

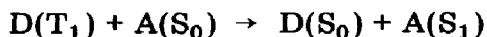
Letter to the Editor

Comments on "The energy transfer from triplet state acetone to 9-bromoanthracene and 9,10-dichloroanthracene: an investigation under high pressure"

The energy transfer from triplet state acetone to 9-bromoanthracene (BA), to 9,10-dichloroanthracene (DCA) and to 9,10-dibromoanthracene (DBA) has recently been investigated [1, 2]. It was concluded that the triplet-triplet (TT) process



was substantially faster than the direct triplet-singlet (TS) process



It was also argued that the $A(S_1)$ level was populated indirectly by inter-system crossing from the $A(T_2)$ state of the acceptor. The yields ϕ_{ISC}^{TS} for this process for DBA, BA and DCA were found to be 0.4, 0.21 and 0.025 respectively.

The conclusion regarding the ineffectiveness of the direct TS process was based on the observation that the total rate of production of the S_1 state of the acceptor in solution was a diffusion-controlled reaction and on the assumption that the rate of the TS energy transfer was the rate k_{ET}^{TS} for long range interaction (*i.e.* independent of viscosity), as observed in polymer systems [3]. The validity of this crucial assumption was not examined or even considered in the original papers.

According to the theory of electronic energy transfer, the total interaction β between a donor and an acceptor can be expressed as a sum of "coulomb" and "exchange" terms [4], *i.e.*

$$\beta = \beta(\text{coulomb}) + \beta(\text{exchange})$$

The first term of the $\beta(\text{coulomb})$ expression is the familiar dipole-dipole interaction term which dominates the interaction at large separation distances. The $\beta(\text{exchange})$ term involves the electrostatic interaction between two charged clouds. This term will contribute significantly to the total interaction if the following spin integral does not vanish:

$$\int \Sigma_{D^{\uparrow}}(1) \Sigma_A(2) \Sigma_D(2) \Sigma_{A^{\uparrow}}(1) d\tau \quad (1)$$

where Σ is a spin wavefunction, and (1) and (2) refer to the two interacting electrons. The integral in eqn. (1) will vanish unless $\Sigma_{D^*} = \Sigma_{A^*}$ and $\Sigma_A = \Sigma_D$, *i.e.* $M(D^*) = M(A^*)$ and $M(D) = M(A)$.

For a TS energy transfer process involving "pure" singlet and triplet spin wavefunctions, $\beta(\text{exchange}) = 0$ because the spin integral is zero, *i.e.* the process is spin forbidden. This spin forbidden rule applies to most organic molecules not containing heavy atoms. However, the triplet and singlet wavefunctions will be perturbed and mixed together in the presence of heavy atoms. Then a "singlet" wavefunction will contain some triplet character and vice versa. Of course, the degree of mixing of the triplet and singlet manifolds depends on the amount of spin-orbit coupling introduced by the heavy atoms. There is plenty of evidence in the literature which shows that the singlet and triplet functions of DBA are indeed thoroughly mixed, *e.g.* the $S_1 \rightarrow T_2$ transition is of the order 10^{13} s^{-1} without the energy factor [5, 6] and the S_1 state of DBA is quenched by naphthalene and other aromatic hydrocarbons to give the triplet state of the quenchers directly [7]. Because the wavefunction of the acceptor (DBA, BA and DCA) is not "pure" with respect to the spin quantum number, the spin integral in the $\beta(\text{exchange})$ term will not vanish even for a TS energy transfer. Thus, it is incorrect to label the TS process in DBA and BA as a "spin forbidden" process.

With $\beta(\text{exchange}) \neq 0$ for DBA, BA and DCA, it is incorrect to assume that the total direct TS energy transfer involves only the long range rate constant $k_{\text{ET}}^{\text{TS}}$ in the $\beta(\text{coulomb})$ term. The total rate of deactivation of triplet acetone by the acceptor has been found to be diffusion controlled and it is more than an order of magnitude larger than $k_{\text{ET}}^{\text{TS}}$ in the polymer system. Therefore the indirect chemiluminescence results should be analyzed using the following scheme:



where $(\text{D}\dots\text{A})^*$ is an "encounter complex" whose rate of formation k_1 is controlled by diffusion. The yield of direct energy transfer $\phi_{\text{ET}}^{\text{TS}}$ from T_1 acetone to S_1 of the acceptor is given by

$$\phi_{\text{ET}}^{\text{TS}} = \frac{\alpha k_1 [\text{A}]}{k_1 [\text{A}] + k_{\text{dea}}^{\text{TA}}}$$

where $\alpha = k_2 / (k_2 + k_3 + k_4)$ and $k_{\text{dea}}^{\text{TA}}$ is the rate of deactivation of triplet acetone by other channels. If α is pressure independent (which it most probably is), this expression for $\phi_{\text{ET}}^{\text{TS}}$ is the same as the expression

$$\phi_{\text{ET}}^{\text{TTS}} = \frac{0.5k_1[A]\phi_{\text{ISC}}^{\text{TS}}}{k_1[A] + k_{\text{dea}}^{\text{TA}}}$$

given in ref. 2 which was used to explain all the experimental observations adequately. Furthermore, it is interesting to note that, if $\alpha = 0.5\phi_{\text{ISC}}^{\text{TS}}$, then $\alpha = 0.2, 0.11$ and 0.013 for DBA, BA and DCA. This is exactly the order that is expected for α from the heavy atom content of the acceptor anthracene. Hence, it is obvious that the experimental data can be explained equally well by the mechanism of direct TS energy transfer. Thus, the investigation of the sensitized emission of anthracenes by triplet acetone under high pressure is unable to provide the answer for the origin of the S_1 state of the acceptor anthracenes and the conclusion reached by that kind of investigation [1, 2] should be examined more carefully.

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