ACTA CHEMICA SCANDINAVICA 27 (1973) 3021–3032

Transfer of Triplet State Energy in Fluid Solution

V. "Nonclassical" Energy Donor and Acceptor Properties of Benzil and Substituted Benzils

KJELL SANDROS

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

Rate constants for triplet energy transfer to and from benzil, *p*-anisil, and *o*-anisil have been determind in cyclohexane solution from measurements of phosphorescence intensity and lifetime. These diketones have different equilibrium conformations in their ground and triplet states. If the energy transfer process is assumed to involve vertical transitions, molecules of this type have less electronic energy available when they act as donors than that which is required when they act as acceptors. Minimum values of the difference between these energies are estimated at 1000, 1000, and 3000 cm^{-1} for benzil, *p*-anisil, and *o*-anisil, respectively.

It is well established that the energy transfer process

$$\text{Donor}_\text{T} + \text{Acceptor}_\text{S0} \rightarrow \text{Donor}_\text{S0} + \text{Acceptor}_\text{T}$$

involves an exchange interaction mechanism. The maximum transfer rate is equal to the rate of encounters between excited donors and acceptors. In an earlier investigation [1] comprising a number of molecule pairs (M, N) in benzene solution, rate constants were determined for energy transfer in both directions, that is

$$\text{M}_\text{T} + \text{N}_\text{S0} \rightleftharpoons \text{M}_\text{S0} + \text{N}_\text{T}$$

It was found that the rate constants (k) obeyed the equation:

$$k = k_\text{D} \exp(-\Delta E_\text{T}/RT)/[1 + \exp(-\Delta E_\text{T}/RT)] \tag{I}$$

where ΔE_T denotes the difference between the electronic excitation energies of the lowest triplet states of acceptor and donor, as obtained from spectroscopic measurements. The equation applies to both positive and negative values of ΔE_T. The value of k_D (6×10^9 M^{-1} sec^{-1}) is not very far from that calculated for a diffusion-controlled process. The results are compatible with the view that for endothermic energy transfer ($\Delta E_\text{T} > 0$) the electronic energy deficit is made up by Boltzmann distributed vibrational energy of the encounter couples.

An energy transfer behaviour such as that outlined above is denoted as "classical" by Herkstroeter and Hammond.[2] They found that *trans*-stilbene behaved classically as an energy acceptor while the rate constants for endothermic energy transfer with *cis*-stilbene and both isomers of α-methylstilbene as acceptors have much higher values than expected from the spectroscopically obtained triplet state electronic energies of these substances. Hammond and Saltiel[3] had earlier coined the term "nonvertical transition" for the excitation process undergone by acceptors of the latter type. Wagner[4a,b] has shown that biphenyl exhibits a similar acceptor behaviour. Common to all these acceptors is that they have significantly different equilibrium geometries in their ground and excited states. In a comprehensive survey[5] of electronic energy transfer in solution, Lamola presents on p. 67 ff. an attractively simple possibility to explain "nonvertical" excitation behaviour. He points out that activation of a suitable twisting vibrational mode in the ground state of the discussed type of molecules would be especially effective because it reduces the energy required for vertical electronic excitation.

To date there seems to have been only one investigation of the donor properties of substances having different ground and excited state conformations. Wagner[4b] has estimated the rate constant for energy transfer from biphenyl to benzophenone. In the present work energy transfer has been studied in systems where benzil and anisils act both as donors and as acceptors. Convincing arguments[6,7] have been presented for the view that in these molecules the carbonyl groups are coplanar both in the lowest singlet and triplet excited states whereas in the ground state the benzoyl units lie at approximately 90° to each other. These molecules may thus be expected to have potential energy profiles similar to those drawn in Fig. 1. Evidently the energy required for excitation of such a molecule (E_{TA}) is higher than the energy available from the excited molecule acting as a donor (E_{TD}). "Hot band" transitions of the type proposed by Lamola may be expected to be operative both when the molecule acts as donor and as acceptor.

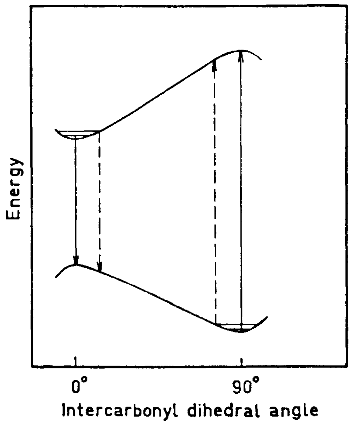

Fig. 1. A potential energy model for the ground and lowest triplet states of benzil and anisils, showing a few vertical transitions. The dashed lines represent "hot band" transitions.

METHODS AND KINETIC ANALYSES

The mixed phosphorescence of a degassed cyclohexane solution of an aromatic diketone (X) and biacetyl (B) upon irradiation by light absorbed mainly by X may be assumed to depend on the following processes:

$$X + h\nu_A \rightarrow X_S' \rightarrow X_T \tag{0}$$

$$X_T + B \rightarrow X + B_T \tag{1}$$

$$B_T + X \rightarrow B + X_T \tag{2}$$

$$X_T \rightarrow X + h\nu_X \tag{3}$$

$$B_T \rightarrow B + h\nu_B \tag{4}$$

$$X_T \rightarrow X \tag{5}$$

$$B_T \rightarrow B \tag{6}$$

The quantum yield of the process (0) is denoted by Φ_T. The rate constants k_5 and k_6 must be regarded as pseudo first order constants, including bimolecular reactions with solvent and impurities. Introducing $k_X = k_3 + k_5$ and $k_B = k_4 + k_6$ the following equations should apply at a constant light absorption rate of I_A:

$$\mathrm{d}[X_T]/\mathrm{d}t = \Phi_T I_A - [X_T](k_X + k_1[B]) + k_2[X][B_T] = 0 \tag{II}$$

$$\mathrm{d}[B_T]/\mathrm{d}t = -[B_T](k_B + k_2[X]) + k_1[B][X_T] = 0 \tag{III}$$

These equations give the following steady-state concentrations:

$$[X_T] = \frac{\Phi_T I_A(k_B + k_2[X])}{k_B k_X + k_X k_2[X] + k_B k_1[B]} \tag{IV}$$

$$[B_T] = \frac{\Phi_T I_A k_1[B]}{k_B k_X + k_X k_2[X] + k_B k_1[B]} \tag{V}$$

For systems where $k_1[B]$ and $k_2[X] \gg k_X$ and k_B, respectively, the eqns. (IV) and (V) may be approximated to:

$$[X_T] = \frac{\Phi_T I_A k_2[X]}{k_X k_2[X] + k_B k_1[B]} \tag{VI}$$

$$[B_T] = \frac{\Phi_T I_A k_1[B]}{k_X k_2[X] + k_B k_1[B]} \tag{VII}$$

The lifetime (τ) of the mixed phosphorescence, when the inequalities given above are valid, may be approximated to:

$$\tau = \frac{k_1[B] + k_2[X]}{k_X k_2[X] + k_B k_1[B]} \tag{VIII}$$

as follows from the general expressions given on p. 2357 in Ref. 1. The phosphorescence intensity contributions from X_T and B_T, as registered by a spectrofluorimeter, are denoted by I_X and I_B, respectively. It follows from eqns. (VI), (VII), and (VIII) that:

$$\tau/I_X = K_1(1 + k_1[B]/k_2[X]) \tag{IX}$$

and

$$\tau/I_B = K_2(1 + k_2[X]/k_1[B]) \tag{X}$$

where $K_1 = (\alpha k_3 \Phi_T I_A)^{-1}$ and $K_2 = (\beta k_4 \Phi_T I_A)^{-1}$, α and β being apparatus constants. Measurements of τ/I_X and of τ/I_B in a series where K_1 and K_2 are kept constant thus both permit calculation of the ratio k_1/k_2. The value of k_2 can be determind from measurements of I_X/I_B in a series where [X]/[B] is kept constant as seen from the following. Eqn. (III) can be written:

$$[X_T]/[B_T] = (k_B + k_2[X])/k_1[B] \tag{XI}$$

Thus:

$$\frac{I_X}{I_B} = \frac{\alpha k_3[X_T]}{\beta k_4[B_T]} = K_3\left(1 + \frac{k_B}{k_2[X]}\right) \tag{XII}$$

where $K_3 = \alpha k_3 k_2[X]/\beta k_4 k_1[B]$.

A plot of I_X/I_B *vs.* $[X]^{-1}$ should give a straight line with a slope to intercept ratio equal to k_B/k_2, and k_B is obtained from the phosphorescence decay in a solution containing biacetyl only.

In the measurements made on the *o*-anisil – biacetyl system, the inequality $k_2[X] \ll k_B$ was found to be valid. This means that eqn. (V) can be approximated to:

$$[B_T] = \frac{\Phi_T I_A k_1[B]}{k_B k_X + k_B k_1[B]} \tag{XIII}$$

It then follows:

$$\tau_B/I_B = K_2(1 + k_X/k_1[B]) \tag{XIV}$$

where $\tau_B = k_B^{-1}$ is the phosphorescence lifetime as measured upon a flash absorbed by the biacetyl.

The ratio k_X/k_1 may thus be determined from a plot of τ_B/I_B *vs.* $[B]^{-1}$, and k_X is obtained from the phosphorescence decay in a solution containing only *o*-anisil.

Some of the energy transfer rate constants have been determined only from phosphorescence lifetime measurements. For the kinetic analyses the reader is referred to appropriate parts of Ref. 1.

EXPERIMENTAL

For the *phosphorescence intensity* measurements a modified Aminco Bowman spectrophotofluorometer was used. The light from a low pressure mercury "pen-ray" lamp (Ultraviolet Products Inc., Cf. USA, Mod SCTI) passed an interference filter (Thin Film Products, Mass. USA, 253.7 nm, bandwidth 20 nm) and a collimating lens. The excitation beam entered the measuring cell, *via* a quartz rod, in line with the emission entrance path to the monochromator. A UV absorbing filter was placed in front of the emission detector in order to exclude excitation light otherwise appearing in the second order spectrum around 507 nm in the first order.

The equipment for degassing the solutions has been described elsewhere.[8] The measuring procedure was as follows. The emission detector sensitivity was adjusted to give a constant recorded value of the fluorescence intensity from an acid solution of 3-aminophthalimide, found to be a suitable reference. The phosphorescence intensity of the degassed cyclohexane solution at 20°C was then measured at the emission maxima of B and X, respectively. The solution was exposed to the exciting light for as short a time as possible to minimize photochemical reactions. The *lifetime* of the mixed phosphorescence was then determined in a flash apparatus described earlier.[9]

From recorded phosphorescence spectra of pure solutions of B and X, respectively, the emission contributions from B and X to the mixed phosphorescence could be separated. The phosphorescence intensities of B and X at their maxima, I_B and I_X, were thus calculated. In series where the concentration of X was kept constant, giving an absorbance of about 2 at 253.7 nm, the values of K_1 and K_2, appearing in eqns. (IX) and (X), were also constant.

Materials. 2,2′-Dimethoxybenzil (*o*-anisil) was prepared by the method of Leonard *et al.*[10] and purified by recrystallisation from ethanol. The purification procedures for other chemicals used have been described earlier.[1,8,11,12]

RESULTS

Absorptive and emittive properties of the diketones. For the molar absorptivities (M^{-1} cm^{-1}) of the diketones at 253.7 nm in cyclohexane solution the following values were obtained: biacetyl 10, benzil 1.7×10^4, *p*-anisil 8×10^3, *o*-anisil 1.7×10^4. In solutions with comparable concentrations of B and X, 253.7 nm light is thus almost exclusively absorbed by X.

The longest phosphorescence lifetimes (μsec) obtained were: biacetyl 700, benzil 280, *p*-anisil 250, *o*-anisil 45. The corresponding lifetimes in benzene solution[11] are: 1000, 70, 60, 15. The triplet excited aromatic diketones thus seem to react with benzene. This is also indicated by changes in emission spectra on excessive irradiation. The phosphorescence lifetime of *o*-anisil is strongly temperature dependent. The lifetime, in heptane solution, increased from 48 μsec to 143 μsec when the temperature was lowered from 20°C to 0°C.

Phosphorescence spectra of biacetyl, benzil, and *p*-anisil in benzene solution have been reported earlier.[11] In the uncorrected phosphorescence spectra of these substances in cyclohexane solution obtained in this work the emission maxima appeared at: biacetyl 523 nm, benzil 564 nm, *p*-anisil 550 nm. The phosphorescence spectrum of *o*-anisil showed a broad maximum around 560 nm. Since its phosphorescence yield is low, no meaningful values of I_X could be calculated from the mixed phosphorescence of *o*-anisil and biacetyl and only a minor correction had to be applied to the recorded intensity at 523 nm in calculating I_B.

Intensity and lifetime measurements of mixed phosphorescence. The results of measurements on solutions of *biacetyl* and *benzil* are given in full detail in Table 1 in order to illustrate the calculation procedure. The intensity measurements on the first two solutions are used in calculating I_B and I_X from measured values of I_{523} and I_{564} from the following solutions. The general trend of the τ values is that expected from eqn. (VIII). In principle, of course, it would be possible to determine the value of k_1/k_2 by means of eqn. (VIII). This is a poor method, however, for the biacetyl-benzil system where the values of k_B and k_X are not very different and are small enough to be sensitive to impurities.

Table 1. Intensities and lifetimes of the mixed phosphorescence from cyclohexane solutions of biacetyl (B) and benzil (X). For further explanations see text.

[B] M $\times 10^4$	[X] M $\times 10^4$	I_{523}	I_{564}	I_B	I_X	τ sec $\times 10^6$	τ/I_B	τ/I_X
29.0	–	56.5	14.5	–	–	422	–	–
–	1.28	8.5	78.5	–	78.5	277	–	3.53
1.39	1.28	33.5	77.0	29.9	70.2	287	11.08	4.09
2.66	1.28	65.0	91.0	56.8	76.3	362	6.37	4.74
3.50	1.28	70.0	83.5	62.7	67.3	343	5.47	5.10
6.98	1.28	108.0	79.0	102.3	52.6	362	3.54	6.88
11.5	1.28	148.0	82.0	143.1	45.2	403	2.82	8.92
15.3	1.28	158.0	76.0	154.1	36.4	414	2.69	11.37
19.7	1.28	163.0	70.0	159.9	29.0	391	2.45	13.48

Plots of τ/I_B *vs.* $[B]^{-1}$ and of τ/I_X *vs.* [B] give straight lines corresponding to:

$$\tau/I_B = 1.75 + 1.28\times 10^{-3}\ [B]^{-1} \text{ and}$$

$$\tau/I_X = 3.37 + 5.12\times 10^{3}\ [B]$$

Identification with eqns. (X) and (IX) gives $k_1/k_2 = 0.175$ and 0.194, respectively. Determinations of I_X/I_B for a series of solutions with a constant value of $[X]/[B] = 0.27$ and with [X] varying from 2×10^{-5} M to 2×10^{-6} M were made to determine the value of k_2 by means of eqn. (XII). The following relationship was obtained:

$$I_X/I_B = 0.844 + 9.04\times 10^{-7}\ [X]^{-1}$$

The ratio k_B/k_2 may thus be calculated as 1.07×10^{-6} M. With $k_B = 1590$ sec^{-1}, obtained from the phosphorescence lifetime of a solution containing only biacetyl, this gives $k_2 = 1.49\times 10^{9}$ M^{-1} sec^{-1}. From the mean value of $k_1/k_2 = 0.184$ it follows that $k_1 = 2.74\times 10^{8}$ M^{-1} sec^{-1}. It should be noted that the inequalities $k_1[B]$ and $k_2[X] \gg k_X$ and k_B were well fulfilled for the solutions presented in Table 1, justifying the application of eqns. (IX) and (X).

The results of measurements on *biacetyl* – p-*anisil* solutions may be summarized as follows. Solutions with $[X] = 2.65\times 10^{-4}$ M and varying biacetyl concentrations gave:

$$\tau/I_B = 1.71 + 3.84\times 10^{-4}[B]^{-1} \text{ and}$$

$$\tau/I_X = 1.67 + 7.37\times 10^{3}[B]$$

These equations give $k_1/k_2 = 1.18$ and 1.17, respectively.

Measurements on solutions with a constant value of $[X]/[B] = 1.06$ gave:

$$I_X/I_B = 0.90 + 2.17\times 10^{-6}[X]^{-1}$$

This relationship, the value obtained for $k_B = 1650$ sec^{-1}, and the mean value of $k_1/k_2 = 1.175$ give $k_2 = 6.8\times 10^{8}$ M^{-1} sec^{-1} and $k_1 = 8.0\times 10^{8}$ M^{-1} sec^{-1}.

As mentioned earlier, only values of I_B could be accurately determined from intensity measurements on *biacetyl* – o-*anisil* solutions. Solutions with $[X] = 1.20\times 10^{-4}$ M gave:

$$\tau_{\mathrm{B}}/I_{\mathrm{B}} = 1.65 + 4.04 \times 10^{-4}[\mathrm{B}]^{-1}$$

Almost constant values of τ_{B}, equal to that in a pure biacetyl solution, were obtained, as expected if $k_2[\mathrm{X}] \ll k_{\mathrm{B}}$. Identification of the given relationship with eqn. (XIV) gives $k_{\mathrm{X}}/k_1 = 2.45 \times 10^{-4}$ M. A value of $k_{\mathrm{X}} = 2.22 \times 10^4$ sec^{-1} was obtained from the phosphorescence lifetime in a pure solution of *o*-anisil and thus $k_1 = 9.1 \times 10^7$ M^{-1} sec^{-1}.

The low solubility of *o*-anisil in cyclohexane prevented a determination of k_2 in this solvent. Some measurements on benzene solutions, presented in Table 2, permit an estimate of the value of k_2. The results may be accounted for by assuming that the *o*-anisil sample contains a mol fraction γ of an impurity that quenches biacetyl triplets with a rate constant of k_q. If $k_{\mathrm{X}} + k_1[\mathrm{B}] \gg k_{\mathrm{B}} + k_2[\mathrm{X}]$ the biacetyl phosphorescence decay constant may be approximated to:

Table 2. Phosphorescence decay rate constants (k) in benzene solutions of biacetyl (B) and/or *o*-anisil (X).

Run No.	[B] M $\times 10^5$	[X] M $\times 10^3$	k sec^{-1} $\times 10^{-3}$
1	5.1	–	1.11
2	5.1	1.27	2.06
3	5.1	2.57	3.05
4	630	–	1.12
5	630	3.79	2.08
6	630	6.05	2.67
7	–	5.00	68

$$k = k_{\mathrm{B}^0} + \left((k_q\gamma + \frac{k_{\mathrm{X}}}{k_{\mathrm{X}} + k_1[\mathrm{B}]}k_2\right)[\mathrm{X}] \qquad \text{(XV)}$$

where k_{B^0} denotes the decay constant in the absence of *o*-anisil. Application of eqn. (XV) to runs $1-3$ and $4-6$, respectively, gives two simultaneous equations from which k_2 and $k_q\gamma$ can be evaluated. Insertion of the value of $k_1 = 9.1 \times 10^9$ M^{-1} sec^{-1}, valid in cyclohexane solution, and of $k_{\mathrm{X}} = 6.8 \times 10^4$ sec^{-1} from run 7 gives $k_2 = 5.9 \times 10^5$ M^{-1} sec^{-1} and $k_q\gamma = 1.9 \times 10^5$ M^{-1} sec^{-1}. If the impurity quenches *o*-anisil triplets with the same rate constant as biacetyl triplets, the neglection of the depencence of k_{X} on [X] (and thus on the impurity concentration) is justified by the much higher value of k_{X} than of k_{B0}. It should also be noted that, with the biacetyl concentrations chosen, the calculated value of k_2 is not strongly dependent on the assumption of equal values of k_1 in cyclohexane and benzene solution. Thus values of k_2 equal to 6.0×10^5 M^{-1} sec^{-1} and 6.4×10^5 M^{-1} sec^{-1} are obtained when the applied value of k_1 is doubled and halved, respectively.

Relative triplet quantum yields of the aromatic diketones can be calculated from the values of K_2 obtained. The relative yields of benzil, *p*-anisil, and *o*-anisil are 1:1.02:1.06. Lamola and Hammond[13] have determined the triplet yield of benzil in benzene solution as 0.92. Applying this value triplet yields of 0.94 and 0.98 are obtained for *p*-anisil and *o*-anisil, respectively.

Energy transfer rate constants from phosphorescence decay measurements. For systems comprising a diketone and an aromatic noncarbonyl compound energy transfer rate constants were determined from phosphorescence decay measurements only. In Table 3, the results have been summarized together with the rate constants obtained for the systems presented in the preceding section.

Table 3. Rate constants for energy transfer from M to N ($k_{\mathrm{M}\rightarrow\mathrm{N}}$) and from N to M ($k_{\mathrm{N}\rightarrow\mathrm{M}}$). The triplet energy of N is denoted by E_{T}.

M	N	E_{T} cm^{-1}	$k_{\mathrm{M}\rightarrow\mathrm{N}}$ M^{-1} sec^{-1}	$k_{\mathrm{N}\rightarrow\mathrm{M}}$ M^{-1}sec^{-1}
Bensil	Biacetyl	19 600 [1]	2.7×10^8	1.5×10^9
p-Anisil	Biacetyl		8.0×10^8	6.8×10^8
o-Anisil	Biacetyl		9.1×10^7	5.9×10^{5}[a]
Biacetyl	Pyrene	16 930 [14]	8.7×10^9	
Biacetyl	1-Chloronaphthalene	20 645 [15]	4.0×10^7	4.7×10^9
Benzil	1-Chloronaphthalene		3.0×10^6	2.8×10^9
p-Anisil	1-Chloronaphthalene		1.4×10^7	2.2×10^9
o-Anisil	1-Chloronaphthalene			3.5×10^7
o-Anisil	Naphthalene	21 180 [14]		9.1×10^7
o-Anisil	Phenanthrene	21 600 [14]		2.9×10^8
o-Anisil	Triphenylene	23 250 [16]		3.0×10^9
o-Anisil	2,2′-Dinaphthyl	19 560 [16]	9.0×10^7	
o-Anisil	1,2-Benzpyrene	18 510 [16]	2.3×10^9	

[a] In benzene solution.

The experimental conditions and calculation precedures for systems involving 1-chloronaphthalene were similar to those presented for the system biacetyl – 1-chloronaphthalene in benzene solution on p. 2368 in Ref. 1.

In the experiments with *o*-anisil and naphthalene, phenanthrene, or triphenylene, a low flash intensity was used in order to suppress the ratio of delayed fluorescence to phosphorescence from the latter compounds. By adding diphenylamine, which reacts much faster with *o*-anisil triplets than with the noncarbonyl triplets (*cf.* p. 2362 of Ref. 1), the *o*-anisil phosphorescence was quenched. The observed emission was thus almost pure phosphorescence from the noncarbonyl compounds.

The rate constants for energy transfer from *o*-anisil to 2,2′-dinaphthyl and to 1,2-benzpyrene were calculated from "first measurable phosphorescence lifetimes" (*cf.* p. 2361 of Ref. 1).

DISCUSSION

The rate constant for energy transfer from biacetyl to pyrene, 8.7×10^9 M^{-1} sec^{-1}; may be taken as a representative value for highly exothermic energy transfer in cyclohexane solution at 20°C. This value is somewhat higher than the corresponding value, 7.6×10^9, obtained in benzene solution.[1] Similarly, the rate constant values for the system biacetyl – 1-chloronaphthalene, 4.0×10^7 and 4.7×10^9, are higher than those measured in benzene solution,[1] 2.9×10^7 and 3.9×10^9. On an average, the ratio of the rate constants in cyclohexane and benzene solutions is equal to 1.2 in spite of the higher viscosity of cyclohexane compared to that of benzene, 0.95 and 0.65 cP at 20°C. This is in accordance with the rate constant ratio, 1.3, given by Wagner and Kochewar [17] in their important paper on "How Efficient is Diffusion-Controlled Triplet Energy Transfer?"

For systems behaving "classically", it is expected [see eqn. (I)] that the rate constant for energy transfer in one of the directions should exceed or be equal to $k_D/2$, which is the value corresponding to $\Delta E_T = 0$. In cyclohexane solution this means a value $\geqq 4 \times 10^9$ M^{-1} sec^{-1}. None of the rate constants for the first three systems presented in Table 3 reach this value, the system *o*-anisil – biacetyl showing the lowest values. This is what may be expected for systems where at least one of the reactants has different ground and excited state geometries. The relative positions of the triplet energy levels of the diketones, as sketched in Fig. 2, should account for the results. No absolute values of the levels for the aromatic diketones can be given since eqn. (I), valid in classical systems, is not applicable. The rate constants obtained for systems involving 1-chloronaphthalene further support Fig. 2.

The logarithms of the rate constant values for systems involving *o*-anisil, the compound showing the most striking nonclassical behaviour, are plotted in Fig. 3 *vs.* the triplet energy of the other solute of the system. The curve drawn through the points for *o*-anisil acting as an acceptor bears a resemblance to the curve drawn in Fig. 1 of Ref. 2 from a more extensive material for *cis*-stilbene acting as an acceptor. A dashed curve has been drawn from the meagre material available for *o*-anisil acting as a donor. The general features

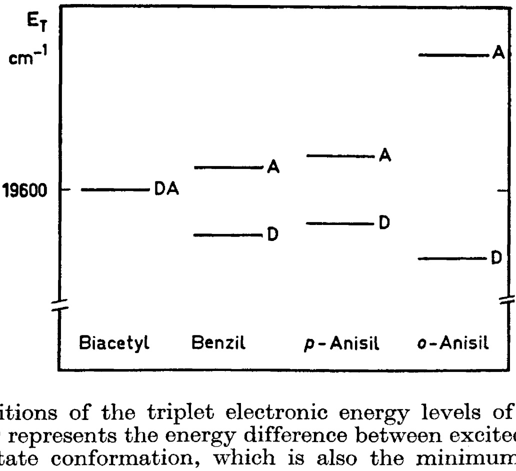

Fig. 2. Relative positions of the triplet electronic energy levels of biacetyl, benzil, *p*-anisil, and *o*-anisil. *D* represents the energy difference between excited and ground states, both with excited state conformation, which is also the minimum value of available electronic energy from the molecule as a donor. *A* represents the energy difference between excited and ground states, both with ground state conformation, or the maximum electronic energy required by the molecule as an acceptor.

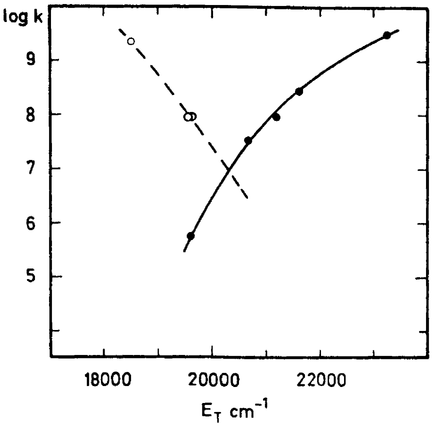

Fig. 3. Log $k_{M \rightarrow N}$ (○) and log $k_{N \rightarrow M}$ (●) *vs.* E_T, the triplet energy of N. M denotes *o*-anisil.

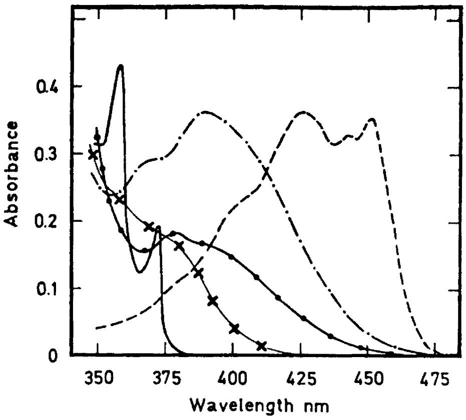

Fig. 4. Absorption spectra of 1.7×10^{-2} M benzaldehyde (—), 1.9×10^{-2} M biacetyl (- - -), 5.8×10^{-3} M benzil (—.—), 1.6×10^{-3} M *p*-anisil (●), and 1.8×10^{-3} M *o*-anisil (×) in cyclohexane solution.

of Fig. 3 are quite different from those of Fig. 1 in Ref. 1. The latter figure represents results from systems involving molecules assumed to have equal values of available energy as donor and required energy as acceptor. This evidently does not apply to *o*-anisil. As pointed out above, the results do not permit a determination of the value of $E_{TA} - E_{TD}$. The reason is that the rate constants are certainly higher than those calculated by putting ΔE_T in eqn. (I) equal to $E_{TA} - E_T$ and to $E_T - E_{TD}$, respectively. However, a minimum value of $E_{TA} - E_{TD}$ may be estimated. The coordinates of the intersection of the curves in Fig. 3 are $E_T = 20300$ cm^{-1} and log $k = 7$. This implies that the rate constant values for energy transfer from *o*-anisil to a molecule with $E_T = 20\,300$ cm^{-1} and for energy transfer from such a molecule to *o*-anisil are both about 10^{-3} of the rate constant value for exothermic energy transfer. The activation energy should thus be at least 1500 cm^{-1} for energy transfer in both directions and a minimum value of $E_{TA} - E_{TD} = 3000$ cm^{-1} is obtained. The true value of $E_{TA} - E_{TD}$ is probably much higher. The full drawn curve shows decreasing slope with increasing E_T indicating appreciable effects of favourable activation modes, as discussed in the introduction.

In this connexion, the *o*-anisil emisson studies performed by Almgren[18] are of great interest. In fluid solution at room temperature (solvent CIP: 95 % isopentane, 5 % cyclohexane) he found a phosphorescence maximum at 555 nm and a weak shoulder at 500 nm. The latter emission should probably be regarded as E-type delayed fluorescence.[19] In CIP glass at 80°K, a broad emission spectrum with a maximum at 485 nm was obtained. This was interpreted as phosphorescence from excited molecules for which the conformational relaxation was more or less inhibited by the glassy matrix. The energy difference between the emisson maxima in the two media, 2600 cm^{-1}, should also represent a minimum value of $E_{TA}-E_{TD}$ since total inhibition of conformational changes is not expected. The broad emission spectrum in the glassy matrix may indicate varying degrees of relaxation for the emitting molecules.

For benzil and *p*-anisil the energy transfer results indicate lower values of $E_{TA}-E_{TD}$. Calculations similar to those for *o*-anisil performed on the results from benzil – biacetyl and *p*-anisil – biacetyl indicate a minimum value of $E_{TA}-E_{TD}$ of about 1000 cm^{-1} for both benzil and *p*-anisil. Morantz and Wright [7] have compared the phosphorescence of benzaldehyde and of benzil. The energy difference between the shortest wavelength phosphorescence peaks is about 18 kcal or 6400 cm^{-1}. Ignoring interaction between the carbonyl groups and adjoining aromatic groups, Morantz and Wright adopt this energy difference as a measure of the energy difference denoted by $E_{TA}-E_{TD}$ in this work. Such a high value of $E_{TA}-E_{TD}$ for benzil does not seem very probable even though the value 1000 cm^{-1} is certainly much too low.

Absorption spectra of benzaldehyde, biacetyl, benzil, *p*-anisil, and *o*-anisil are given in Fig. 4. The resemblance between the absorption spectra of benzaldehyde and benzil found by Morantz and Wright [7] does not seem very striking. While the long wavelength tail of the benzaldehyde spectrum falls steeply, as does also that of biacetyl, all the aromatic diketones show absorption spectra with long tails. The latter behaviour is to be expected for molecules with different ground and excited state conformations.

It may be noted that Richtol and Belorit [20] have studied the mixed phosphorescence from solutions of benzil and biacetyl excited by 436 nm light. Their interpretation of the results is quite different from that given here. They assume that the energy transfer from benzil to biacetyl is negligible. If this were true no biacetyl phosphorescence should have been observed in the present measurements where the exciting light of wavelength 254 nm was almost exclusively absorbed by benzil. It is then not surprising that the rate constant value obtained for energy transfer from biacetyl to benzil, 5.6×10^5 M^{-1} sec^{-1}, is quite different from the value, 1.5×10^9 M^{-1} sec^{-1}, calculated in the present work.

The reaction scheme proposed by Richtol and Belorit includes the following process:

$$\text{biacetyl}_T + \text{benzil} \rightarrow \text{biacetyl} + \text{benzil}$$

The rate constant for this process is given a value of 7.4×10^5 M^{-1} sec^{-1}. The validity of triplet quantum yield determinations based on measurements of sensitized isomerization reactions,[13] delayed fluorescence,[21] or phosphorescence [8] critically depends on whether the rate of such an energy degradation process is small compared to that of the energy transfer process. The determinations are always performed in systems where the sensitization is an exothermic energy transfer process with close to diffusion-controlled rate. Closely agreeing values of triplet yields for a number of sensitizers have been obtained by the three methods mentioned in which quite different energy acceptors have been involved. This indicates that the energy degradation process cannot compete significantly with the energy transfer process in the systems investigated.

As mentioned in the introduction both the donor and acceptor properties of biphenyl, a substance with different ground and excited state conformations, have been investigated. Making some reasonable assumptions, Wagner [4b] has calculated the rate constants for energy transfer in benzene solution from benzophenone to biphenyl and from biphenyl to benzophenone as 2.5×10^8 and 3.5×10^7 M^{-1} sec^{-1}, respectively. The E_T value of benzophenone is chosen as 69.5 kcal while the lowest energy T←S absorption band and highest energy phosphorescence band of biphenyl correspond to 75.5 and 65.5 kcal, respectively.[4b] Wagner postulates [4a,b] that energy transfer both to and from biphenyl involves a nonvertical transition, the energy difference between the upper and lower states being close to 68.5 kcal. The fact that the energy transfer rate constants both have much lower values than that for a diffusion-controlled process should be a consequence of the greater steric requirements of a process involving nonvertical transitions compared to a process with only vertical ones. Lamola [5] points out that the details of the transfer process are not known and gives preference neither to the model used by Wagner nor to that used in the present work.

Acknowledgements. I am indebted to Professor Hans L. J. Bäckström for comments and suggestions on the manuscript. My thanks are also due to Dr. Mats Almgren for many helpful discussions, and to Mrs. I.-L. Samuelsson for experimental assistance.

REFERENCES

1. Sandros, K. *Acta Chem. Scand.* **18** (1964) 2355.
2. Herkstroeter, W. G. and Hammond, G. S. *J. Am. Chem. Soc.* **88** (1966) 4769.
3. Hammond, G. S. and Saltiel, J. *J. Am. Chem. Soc.* **85** (1963) 2516.
4. a. Wagner, P. J. *J. Am. Chem. Soc.* **89** (1967) 2820; b. Wagner, P. J. *Mol. Photochemistry* **1** (1969) 71.
5. Lamola, A. A. *Technique of Org. Chemistry*, Interscience, New York 1969, Vol. XIV, p. 17.
6. Evans, T. R. and Leermakers, P. A. *J. Am. Chem. Soc.* **89** (1967) 4380.
7. Morantz, D. J. and Wright, A. J. C. *J. Chem. Phys.* **54** (1971) 692.
8. Sandros, K. *Acta Chem. Scand.* **53** (1969) 2815.
9. Bäckström, H. L. J. and Sandros, K. *Acta Chem. Scand.* **12** (1958) 823.
10. Leonard, N. J., Rapala, R. T., Herzog. H. L. and Blout, E. R. *J. Am. Chem. Soc.* **71** (1949) 2997.
11. Bäckström, H. L. J. and Sandros, K. *Acta Chem. Scand.* **14** (1960) 48.
12. Sandros, K. and Bäckström, H. L. J. *Acta Chem. Scand.* **16** (1962) 958.
13. Lamola, A. A. and Hammond, G. S. *J. Chem. Phys.* **43** (1965) 2129.
14. Evans, D. F. *J. Chem. Soc.* **1957** 1351.
15. Ferguson, J., Iredale, T. and Taylor, J. A. *J. Chem. Soc.* **1954** 3160.
16. Clar, E. and Zander, M. *Chem. Ber.* **89** (1956) 749.
17. Wagner, P. J. and Kochewar, I. *J. Am. Chem. Soc.* **90** (1968) 2232.
18. Almgren, M. *Photochem. and Photobiol.* **9** (1969) 1.
19. Parker, C. A. and Joyce, T. A. *Chem. Commun.* **1968** 1421.
20. Richtol, H. H. and Belorit, A. *J. Chem. Phys.* **45** (1966) 35.
21. Parker, C. A. and Joyce, T. A. *Trans. Faraday Soc.* **62** (1966) 2785.

Received April 7, 1973.