Table II. Comparison of Selected Catalysts with 1,2-$C_2B_{10}H_{12}$ as Substrate

System	Catalyst	Conditions[a]	Av no. of D in product[b]
1	10% Pd on C (1 g)	3 days, 100°	2
2	$(PPh_3)_3RhCl$[c]	18 hr, 80°	2
3	$(PPh_3)_3RuHCl$	18 hr, 80°	5
4	$(PPh_3)_3RuHCl$	3 days, 100°	8
5	II	1 day, 65°	10
6	III	1 day, 65°	10

[a] Except where noted, reactions were with 1 mmol of 1,2-$C_2B_{10}H_{12}$ and 0.05 mmol of catalyst in 20 ml of toluene with D_2 bubbling at ~3 ml/min. [b] Estimated from ir, ^{11}B nmr, and mass spectra. [c] Formed nearly insoluble dimer and slowly decomposed under these conditions.

deuteration of 1,2-$C_2B_{10}H_{12}$ at least one order of magnitude faster than any other catalyst so far examined.

The results obtained with the catalytic systems described in Table II provide an example of the relative activity and selectivity exhibited by these catalysts with a variety of substrates. The order of rates of deuterium incorporation at the four chemically nonequivalent sets of sites in 1,2-$C_2B_{10}H_{12}$ was followed by 80.5-MHz ^{11}B nmr spectroscopy. With increasing deuterium exchange at a site represented by a given resonance, the doublet due to hydrogen coupling collapsed smoothly to a singlet.

The deuterated carboranes produced by system 1 in Table II had a ^{11}B nmr spectrum which showed a small degree of collapse at all four resonances, indicating little if any selectivity with this catalyst. System 2 produced a deuterated carborane with a ^{11}B nmr spectrum which exhibited considerable collapse of the resonance assigned to B(3,6),[11] slight collapse of that assigned to B(4,5,7,11), and no significant change in the B(8,10) and B(9,12) resonances. The ^{11}B nmr spectrum of the product of system 3 consisted of an unsymmetrical singlet for B(3,6) and B(4,5,7,11), and slightly collapsed doublets for B(8,10) and B(9,12). Under the more vigorous conditions of system 4, $(PPh_3)_3RuHCl$ produced deuterated carborane with a ^{11}B nmr spectrum consisting of a sharp singlet for B(3,6) and B(4,5,7,11), a broad singlet for B(8,10), and a poorly resolved doublet for B(9,12). Systems 5 and 6 produced carboranes which were more than 95% deuterated.

None of these catalysts caused exchange at the carbon atoms of 1,2-$C_2B_{10}H_{12}$[12] (no C–D stretching absorptions in the ir spectra of the deuterated carboranes) and no exchange was observed for the bridge hydrogens of $B_{10}H_{14}$ (no B–D bridge absorptions in the ir spectrum of deuterated decaboranes). Although $(PPh_3)_3RhCl$ rapidly forms the nearly insoluble dimer[13] at the required temperatures, and slowly decomposes, $(PPh_3)_3$-RuHCl, II, and III can all be recovered from some of the catalytic solutions.[14]

(11) The assignment of the ^{11}B nmr spectrum of 1,2-$C_2B_{10}H_{12}$ is that of J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, J. Amer. Chem. Soc., 88, 628 (1966).
(12) However, Raney nickel and D_2 effect slow exchange at carbon and none at boron, while $Co(CN)_5D^{3-} + D_2 + D_2O$ is very effective for specific exchange at carbon.
(13) J. A. Osborn, F. H. Jardine, and G. Wilkinson, J. Chem. Soc. A, 1711 (1966).
(14) Under the reaction conditions, these three catalysts undergo self-deuteration, $(PPh_3)_3RuHCl$ forms $[(2,6-D_2C_6H_3)_3P]_3RuDCl$,[9] and the metallocarboranes are extensively deuterated in the cage and hydride but not in the triphenylphosphine ligands.

The observed order of rates of deuteration at available sites on 1,2-$C_2B_{10}H_{12}$, B(3,6) > B(4,5,7,11) > B(8,10) > B-(9,12), is the reverse of that established for electrophilic substitution[15] and is therefore the order which might be expected for nucleophilic substitution. The pattern of substitution found for 1,7-$C_2B_{10}H_{12}$ [B(2,3), B(5,12), B(4,6,8,11) > B(9,10)][16] and $B_{10}H_{14}$ [B(6,9) > B(5,7,-8,10) > B(2,4), B(1,3)] is also in accord with expected patterns of nucleophilic substitution.[15,19]

The correlation of the pattern of reactivity for these deuterations with patterns of nucleophilic substitution is in accord with a mechanism involving oxidative addition of a transition metal complex to a terminal B–H bond.[20] The nucleophilic character of transition metal complexes in ortho metallation and other oxidative additions has been discussed.[8,21] Further studies with other substrates and catalysts, including detailed kinetic and mechanistic investigations, are in progress.

(15) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.
(16) This observation is based on the latest interpretation of the ^{11}B nmr spectrum of 1,7-$C_2B_{10}H_{12}$[17] and lends further support to it. The assignment of Stanko, et al.,[18] appears to be in error.
(17) H. V. Hart and W. N. Lipscomb, Inorg. Chem., 12, 2644 (1973).
(18) V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim., 11, 627 (1970).
(19) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Amer. Chem. Soc., 94, 4467 (1972).
(20) Our previous prediction of an electrophilic substitution pattern for oxidative addition to a B–H bond[7] was based on an erroneous interpretation of the results of Bennett and Milner.[8]
(21) J. P. Collman and W. R. Roper, Advan. Organometal. Chem., 7, 53 (1968).

Elvin L. Hoel, M. Frederick Hawthorne*
Contribution No. 3330, Department of Chemistry
University of California
Los Angeles, California 90024
Received April 1, 1974

Electronic Excitation Transfer in Polymers. I. Demonstration of Singlet–Singlet, Triplet–Singlet, and Triplet–Triplet Transfer in a Polystyrene Matrix Studied by a Chemiexcitation Method. Evidence for Forbidden and for Allowed Long Range Mechanisms

Sir:

Energy transfer processes which occur in solid polymeric systems are of interest from the standpoint of elucidation of energy transfer mechanisms[1] and design of strategies both to inhibit polymer photodegradation and to control the biodegradation of polymers.[2,3] During the last decade, a number of reports concerning

(1) Review of energy transfer mechanisms: A. A. Lamola, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969.
(2) (a) A. M. Trozzolo and F. H. Winslow, Macromolecules, 1, 98 (1968); (b) A. M. Trozzolo in "Polymer Stabilization," W. L. Hawkins, Ed., Interscience, New York, N. Y., 1974; (c) E. Dan and J. E. Guillet, Macromolecules, 6, 230 (1973), and earlier papers in this series.
(3) (a) R. B. Fox, Pure Appl. Chem., 34, 235 (1972); 30, 87 (1973); (b) C. David, M. Piens, and G. Geuskens, Eur. Polym. J., 9, 533 (1973), and references therein; A. C. Somersall and J. E. Guillet, Macromolecules, 6, 218 (1973).
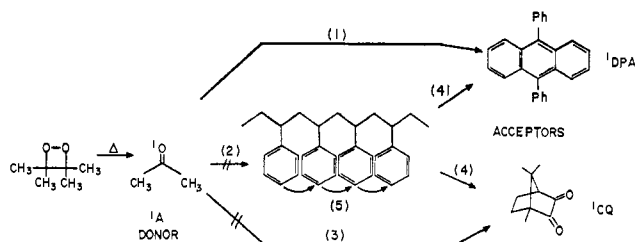
Figure 1. Path 1 is the long range, through space singlet–singlet energy transfer from ^1A to DPA. Path 2 is the singlet excitation of a phenyl group in the polymer followed by energy migration along the polymer chain(s). Path 3 is the singlet–singlet excitation of CQ by diffusion of ^1A to CQ followed by collision, exchange energy transfer. Path 4 is the excitation of DPA or CQ after the migration of singlet excitation along the polymer chain. Only path 1 operates with detectable efficiency under the reported conditions.

Figure 2. Path 1 is the long range, through space triplet–singlet energy transfer from ^3A to ^1DBA. Path 2 is the triplet–triplet excitation of a phenyl group in the polymer, followed by path 3, the migration of triplet energy migration along the polymer chain, and then by either path 4, triplet–singlet energy transfer to ^1DBA, or path 5 triplet–triplet energy transfer to ^3DBN. Path 6 is the diffusion of ^3A through the medium and collisional-exchange triplet–triplet energy transfer to ^3DBN.

energy transfer mechanisms in polymers, studied by photoexcitation, have appeared.[3] We report here (a) a study of energy transfer in polymers which utilizes chemiexcitation and thereby allows the examination of mechanisms which are technically difficult or impossible to study by means of standard photoexcitation techniques and (b) evidence for the occurence of long range singlet–singlet and triplet–singlet energy transfer mechanisms.

It has been shown that the thermolysis of tetramethyl-1,2-dioxetane (1) yields both excited acetone singlets (^1A) and acetone triplets (^3A), with the latter species being produced predominately.[4] We find that both the activation energy for *chemiluminescent* decomposition[5] of 1 and the ratio for primary excitation[6,7] of ^3A to ^1A are quite comparable in a polystyrene matrix or benzene solution. *From these data we conclude that the polymer matrix has no significant effect on the chemiluminescent pathways for fragmentation of 1 into excited acetone molecules.*

The chemiexcited acetone from 1 can be employed as a donor in energy transfer processes to a wide variety of energy acceptors, since in contrast to photoexcitation, absorption of light by acceptor has no effect on the production of ^1A or ^3A. Thus, transfer of energy from both of the latter states to the S_1 or T_1 states of strongly absorbing acceptors is possible. According to the Forster theory,[8] efficient long range energy transfer requires a strong absorption strength of the *acceptor* but not necessarily in the donor. For example, this means that *both* long range singlet–singlet and long range triplet–singlet energy transfer from acetone to anthracenes should be possible. On the other hand, triplet–triplet transfers, which are required by theory to occur by a collisional method,[1,9] must be short range in nature. In a rigid polymer matrix in which material

diffusion is strongly inhibited, two types of long range energy transfers are possible: (a) a long range, "through space" interaction between donor and acceptor[8] and (b) migration of energy through the polymer units.[3] We selected polystyrene as a matrix for our initial studies because both long range mechanisms are possible in this matrix and because polystyrene was found to form transparent, rigid glasses in which chemiluminescence could be observed with good reproducibility ($\pm 5\%$).[10]

Experimentally, 1 was employed to chemiexcite emission from a number of acceptors: 9,10-dibromoanthracene (DBA), 9,10-diphenylanthracene (DPA), 1,4-dibromonaphthalene (DBN), and camphoroquinone (CQ). Figure 1 lists the possibilities for energy transfer from ^1A to these acceptors and Figure 2 lists the possibilities for energy transfer from ^3A to these acceptors.

In the absence of acceptors, only the fluorescence from ^1A is observed. Thus, as expected, from energetic considerations, excitation of the S_1 state of the polymer by ^1A is unimportant. That diffusion is inhibited in the polymer was established by the observation that fluorescence from ^1A is not significantly quenched ($k < 10^8\ M^{-1}\ sec^{-1}$) by CQ which can only accept energy by a short range singlet–singlet mechanism.[11] On the other hand, the fluorescence of ^1A is specifically quenched by DPA[7,12] and the fluorescence of DPA is chemiexcited ($k_q \sim 10^{10}\ M^{-1}\ sec^{-1}$). This contrasting behavior of CQ and DPA toward ^1A strongly suggests a difference in mechanisms of energy transfer, CQ being of short range type of energy acceptor and DPA being a long range energy acceptor.

Since we found that the singlet state of the polymer is not excited by ^1A, *we conclude that DPA quenches ^1A by a long range through space mechanism.* The calculated half quenching radius from the ^1A–DPA system is ~ 20 Å. Thus, on the average, an energy transfer event *can occur with 50% efficiency even when ^1A and DPA are separated by 4–5 phenyl units.*

Chemiexcited phosphorescence from ^3A is very weak

(4) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972); *Pure Appl. Chem.*, **33**, 363 (1973).
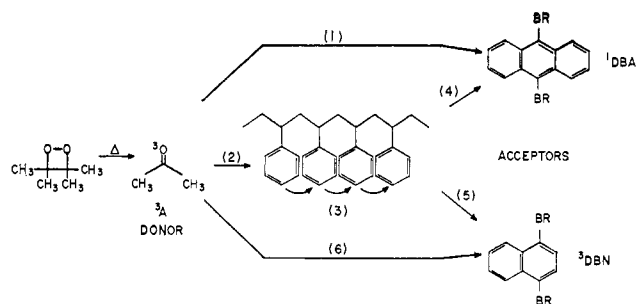
(5) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **96**, 282 (1974).

(6) T. Wilson, M. E. Landis, A. L. Baumstark, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **95**, 4765 (1973).

(7) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Amer. Chem. Soc.*, **96**, 1627 (1974).

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

(9) By this we mean the energy transfer step is short range and requires a collision between the triplet donor and triplet acceptor. Triplet–triplet transfer may become long range in nature if energy migration through the medium (*e.g.*, solvent or polymer backbone) is possible. Even in this situation, however, each transfer event is short range in nature.

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 ($k_{\text{ET}}^{\text{TS}} \sim 10^9 \ M^{-1}$ 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) $k_{\text{ET}}^{\text{TS}}$ is appreciably faster than $k_{\text{ET}}^{\text{SS}}$ for the short range ^{1}A $\rightarrow$ ^{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 solution. 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*

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]

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

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).