	—
0.297	1.00	1942	9 997	90	1.53	5.15
0.627	1.00	3195	10 000	90	2.98	4.75
1.24	1.00	5000	10 004	90	6.23	5.02
2.29	1.00	6390	10 012	90	10.8	4.72
						Av. 4.91

Determinations of "the first measurable phosphorescence lifetime" of biacetyl-1,2-benzpyrene solutions are presented in Table 8. The calculated mean value of  $k_1$  from these experiments is  $5.84 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$ .

Measurements of the rate of phosphorescence decay of biacetyl-1,2-benzpyrene solutions containing diphenylamine are to be found in Table 9. From these measurements  $k_2$  was found equal to  $4.91 \times 10^7 \text{ sec}^{-1} \text{ M}^{-1}$ .

*Biacetyl-pyrene.* The large difference in triplet state energy between biacetyl and pyrene ( $\Delta E_T = 2850 \text{ cm}^{-1}$ ) means that  $k_2$  is small for this system. In this way the separate determination of  $k_1$  is facilitated.

Table 10. Determination of  $k_1$  from the "first observable phosphorescence lifetime"  $\tau_*$  of biacetyl ( $4.5 \times 10^{-5}$  M) in solutions of pyrene in varying concentration [X].

[X] M $\times 10^6$	$1/\tau_* = k_*$ sec $^{-1}$	$k_B$ sec $^{-1}$	$k_1 \text{ sec}^{-1} \text{ M}^{-1}$ $\times 10^{-9}$
—	1 038	1038	—
0.337	3 521	1038	7.37
0.653	6 098	1039	7.75
1.24	10 680	1039	7.77
1.68	13 790	1040	7.59
			Av. 7.62

Table 11. Determination of  $k_2$  from the biacetyl phosphorescence lifetime  $\tau$  in solutions of biacetyl B, pyrene X and diphenylamine ( $6.05 \times 10^{-7}$  M). In calculating  $k_2[B]$  the values of  $k_1 = 7.62 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$  and of  $k_X = 48 \text{ sec}^{-1}$  have been used.

[B] M	[X] M $\times 10^6$	$1/\tau = k$ sec $^{-1}$	$k_B$ sec $^{-1}$	$k_2[B]$ sec $^{-1}$ $\times 10^{-3}$	$k_2 \text{ sec}^{-1} \text{ M}^{-1}$ $\times 10^{-4}$
0.005	—	5086	5086	—	—
0.121	1.07	780	5138	2.10	1.74
0.239	1.07	1429	5190	4.37	1.83
0.451	1.07	2123	5284	7.43	1.65
0.729	1.07	2833	5407	11.61	1.59
					Av. 1.70

In these experiments a newly distilled batch of biacetyl was used, for which  $k_4\alpha$  was found to be  $444 \text{ sec}^{-1}\text{M}^{-1}$ . For the pyrene sample used,  $k_3 = 48 \text{ sec}^{-1}$  and  $k_6\beta = 1.00 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ . The value of  $k_{10}$  was determined at  $2.4 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ .

Determinations of the "first measurable phosphorescence lifetime" from biacetyl-pyrene solutions, shown in Table 10, give  $k_1 = 7.62 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ .

Measurements of the rate of phosphorescence decay of biacetyl-pyrene solutions containing diphenylamine are presented in Table 11. With the low pyrene content chosen, the intensity of the delayed fluorescence was insufficient for determining  $k_x$ . It was therefore calculated from data for  $k_3$ ,  $k_6\beta$  and  $k_{10}$ . The series of experiments gives  $k_2 = 1.70 \times 10^4 \text{ sec}^{-1}\text{M}^{-1}$ .

*Biacetyl-2,2'-dinaphthyl.* In these experiments the same biacetyl sample was used as in the experiments with biacetyl-pyrene. Measurements of the lifetime of phosphorescence from solutions of 2,2'-dinaphthyl containing diphenylamine gave  $k_3 = 70 \text{ sec}^{-1}$ ,  $k_6\beta = 5.30 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$  and  $k_{10} = 4.2 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$ .

Since the triplet state energies of biacetyl and of 2,2'-dinaphthyl are nearly equal, a separate determination of  $k_1$  by the previous technique is not possible. On the other hand,  $k_2$  can be determined by measuring the rate of decay of the total emission from biacetyl-2,2'-dinaphthyl solutions in which the lifetime of triplet biacetyl is sufficiently reduced by adding diphenylamine.

Table 12. Determination of  $k_2$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ([B] M) and 2,2'-dinaphthyl ( $7.64 \times 10^{-6}$  M) containing benzophenone ( $2.0 \times 10^{-3}$  M) and diphenylamine ( $2.80 \times 10^{-4}$  M).

[B] M $\times 10^6$	$1/\tau = k$ sec <sup>-1</sup>	$k_x$ sec <sup>-1</sup>	$k_2 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-9}$
—	1362	1362	—
1.02	2766	1362	1.38
1.93	4018	1362	1.38
3.59	5882	1362	1.26
5.03	8097	1362	1.34
			Av. 1.34

Table 13. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl B and 2,2'-dinaphthyl X containing benzophenone ( $2.0 \times 10^{-3}$  M) and diphenylamine ( $1.56 \times 10^{-6}$  M). In calculating  $k_1$  the value of  $k_2 = 1.34 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  has been used.

[B] M $\times 10^5$	[X] M $\times 10^5$	$1/\tau = k$ sec <sup>-1</sup>	$k_B$ sec <sup>-1</sup>	$k_x$ sec <sup>-1</sup>	$k_1 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-9}$
2.32	—	11 470	11 470	—	—
—	1.34	160	—	160	—
0.81	1.34	2 188	11 540	160	3.04
1.90	1.34	4 127	11 540	160	3.00
3.72	1.34	6 231	11 540	160	2.86
5.96	1.34	7 474	11 540	160	3.01
					Av. 2.98

When sufficient time has elapsed after a flash,  $[B_T]$  is proportional to  $[X_T]$  (see eqns. (III) and (IV)), and the expression for the decay of the total emission may be written:

$$\frac{1}{\tau} = k = \frac{1}{[B_T]} \frac{d[B_T]}{dt} = a - b \quad (\text{XIV})$$

If the diphenylamine concentration is chosen so that  $k_B \gg k$ ,  $k_1[X]$ , and  $k_X$ , eqn. (XV) should hold approximately:

$$k = k_X + k_2[B] \quad (\text{XV})$$

A series of experiments presented in Table 12 gives  $k_2 = 1.34 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ . Using this value of  $k_2$ ,  $k_1$  was obtained from similar experiments where higher concentrations of biacetyl and much lower concentration of diphenylamine were used (Table 13). The value of  $k_1$  was calculated by means of eqn. (XVI):

$$k_1[X] = \frac{k_B(k_2[B] + k_X) - k(k_B + k_2[B] + k_X - k)}{k - k_X} \quad (\text{XVI})$$

The mean value found for  $k_1$  is  $2.98 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ .

*Naphthalene-biacetyl.* Measurements of naphthalene phosphorescence lifetimes in solutions containing benzophenone and diphenylamine gave  $k_3 = 405 \text{ sec}^{-1}$ ,  $k_3\beta = 4.3 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$  and  $k_{10} = 8.5 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ .

In experiments with naphthalene and its derivatives, the conditions were chosen so as to localize the excitation energy immediately after the flash mainly in these substances. The absorption spectrum of naphthalene necessitated sensitizing with benzophenone, whereas in experiments with the naphthyl halides direct excitation occurred. Thus, immediately after excitation of a solution containing benzophenone and naphthalene in much greater concentrations than biacetyl,  $[B_T] \simeq 0$ . Thereafter, eqn. (XVII) applies:

$$[B_T] = C_1 \exp[-(a-b)t] - C_1 \exp[-(a+b)t] \quad (\text{XVII})$$

The ratio between the first and the second term is  $\exp(2bt)$ , from which it is possible to estimate the time after the flash when the second term may be neglected. This was the case in the measurements reported below.

Table 14. Determination of  $k_2$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $[B]$  M) and naphthalene ( $2.0 \times 10^{-4}$  M) containing benzophenone ( $5.0 \times 10^{-3}$  M) and diphenylamine ( $1.27 \times 10^{-4}$  M).

$[B]$ M $\times 10^7$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_2 \text{sec}^{-1}\text{M}^{-1}$ $\times 10^{-9}$
—	513	513	—
3.13	3 257	513	8.77
5.96	5 882	513	9.01
8.75	8 264	513	8.86
11.1	10 160	513	8.69
			Av. 8.83

Table 15. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $0.98 \times 10^{-6}$  M) and naphthalene ( $[X]$  M) containing benzophenone ( $5.0 \times 10^{-3}$  M) and diphenylamine ( $3.80 \times 10^{-6}$  M). In calculating  $k_1[X]$  the values of  $k_2 = 8.83 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  and of  $k_B = 2.68 \times 10^4 \text{ sec}^{-1}$  have been used.

$[X]$ M $\times 10^3$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_1[X] \text{ sec}^{-1}$ $\times 10^{-4}$	$k_1 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-6}$
0.443	5875	427	1.23	2.78
1.35	3931	466	3.43	2.54
2.14	3186	500	5.25	2.45
3.70	2242	567	10.2	2.76
4.98	1961	622	13.6	2.73
				Av. 2.65

Table 14 gives the results of experiments with naphthalene similar to those with 2,2'-dinaphthyl reported in Table 13. The calculated value of  $k_B \approx 8 \times 10^5 \text{ sec}^{-1}$ . The resulting value of  $k_2$  is  $8.83 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ .

The results of experiments to determine  $k_1$  are presented in Table 15. In calculating  $k_B$ , the contribution due to  $k_5\beta [X]$  has been neglected. The resulting value of  $k_1$  is  $2.65 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$ .

Table 16. Determination of  $k_2$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $[B]$  M) and 1-chloronaphthalene ( $3.1 \times 10^{-4}$  M) containing diphenylamine ( $8.0 \times 10^{-6}$  M).

$[B]$ M $\times 10^7$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_2 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-9}$
—	645	645	—
1.04	1062	645	4.01
3.69	2183	645	4.17
6.52	3021	645	3.64
9.30	4098	645	3.71
23.6	9690	645	3.83
			Av. 3.87

Table 17. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $6.46 \times 10^{-6}$  M) and 1-chloronaphthalene ( $[X]$  M) containing diphenylamine ( $1.125 \times 10^{-5}$  M). In calculating  $k_1[X]$  the values of  $k_2 = 3.87 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  and of  $k_B = 7.75 \times 10^4 \text{ sec}^{-1}$  have been used.

$[X]$ M $\times 10^3$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_1[X] \text{ sec}^{-1}$ $\times 10^{-4}$	$k_1 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-7}$
2.98	11 430	623	8.68	2.91
5.06	8 937	637	13.8	2.73
7.23	6 807	653	21.6	2.99
12.2	4 543	687	40.0	3.28
22.2	3 411	758	62.4	2.81
				Av. 2.94

Table 18. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $2.05 \times 10^{-6}$  M) and 1-chloronaphthalene ( $[X]$  M) containing diphenylamine ( $4.58 \times 10^{-6}$  M). In calculating  $k_1[X]$  the values of  $k_2 = 3.87 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  and of  $k_B = 3.21 \times 10^{-4} \text{ sec}^{-1}$  have been used.

$[X]$ M $\times 10^3$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_1[X]$ $\text{sec}^{-1}$ $\times 10^{-4}$	$k_1 \text{sec}^{-1}\text{M}^{-1}$ $\times 10^{-7}$
0.544	5650	602	1.51	2.78
1.20	4338	606	3.13	2.61
3.21	2500	620	9.53	2.97
6.22	1811	642	17.5	2.81
				Av. 2.79

*1-Chloronaphthalene-biacetyl.* For the 1-chloronaphthalene used, the values  $k_3 = 595 \text{ sec}^{-1}$  and  $k_{\beta} = 7.0 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$  were obtained. The value of  $k_{10}$  was determined at  $6.3 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ . Experiments for the determination of  $k_2$  are reported in Table 16. For the diphenylamine concentration used,  $k_B$  can be calculated at  $5.4 \times 10^5$ , showing that the conditions  $k_B \gg k$ ,  $k_1[X]$ , and  $k_X$  are well satisfied. These experiments give  $k_2 = 3.87 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ .

Table 19. Determination of  $k_2$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $[B]$  M) and 1-bromonaphthalene ( $2.4 \times 10^{-4}$  M) containing diphenylamine ( $2.0 \times 10^{-4}$  M).

$[B]$ M $\times 10^7$	$1/\tau = k$ $\text{sec}^{-1}$	$k_X$ $\text{sec}^{-1}$	$k_2 \text{sec}^{-1}\text{M}^{-1}$ $\times 10^{-9}$
—	1 110	1110	—
5.14	2 739	1110	3.17
8.98	4 219	1110	3.46
17.8	7 246	1110	3.45
28.8	10 790	1110	3.36
37.7	14 220	1110	3.48
			Av. 3.38

Table 20. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $2.60 \times 10^{-6}$  M) and 1-bromonaphthalene ( $[X]$  M) containing diphenylamine ( $3.13 \times 10^{-6}$  M). In calculating  $k_1[X]$  the values of  $k_2 = 3.38 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  and of  $k_B = (2.23 \times 10^4 + k_{\beta}\beta[X]) \text{ sec}^{-1}$  have been used.

$[X]$ M $\times 10^3$	$1/\tau = k$ $\text{sec}^{-1}$	$k_B \text{sec}^{-1}$ $\times 10^{-4}$	$k_X$ $\text{sec}^{-1}$	$k[X]$ $\text{sec}^{-1}$ $\times 10^{-4}$	$k \text{sec}^{-1}\text{M}^{-1}$ $\times 10^{-7}$
0.321	6532	2.24	1014	0.941	2.93
0.826	4805	2.25	1114	2.44	2.95
1.95	3434	2.27	1332	6.13	3.14
3.72	2944	2.30	1677	11.9	3.20
6.50	3021	2.36	2220	20.5	3.15
					Av. 3.07

Table 21. Determination of  $k_1$  from the lifetime  $\tau$  of the mixed phosphorescence from solutions of biacetyl ( $2.11 \times 10^{-6}$  M) and 1-bromonaphthalene ( $[X]$  M) containing diphenylamine ( $5.22 \times 10^{-6}$  M). In calculating  $k_1[X]$  the values of  $k_2 = 3.38 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$  and of  $k_B = (3.65 \times 10^4 + k_5\beta[X]) \text{ sec}^{-1}$  have been used.

$[X]$ M $\times 10^3$	$1/\tau = k$ $\text{sec}^{-1}$	$k_B \text{ sec}^{-1}$ $\times 10^4$	$k_X$ $\text{sec}^{-1}$	$k_1[X] \text{ sec}^{-1}$ $\times 10^{-4}$	$k_1 \text{ sec}^{-1}\text{M}^{-1}$ $\times 10^{-7}$
0.351	6410	3.66	1021	0.976	2.78
1.05	4963	3.67	1158	2.77	2.64
1.58	4149	3.68	1261	4.80	3.04
3.36	3604	3.72	1608	8.72	2.60
					Av. 2.77

Two series of experiments for the determination of  $k_1$ , using different concentrations of diphenylamine, are presented in Tables 17 and 18. In calculating  $k_B$ ,  $k_5\beta[X]$  was neglected. From the two series, values of  $k_1$  equal to  $2.94 \times 10^7$  and  $2.79 \times 10^7 \text{ sec}^{-1}\text{M}^{-1}$ , respectively, are obtained.

*1-Bromonaphthalene-biacetyl.* For the 1-bromonaphthalene sample used,  $k_3 = 950 \text{ sec}^{-1}$  and  $k_6\beta = 1.95 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ . The value of  $k_{10}$  was determined at  $5.4 \times 10^5 \text{ sec}^{-1}\text{M}^{-1}$ . Experiments performed to determine  $k_2$  using solutions containing diphenylamine are reported in Table 19. From these experiments  $k_2$  is found to be  $3.38 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ .

Two series of experiments for the determination of  $k_1$  using different concentrations of diphenylamine are presented in Tables 20 and 21. In calculating  $k_B$ , it was assumed that  $k_5 = k_6$ . From these series, values of  $k_1$  equal to  $3.07 \times 10^7$  and  $2.77 \times 10^7 \text{ sec}^{-1}\text{M}^{-1}$ , respectively, are obtained.

## DISCUSSION

It was pointed out in a previous paper<sup>1</sup> that many of the rate constants for quenching of biacetyl phosphorescence by energy transfer given there had to be regarded as preliminary since they were not corrected for energy transfer in the reverse direction. The only exception was a value for 1-iodonaphthalene. The results obtained in the present work are summarized in Table 22. As expected, the values of the quenching constants given in Table 1 of the previous paper (determined for  $3 \times 10^{-3}$  M biacetyl solutions) agree with the values of  $k_1$  determined in this work only for quenchers whose triplet state energies are much lower than that of biacetyl. One such substance is pyrene. Other substances for which the value of the quenching constant, previously given, may be expected to agree with the corresponding value of  $k_1$  are 3,4-benzpyrene, anthracene, 1,2-benzanthracene, and *trans*-stilbene. The logarithms of the values given for these substances are 9.91, 9.91, 9.84, and 9.60, respectively.

It is evident from Table 22 and from the values given above that the rate constant for transfer of triplet state energy in benzene solution has nearly the same value for all systems in which the triplet state energy of the donor is at least about  $1000 \text{ cm}^{-1}$  higher than that of the acceptor. This value is

Table 22. The logarithm of the rate constant ( $k_1$ ,  $\text{sec}^{-1}\text{M}^{-1}$ ) of triplet state energy transfer from biacetyl to different substances (X) and the logarithm of the rate constant ( $k_2$ ,  $\text{sec}^{-1}\text{M}^{-1}$ ) of triplet state energy transfer from X to biacetyl.  $E_T$  denotes triplet state energy and  $\Delta E_T$  difference of triplet state energy between energy acceptor and energy donor. For biacetyl  $E_T = 19\,700\text{ cm}^{-1}$  is assumed.<sup>1</sup>

X	$E_T$ $\text{cm}^{-1}$	$\log k_1$	$\log k_2$	$\log[k_1 \exp(-\Delta E_T/kT)]$	$\log[k_2 \exp(-\Delta E_T/kT)]$
Pyrene	16 930 <sup>13</sup>	9.88	4.23	3.98	—
1,2-Benzpyrene	18 510 <sup>14</sup>	9.77	7.69	7.23	—
Fluoranthene	18 510 <sup>14</sup>	9.72	7.33	7.17	—
2,2'-Dinaphthyl	19 560 <sup>14</sup>	9.47	9.13	9.17	—
1,5-Dinitronaphthalene	19 900 <sup>15</sup>	9.37	—	—	—
1,8-Dinitronaphthalene	20 000 <sup>15</sup>	9.41	—	—	—
1-Iodonaphthalene	20 500 <sup>6</sup>	7.54 <sup>a</sup>	—	—	—
1-Chloronaphthalene	20 645 <sup>16</sup>	7.46	9.59	—	7.58
1-Bromonaphthalene	20 650 <sup>15</sup>	7.47	9.53	—	7.51
2-Iodonaphthalene	21 040 <sup>15</sup>	6.77	—	—	—
Naphthalene	21 180 <sup>13</sup>	6.42	9.95	—	6.80

<sup>a</sup> From Ref.<sup>1</sup>



approximately equal to that which can be calculated to apply to a diffusion-controlled process. For such a bimolecular reaction in benzene solution at 20°C, a rate constant of  $1.0 \times 10^{10} \text{ sec}^{-1}\text{M}^{-1}$  can be calculated using Debye's approximation.<sup>7</sup>

When the electronic excitation energy of the donor in the triplet state is less than that of the acceptor, it appears valid to set the rate constant for energy transfer equal to  $k_r \exp(-\Delta E_T/kT)$ , where  $k_r$  denotes the rate constant for energy transfer in the opposite direction and  $k$  Boltzmann's constant equal to  $0.695 \text{ cm}^{-1} \text{ degree}^{-1}$ , if energy is expressed in wave numbers ( $\text{cm}^{-1}$ ). The agreement between the values in columns 4 and 5 and between those in columns 3 and 6 in Table 22 must be considered satisfactory if one takes into account the uncertainty of the triplet state energies used. When possible, these were obtained from measurements of  $T \leftarrow S$  absorption in liquid solution at room temperature. However, most of the values are based on phosphorescence spectra of solid solutions at low temperatures.

These results might be explained as follows. Consider an encounter between a triplet excited biacetyl molecule  $B_T$  and a molecule X in its ground state, the electronic excitation energy of  $B_T$  being higher than that of  $X_T$  by the amount  $\Delta E_T$ . Assume that, during such an encounter comprising several collisions between B and X, these molecules come into thermal equilibrium with the surroundings between every two collisions. Assume further that the probability of energy transfer from  $B_T$  to X in a collision is equal to the probability of energy transfer from  $X_T$  to B provided that the vibration energy of the collision couple in the latter case is equal to or greater than  $\Delta E_T$ . Then, according to the Boltzmann distribution law, the ratio between the probabilities that the molecules will leave the "solvent cage" with the excitation energy localized in X and in B will be  $1/\exp(-\Delta E_T/kT)$ . If the diffusion-controlled rate constant of energy transfer is denoted by  $k_D$ , one thus obtains:

$$k_1 = k_D \frac{1}{1 + \exp(-\Delta E_T/kT)} \quad (\text{XVIII})$$

Assuming that the diffusion conditions are the same for the system  $B_T-X$  as for the system  $B-X_T$ , we get in the same way:

$$k_2 = k_D \frac{\exp(-\Delta E_T/kT)}{1 + \exp(-\Delta E_T/kT)} \quad (\text{XIX})$$

It then follows:

$$k_2 = k_1 \exp(-\Delta E_T/kT) \quad (\text{XX})$$

For  $\Delta E_T = 0$ , the relations  $k_1 = k_2 = \frac{1}{2}k_D$  apply.

The relations (XVIII), (XIX), and (XX) are not restricted to the assumption made that  $E_T(B) > E_T(X)$ ; on the contrary, they are quite generally valid. To prove that, let  $\Delta E_T$  be negative, and let  $|\Delta E_T|$  be its absolute value; then we get:

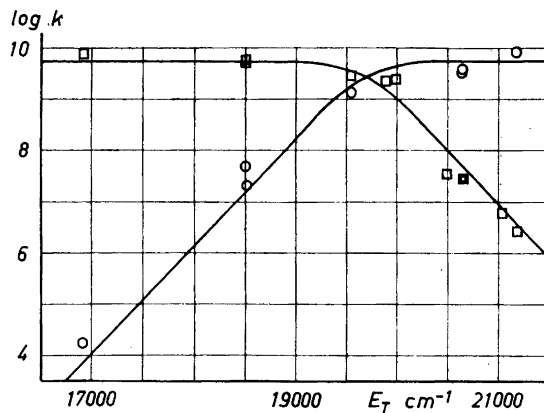


Fig. 1. Log  $k_1$  ( $\square$ ) and log  $k_2$  ( $\circ$ ) vs. triplet state energy ( $E_T$ ) of X.  $k_1$  and  $k_2$  in  $\text{sec}^{-1}\text{M}^{-1}$ . For explanation of the curves drawn, see text.

$$k_1 = k_D \frac{\exp(-|\Delta E_T|/kT)}{1 + \exp(-|\Delta E_T|/kT)} = k_D \frac{1}{\exp(|\Delta E_T|/kT) + 1} =$$

$$= k_D \frac{1}{1 + \exp(-\Delta E_T/kT)}$$

which is identical with (XVIII).

The results are represented in graphic form in Fig. 1, in which log  $k_1$  and log  $k_2$  are plotted against  $E_T$  for X. Results of experiments on systems in which X has a short lifetime in the triplet state in solution, meaning that only  $k_1$  could be determined by the technique employed, are also included. In cases where the rate constant for energy transfer is expected to be diffusion-controlled, logarithmic values ranging from 9.53 to 9.95 have been obtained in this and the previous work.<sup>1</sup> The mean is 9.77. Using this value for log  $k_D$  and assuming that the triplet state energy of biacetyl<sup>1</sup> is 19 700  $\text{cm}^{-1}$ , the functions  $\log [k_D/1 + \exp(-\Delta E_T/kT)]$  and  $\log [k_D \exp(-\Delta E_T/kT)/1 + \exp(-\Delta E_T/kT)]$ , where  $\Delta E_T$  denotes the difference between the triplet state energies of biacetyl and the substance X, have been drawn in the figure. The experimental values agree with these curves as well as can be expected taking into consideration the variations in  $k_D$  for the different systems and the uncertainty of the values used for the triplet state energies. If the triplet state energy of biacetyl is assumed to be 19 600  $\text{cm}^{-1}$ , there is even better agreement.

The systems investigated comprise the following combinations of lowest triplet states of donor and acceptor: donor  $^3(\pi^*n)$ —acceptor  $^3(\pi^*\pi)$ ; donor  $^3(\pi^*\pi)$ —acceptor  $^3(\pi^*n)$ ; donor  $^3(\pi^*n)$ —acceptor  $^3(n^*\pi)$ . The results do not permit to establish a possible influence from the character of the triplet states of donor and acceptor on the energy transfer rate constant.

The results agree only partly with those obtained by Porter and Wilkinson<sup>8</sup> in a study of the transfer of triplet state energy using flash photolysis methods.

These authors, too, found a diffusion-controlled energy transfer when  $E_T$  for the donor is much greater than that for the acceptor. However, in the case of systems where the triplet energy level of the donor lies only slightly above that of the acceptor, the rate constant for energy transfer was found to be appreciably reduced. Thus, the rate constant for energy transfer from phenanthrene to naphthalene ( $\Delta E_T = 300 \text{ cm}^{-1}$ ) in hexane solution was found to be  $2.9 \times 10^6 \text{ sec}^{-1}\text{M}^{-1}$ , whereas from the present results the energy transfer would be expected to be almost diffusion-controlled for this system. In cases where the triplet level of the donor lies below that of the acceptor, no energy transfer could be observed. The reason for the disagreement between Porter and Wilkinson's results and those reported here is not clear. The fact that Porter and Wilkinson obtained a considerably larger rate constant for energy transfer in hexane solution from phenanthrene to 1-iodonaphthalene ( $7 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ ) than for energy transfer from phenanthrene to 1-bromonaphthalene ( $1.5 \times 10^8 \text{ sec}^{-1}\text{M}^{-1}$ ) indicates the possibility that the experimental conditions did not permit the reversed energy transfer to be taken into account in the interpretation of the results. The values of  $\Delta E_T$  for these two systems do not differ appreciably ( $1100 \text{ cm}^{-1}$  and  $950 \text{ cm}^{-1}$ , respectively), whereas the lifetime of 1-iodonaphthalene in the triplet state is much shorter than that of 1-bromonaphthalene, with the thereby concomitant altered conditions for reversed energy transfer to the phenanthrene.\*

As pointed out earlier,<sup>9,1</sup> the 1-halogeno derivatives of naphthalene are well suited for testing whether or not the rate constant for triplet energy transfer depends on the oscillator strength of the  $T \leftarrow S$  transition for the acceptor. Whereas  $E_T$  for these substances is approximately the same, the oscillator strengths for their  $T \leftarrow S$  transition differ markedly from each other. From Ermolaev and Svitashv's<sup>10</sup> measurements of phosphorescence lifetime in solid solution at low temperatures and of the fluorescence and phosphorescence quantum yields for these substances, it can be calculated that the ratios between the oscillator strengths of the  $T \leftarrow S$  transitions of 1-chloronaphthalene, 1-bromonaphthalene, and 1-iodonaphthalene are 1:14:170. The previously reported experiments<sup>1</sup> on quenching of biacetyl phosphorescence by these substances indicated that the value of the rate constant for energy transfer increases with increasing oscillator strength. When these experiments were published, the writers were unaware of the unexpectedly long lifetimes of 1-chloronaphthalene and 1-bromonaphthalene in the triplet state, as later found by Hoffman and Porter.<sup>11</sup> These authors found triplet state lifetimes of about  $10^{-3}$  sec for these compounds in liquid solution at room temperature, whereas a corresponding lifetime for 1-iodonaphthalene of about  $10^{-8}$  sec can be calculated from data in reference.<sup>1</sup> Therefore, in the experiments with 1-chloronaphthalene and biacetyl unsuitably high biacetyl concentrations were chosen, which led to almost complete return of energy from the 1-chloronaphthalene in triplet state and a partial recovery of energy from the small fraction of impurities in the 1-chloronaphthalene, the recovery increasing with increase in biacetyl concentration. Therefore,

\* Note added in proof: This suggestion seems to be confirmed by two papers recently published by Stevens and Walker (*Proc. Chem. Soc.* 1964 26, 109).

the calculated quenching constant ( $4.1 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$ ) corresponds to the constant denoted by  $k_5\beta$  in this paper. Using the same chloronaphthalene sample (2 years old),  $k_6\beta$  has been found to be  $7.0 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$ , indicating that the assumption  $k_5 = k_6$  is approximately correct.

From the present results it seems possible to exclude a dependence between the rate of energy transfer and the oscillator strength of the acceptor T  $\leftarrow$  S transition. Thus, for 1-chloronaphthalene, 1-bromonaphthalene, and 1-iodonaphthalene nearly the same value for the rate constant  $k_1$  has been found.

Ermolaev and Terenin<sup>9</sup> found naphthalene and its 1-halogen derivatives, within the limits of error, to be equally effective as quenchers of benzophenone phosphorescence in solid solution at the temperature of liquid air. Since in this case the triplet state energy of the donor is more than  $3000 \text{ cm}^{-1}$  greater than that of any of the acceptors, the conditions cannot be compared with those prevailing in the experiments discussed here, performed in liquid solution where the triplet state energy of the donor (biacetyl) is lower than that of any of the acceptors.

As has been pointed out earlier,<sup>9,12,1</sup> the experimental results for transfer of triplet state energy in solid as well as in liquid solution are in agreement with the idea of an exchange interaction mechanism. In liquid solution the energy transfer seems, at least in solutions of not too low viscosity, to be a diffusion-controlled process which occurs at every encounter (comprising several collisions) provided that the energy requirements are satisfied.

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