under our conditions.[13] However, that ^{3}A is formed in plentiful yield is firmly established by the observation of chemiexcitation of DBN *phosphorescence* by **1** and knowledge that *singlet* excitation of DBN does not occur. Furthermore, the fluorescence of DBA is chemiexcited by **1**. Significantly, however, this chemiluminescence is much more intense than that of DPA (both acceptors at identical concentrations), in spite of the higher inherent fluorescence yield of DPA. We thus must conclude that the major mechanism of chemiexcited DBA fluorescence ($k_{ET}^{TS} \sim 10^9 \ M^{-1}$ sec^{-1}) is *triplet–singlet energy transfer*.[7,12] Does this "forbidden" energy transfer occur *via* a long range or a short range mechanism? We propose that, in fact, the mechanism is long range as a result of the observation that (a) k_{ET}^{TS} is appreciably faster than k_{ET}^{SS} for the short range ^{1}A → ^{1}CQ system and (b) at 10^{-3} DBA a concentration of $10^{-1} \ M$ of DBA is required to quench half of the initial DBA chemiluminescence! Since DBN can only quench ^{3}A by a short range mechanism,[1] we therefore conclude that the ^{3}A–DBA transfer is long range through space in nature.[16]

This latter conclusion[17] allows us to distinguish between three mechanisms which may be proposed for energy transfer from ^{3}A to DBA (S_1): (a) collisional exchange energy transfer from ^{3}A to T_2 of DBA followed by intersystem crossing from T_2 to S_1 of DBA, (b) collisional exchange energy transfer from ^{3}A directly to S_1 of DBA, and (c) long range, radiationless transfer from ^{3}A to S_1 of DBA. Only mechanism c is consistent with our observations.

It is interesting to note that although DBN poorly competes with DBA in quenching of ^{3}A, the experimental rate constant for the ^{3}A–DBN quenching step is $\sim 10^7$–$10^8 \ M^{-1}$ sec^{-1}. This value is far too large to be due to quenching by immobilized DBN if only a short range mechanism for triplet–triplet transfer is occurring. We suggest that either triplet energy migration through the phenyl groups or a certain amount of local fluidity accounts for the results.[18] Experiments designed to decide between these possibilities are in progress.

(13) The weakness of chemiluminescence due to acetone phosphorescence[14] is wholly consistent with quenching by the phenyl groups of polystyrene, since benzene is a good quencher of acetone phosphorescence[15] and only a negligible amount of acetone phosphorescence is observed from **1** in benzene. It is possible that a benzene triplet may result from this quenching.

(14) N. J. Turro, H.-C. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **95**, 6468 (1973).

(15) R. O. Loufty and R. W. Yip, *Can. J. Chem.*, **51**, 1881 (1973).

(16) This conclusion, which is *not* expected on the basis of the Foster theory,[8] would be vitiated if a specific "complex" occurred between DBA and **1**, in the polymer matrix. We consider this possibility unlikely in view of (a) the experimentally indistinguishable values of E_a for the chemiluminescent fragmentation of **1** on polystyrene or in benzene (monitoring ^{1}A fluorescence by step analysis[6]) and (b) the comparable ratios of ^{3}A to ^{1}A formation in the polymer and in benzene.

(17) Previous workers have suggested a long range mechanism for energy transfer in polymers in which chemiluminescence was generated by radical recombination reactions: V. N. Anisimov, D. Phillips, O. N. Karpuhin, and V. Shlyapintokh, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **34**, 1529 (1970). This conclusion was later reversed: V. M. Aniaimov, K. Burnstein, O. Karpukhen, and M. A. Koshushner, *Opt. Spectrosc. (USSR)*, **31**, 602 (1971).

(18) A referee has quite properly been concerned about the possibility that the effects we have observed may be complicated by aggregation of the dioxetane and the acceptor molecules in the polymer matrix and that we may not be dealing with true solutions. Some evidence against this possibility is given in the text. We also wish to point out that the ratio of the limiting intensity from DBA to that from DPA is about three times greater in the polystyrene polymer matrix than the ratio for the same systems in fluid benzene solution. This increase is precisely the magnitude of the increase (a factor 3) expected from previous work[7,12] if the efficiency for triplet–singlet energy transfer approaches unity *and* the triplet–singlet excitation yield from **1** is the *same* in the polymer and in benzene. In addition, the activated chemiluminescence of DBN in polystyrene is a strictly linear function of DBN concentration up to 0.1 *M* DBN. Linearity is also observed in plots of the activated chemiluminescence intensity of DBA and DPA under the conditions employed to extract our kinetic parameters.

Nicholas J. Turro,* Han-Christian Steinmetzer
Department of Chemistry, Columbia University
New York, New York 10027
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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 anthracenes[2] by tetramethyl-1,2-dioxetane (**1**): (a) singlet acetone (^{1}A) to anthracene acceptor singlet (*e.g.*, 9,10-diphenylanthracene, DPA) and (b) triplet acetone (^{3}A) 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 transfer[4] relative to short range triplet–triplet energy transfer.[5]

The efficiency of indirect chemiluminescence (ϕ_{CL}) of our system is given by the general expression[6]

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

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-

(1) N. J. Turro and H.-C. Steinmetzer, *J. Amer. Chem. Soc.*, **96**, 4677 (1974).

(2) H.-C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebigs Ann. Chem.*, 1984 (1973).

(3) A. A. Lamola, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969.

(4) T. Forster, *Discuss. Faraday Soc.*, **29**, 7 (1959).

(5) V. L. Ermolaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **32**, 1193 (1968).

(6) (a) T. Wilson and P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971); (b) R. F. Vasilev, *Russ. Chem. Rev.*, **39**, 529 (1970).
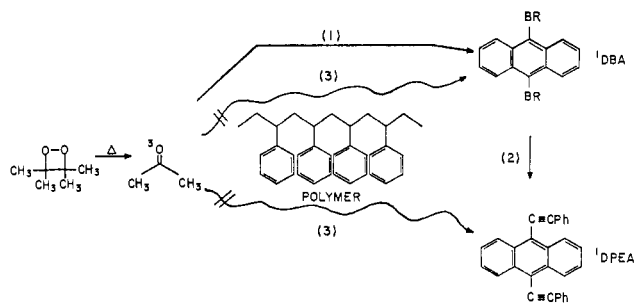
Figure 1. Amplification of chemiluminescence by double energy transfer in a polymer system. The "native" chemiluminescence of **1** in the polymer is weak fluorescence and phosphorescence. Chemiluminescence can be amplified by energy transfer to DBA ($\phi_F \sim 0.1$)[9] but the transfer step is inefficient if diffusional triplet–triplet energy occurs (path 3). Transfer from ^{3}A to the efficient emitter DPEA ($\phi_F \sim 1$)[11] is inefficient by all mechanisms. The long range energy transfer from ^{3}A to ^{1}DBA in a polymer (path 1) removes the inefficiency of path 3 and the tandem energy transfer from ^{1}DBA to ^{1}DPEA (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 shown[7] that **1** (in analogy to other dioxetanes)[6a,8] thermolyzes into ^{3}A 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 ^{3}A 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 ^{3}A to DBA is severely inhibited under these conditions.* Furthermore, if ^{1}DBA 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 ^{3}A with good efficiency, that the latter will transfer *via* a long range efficient mechanism to ^{1}DBA, and finally that ^{1}DBA 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 4×10^{-2} M **1**, 2×10^{-3} M DBA, and varying concentrations of DPEA was studied at 49°. At 2×10^{-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 $\sim$14 (at 49°), so that the product $\phi_{ET}^{TS}(^3A \to {}^1DBA) \times \phi_{ET}^{SS}(^1DBA \to {}^1DPEA) \times \phi_F^{DPEA}$ 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** $\to$ ^{3}A and ^{3}A $\to$ ^{1}DBA) and one long range spin allowed step (^{1}DBA $\to$ ^{1}DPEA) 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, be definition, equal unity.

(11) The sample of DEPA 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 DEPA is comparable to that of DPA, which is reported[9] to be close to 1.0.

Nicholas J. Turro,* Hans-Christian Steinmetzer
Chemistry Department, Columbia University
New York, New York 10027
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Geometric Isomers of Vinylmethylene

Sir:

We have observed the electron paramagnetic resonance spectrum of the ground state triplet vinylmethy-