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**Energy Transfer Mechanisms in Polymer Systems.
 II. Design and Demonstration of an Enhancement of
 the Efficiency of a Solid Phase Chemiluminescent
 System Based upon Spin Forbidden Steps and a
 Tandem Energy Transfer**

Sir:

In a previous report,¹ we have provided evidence that, in a polystyrene matrix, two different long range mechanisms are involved in the indirect chemiluminescence of anthracenes² by tetramethyl-1,2-dioxetane (1): (a) singlet acetone (¹A) to anthracene acceptor singlet (*e.g.*, 9,10-diphenylanthracene, DPA) and (b) triplet acetone (³A) to anthracene acceptor singlet (*e.g.*, 9,10-dibromoanthracene, DBA). We also demonstrated that in a polystyrene polymer matrix, diffusional triplet-triplet exchange energy transfer (which is required to occur by a collisional exchange mechanism) is strongly inhibited.³

We report here the construction of a chemiluminescence polymeric system which is designed to be much more efficient than its fluid solution counterpart and whose mechanism of enhanced efficiency is based on the different distance dependences of long range singlet-singlet (and triplet-singlet) energy transfer⁴ relative to

short range triplet-triplet energy transfer.⁵

The efficiency of indirect chemiluminescence (ϕ_{CL}) of our system is given by the general expression⁶

$$\phi_{CL} = \frac{I_{CL}}{R} = \phi_* \phi_{ET} \phi_F \quad (1)$$

in which I_{CL} is the number of moles of activated chemiluminescent photons (anthracene fluorescence) emitted per second, R is the rate of disappearance of 1 by all paths, ϕ_* is the probability that a molecule of 1 will decompose to produce an excited acetone molecule, ϕ_{ET} is the probability that the latter will transfer electronic excitation to an anthracene singlet, and ϕ_F is the fluorescence emission efficiency of the anthracene. In order to have an efficient system based on activated chemi-

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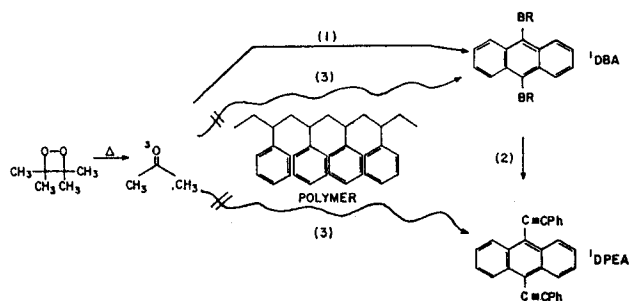


Figure 1. Amplification of chemiluminescence by double energy transfer in a polymer system. The "native" chemiluminescence of **1** in the polymer is weak fluorescence and phosphorescence. Chemiluminescence can be amplified by energy transfer to DBA ($\phi_F \sim 0.1$)⁹ but the transfer step is inefficient if diffusional triplet-triplet energy occurs (path 3). Transfer from 3A to the efficient emitter DPEA ($\phi_F \sim 1$)¹¹ is inefficient by all mechanisms. The long range energy transfer from 3A to 1DBA in a polymer (path 1) removes the inefficiency of path 3 and the tandem energy transfer from 1DBA to 1DPEA (path 2) occurs resulting in a potential increase in chemiluminescence efficiency above and beyond that of **1** alone or the **1**-DBA and **1**-DPEA systems.

luminescence, all three probabilities, ϕ_* , ϕ_{ET} , and ϕ_F must be high. It has been shown⁷ that **1** (in analogy to other dioxetanes)^{6a,8} thermolyzes into 3A with a high efficiency ($\phi_* \sim 1$). Thus for high overall efficiency, $\phi_{ET}\phi_F$ must now correspond to an efficient triplet-singlet (TS) energy transfer followed by efficient fluorescence. Such a situation is extremely difficult to obtain in fluid solution because (a) all triplet-singlet acceptors also will be triplet-triplet acceptors (thereby causing a competitive nonluminescent path for deactivation of 3A and a low value of ϕ_{ET}) and (b) the most effective triplet-singlet acceptors (e.g., DBA) have inherently low fluorescence yields ($\phi_F < 0.1$).⁹

From our previous results,¹ it is clear that *the inefficiency in ϕ_{ET} can be circumvented by employing DBA as a triplet-singlet acceptor in a polymer matrix, since the competitive triplet-triplet energy transfer from 3A to DBA is severely inhibited under these conditions.* Furthermore, if 1DBA can be made to efficiently transfer to an acceptor which possesses a high ϕ_F , the product $\phi_{ET}\phi_F$ may approach a much higher value than that obtained in fluid solution (since the second acceptor cannot compete *via* triplet-triplet energy transfer). This strategy would thus allow for a highly efficient chemiluminescent system to be based on *two* spin forbidden steps (Figure 1)!

Experimentally, we find that the limiting intensity of DBA *vs.* DPA chemiluminescence (which equals $\phi_{ET}^{TS}\phi_{ET}^{SS}\phi_F^{DPA}$)^{2,10} is two to three times as great in a polymer matrix than in fluid solution. This observation is consistent with our expectations that the inhibition of diffusion in the polymer would lead to an enhanced value of ϕ_{ET}^{TS} for DBA, since we do not expect the fluorescence yield ratio or the singlet-singlet

transfer efficiency to DPA to change upon proceeding from benzene solution to a polymer system. A more dramatic effect was observed when 9,10-dichloroanthracene (DCA) was employed as acceptor. In fluid solution, ϕ_{ET}^{TS} for this acceptor is much lower than for DBA. In the polymer the chemiluminescence limiting emission from DCA excited by decomposition of **1** is nearly ten times greater than it is for benzene solutions!

Even a more impressive and convincing experimental confirmation of the general idea proposed on Figure 1 is possible. The tertiary system, **1**, DBA, and DPEA (9,10-diphenylethylanthracene),¹¹ in polystyrene was employed. The strategy of this chemiluminescence system is that **1** will yield 3A with good efficiency, that the latter will transfer *via* a long range efficient mechanism to 1DBA , and finally that 1DBA will transfer to the strongly fluorescent DPEA *via* a long range singlet-singlet energy transfer.^{3,4} Note again that the polymer system inhibits the nonlight producing triplet-triplet transfers to *both* DBA and DPEA.

Experimentally, a system of $4 \times 10^{-2} M$ **1**, $2 \times 10^{-3} M$ DBA, and varying concentrations of DPEA was studied at 49°. At $2 \times 10^{-3} M$ DPEA, the chemiluminescence (essentially pure DPEA fluorescence) is twice that of DBA as acceptor alone and more than *ten times* that of DPEA as acceptor alone. Extrapolation to a limiting concentration of DPEA (with appropriate substitution of DPEA chemiluminescence on the absence of DBA) allows determination of a value of DPEA chemiluminescence which is *10-15 times* the value of DBA alone. Indeed, the ratio of fluorescence yields of DPEA to DBA is ~ 14 (at 49°), so that the product $\phi_{ET}^{TS}(^3A \rightarrow ^1DBA) \times \phi_{ET}^{SS}(^1DBA \rightarrow ^1DPEA) \times \phi_F^{DPEA}$ must be approaching a value of unity in the limit!

In conclusion, we provide evidence that the efficiency of indirect chemiluminescence on polymer systems can be made to greatly exceed that for fluid solutions and furthermore that, in principle, a highly efficient chemiluminescent system based on *two* spin forbidden steps ($^1 \rightarrow ^3A$ and $^3A \rightarrow ^1DBA$) and one long range spin allowed step ($^1DBA \rightarrow ^1DPEA$) can be designed by employing a double energy transfer and a rigid medium.

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(10) This follows from eq 1 since the comparison of I_{CL} values is made under conditions of identical rates of decomposition and since the extrapolated value of ϕ_{ET} for singlet-singlet transfer to DPA must, by definition, equal unity.

(11) The sample of DPEA employed in this work was the kind gift of Dr. Arthur Mohan, American Cyanamid Co., Bound Brook, N. J. The quantum yield of fluorescence of DPEA is comparable to that of DPA, which is reported⁹ to be close to 1.0.

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