"Through Space" Triplet Energy Transfer: Movement of Electrons through the Hemicarcerand Skeleton

Angeles Farrán, Kurt Deshayes,* Christopher Matthews, and Ileana Balanescu

*Department of Chemistry and Center for
Photochemical Sciences, Bowling Green State University
Bowling Green, Ohio 43403*

A great deal of interest has developed concerning the influence of the nature of the intervening media on electron transfer reactions in which electrons move from donor to acceptor sites separated by "insulating" material.[1] Details of such processes can be probed by the study of triplet energy transfer based on the proposal of Dexter that transfer involves exchange of electrons between energy donor and acceptor.[2] Recently this approach was verified when Closs showed that energy transfer can occur between chromophoric groups separated by long distances, but connected by networks of single bonds.[3] The rates of energy transfer within a number of related molecules, with varying interchromophoric distances and orientations, were correlated quantitatively with rates of charge transfer involving both electron and hole transfer in the same molecular system.[4] The results lent increased credibility to the Dexter mechanism but did not resolve the question as to whether or not the intervening saturated structures played a special role in the process (through-bond mechanism). Here we describe the unambiguous observation of triplet energy transfer between unconnected systems separated by a molecular barrier (through-space mechanism).

An encapsulating host molecule ("hemicarcerand") was used to separate the donor and acceptor in solution so that the through-bond mechanism as it is commonly defined would not be operative, but the path of closest approach could still be estimated with good certainty. Hemicarcerands are closed-surface hosts with rigid, physically isolated interiors that form kinetically stable complexes when large energetic barriers prevent guest egress.[5] Work by Cram et al. in which the normally highly reactive cyclobutadiene was created inside a hemicarcerand confirms that species deeply buried within hemicarcerand interiors have no "bond-forming" contact with the external milieu.[6] Therefore, a triplet energy donor placed inside a hemicarcerand would not come into direct contact with the energy acceptor.

Both CPK molecular model examination and force field calculations[7] predict that acetophenone would fit tightly within hemicarcerand **1** to give a kinetically stable complex **1·acetophenone** (**1·Ac**), Figure 1.

The formation of **1·Ac** involves the synthesis of **1·dimethyl acetamide** (**1·DMA**) according to the literature procedure[8] and the subsequent exchange of encapsulated DMA guest with acetophenone.[9] Upfield shifts in NMR peak position of the guest protons by as much as 4.4 ppm provide evidence that the acetophenone is isolated within the shielding environment of the hemicarcerand interior. Analysis of peak integration areas shows that exactly one acetophenone was encapsulated within each hemicarcerand cage. Specific ROESY cross peaks between the two hemispheres of **1** and the acetophenone guest indicate that acetophenone adopts a single conformation along the long axis of hemicarcerand **1**. Variable temperature experiments[10] show the **1·Ac** complex to be quite stable at 25 °C with a $\Delta G^{\ddagger}$ of acetophenone egress of 25.3 kcal/mol containing $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ components of 19.7 kcal/mol and −18.7 eu, respectively. Indeed, solutions of **1·Ac** show no evidence of decomplexation after standing for weeks at room temperature. The structural data suggests that the most direct path by which triplet energy can be transferred is directly through the walls of hemicarcerand **1** with a closest direct path of 7 Å between the carbonyl within **1·Ac** and an external energy acceptor.

The absorption of the cage drops off at 300 nm, making the (n,π^*) transition of acetophenone accessible by the direct absorption of light. The absorption spectra of **1·Ac** and acetophenone are superimposable, showing that incarceration does not distort the absorption spectrum of acetophenone. Irradiation of **1·Ac** at 320 nm in a methyltetrahydrofuran (MTHF) matrix at 77 K yields a species with a lifetime of 10.1 ms and an emission spectrum containing the four vibrational bands charcteristic of acetophenone phosphorescence. In order to determine if triplet energy would be transferred through the skeleton of **1·Ac**, samples in which naphthalene was added to the MTHF matrix were irradiated. As the concentration of naphthalene in the MTHF matrix was increased, **1·Ac** phosphorescence intensity decreased while naphthalene phosphorescence was induced. Naphthalene phosphorescence was not seen upon direct irradiation of naphthalene, so triplet energy must be transferred through the skeleton of **1** in these experiments. The method of Terenin and Ermolaev[11] was used to obtain formal rate constants of triplet energy transfer of 79 s^{-1} for **1·Ac** and 300 s^{-1} for uncomplexed acetophenone. Since the radial distribution of quencher molecules about the **1·Ac** and acetophenone donors should be the same in the glass, there is only a modest difference in transfer efficiencies in this case. This is consistent with the observation that the millisecond triplet lifetimes feasible at 77 K enable triplet energy transfer to span 10–15 Å distances.[12]

Rates of triplet energy transfer at ambient temperature were addressed by the investigation of the photosensitized isomerization of *cis*-piperylene.[13] The transfer of triplet energy to *cis*-piperylene results in cis/trans isomerization so that triplet energy transfer can be monitored by the appearance of the *trans*-

(1) (a) Stemp, E. D. A.; Arkin, M. R.; Barton, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 2375. (b) Meade, T. J.; Kayyem, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 352. (c) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. (d) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossman, S. H.; Turro, N. J.; Barton, J. K. *Science* **1993**, *262*, 1025. (e) Jacobs, B. A.; Mauk, M. R.; Funk, W. D.; MacGillivray, R. T. A.; Mauk, A. G.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 4390. (f) Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1992**, *114*, 3656.

(2) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(3) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652.

(4) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(5) Cram, D. J.; Jaeger, R.; Deshayes, K. *J. Am. Chem. Soc.* **1993**, *115*, 10111 and references within.

(6) Cram, D. J.; Tanner, M. E.; Thomas, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1024.

(7) The commercial SPARTAN 3.0 modeling package from Wavefunction, Inc., 18401 Van Karman Ave., Suite 370, Irvine, CA 92715, running the SYBIL force field was used in the docking experiments.

(8) Cram, D. J.; Blanda, M. T.; Paek, K.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7765.

(9) The **1·Ac** complex is formed by heating **1·DMA** at 120 °C in acetophenone for 2 days under a nitrogen atmosphere. The **1·Ac** complex is precipitated by the addition of hexane to solution and purified by silica gel chromatography using CHCl$_3$ as eluent.

(10) For a description of the methodology used to determine activation parameters using NMR, see: Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985.

(11) Terenin, A. N.; Ermolaev, V. L. *Trans. Faraday Soc.* **1956**, *52*, 1042.

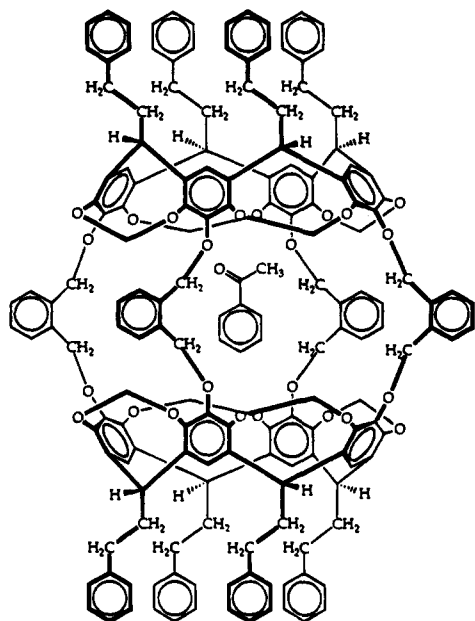(12) Bennett, R. G.; Kellogg, R. E. *Prog. React. Kinet.* **1967**, *4*, 215.

Communications to the Editor

J. Am. Chem. Soc., Vol. 117, No. 37, 1995 **9615**

Figure 1. Structure of 1·Ac.

Figure 2. Reciprocal plot for isomerization of *cis*-piperylene using 1·Ac (O) and acetophenone (■) as sensitizers.

piperylene. No measurable isomerization was observed when solutions containing only *cis*-piperylene were irradiated, while isomerization was observed on irradiation of solutions containing both acetophenone and 1·Ac. These results confirm that triplet energy transfer occurs from both acetophenone and 1·Ac. The Stern—Volmer analysis is shown in Figure 2, in which the initial rate of apperance of *trans*-piperylene is correlated with *cis*-piperylene concentration using a conventional reciprocal plot.

The ratio of the slopes obtained with 1·Ac sensitization and acetophenone sensitization is 4.0 ± 0.8. The lifetimes of the 1·Ac and acetophenone triplets were found using standard laser flash photolysis techniques to be 160 and 240 ns, respectively, so the observed variance in slope can be translated into a ratio of triplet energy transfer rates of 2.7 between naked acetophenone and 1·Ac. The rate constant for triplet energy transfer from acetophenone to *cis*-piperylene was verified to be 1.0×10^{10} M^{-1} s^{-1}, the diffusion-controlled limit for benzene solvent.[14] Our results show that the rate constant for triplet energy transfer from 1·Ac to *cis*-piperylene must be 3.7×10^{9} M^{-1} s^{-1}. The rate of triplet energy transfer is at, or near, the diffusion-controlled limit for both acetophenone and 1·Ac.

Triplet energy transfer is spin forbidden and cannot proceed by a dipole—dipole, or Förster, mechanism. Therefore triplet energy is almost certainly transferred by the electron exchange mechanism in these experiments. Electron exchange in solution is believed to require close contact between the donor and acceptor in order to create sufficient orbital overlap for the exchange of electrons. When the acetophenone resides within the interior of **1**, direct contact between the donor and acceptor is not possible, yet triplet energy transfer still occurs. If triplet energy transfer does in fact involve the exchange of electrons, our results demonstrate that there is sufficient orbital overlap between the donor and acceptor through the hemicarcerand skeleton for the simultaneous exchange of electrons between the HOMO and LUMO of the donor—acceptor pair.

In conclusion, triplet energy is transferred from an aryl ketone even when a hemicarcerand cage blocks atom-to-atom contact with the energy acceptor. Work to elucidate the precise role of the aromatic rings through the variation of the nature of the intervening hemicarcerand cage, the examination of different donor—acceptor pairs, and complementary studies on single electron transfer are currently underway in this laboratory.

Supporting Information Available: Low-temperature phosphorescence, 2D-TOCSY, and 2D-ROESY spectra of the 1·Ac hemicarceplex (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951346Q

(13) Although quenching of the 1·Ac triplet was observed, the low molar absorptivity of the acetophenone chromophore at 355 nm and the limited solubility of 1·Ac precluded the generation of sufficient triplet for accurate laser flash determination of quenching constants. Fortunately, relative rates of triplet energy transfer could be unambiguously obtained for 1·Ac and acetophenone using a classical method: Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129. Degassed solutions of 1·Ac and acetophenone in benzene were irradiated between 300 and 360 nm using a merry-go-round photoreactor in the presence of 0.02—0.1 M pure *cis*-piperylene. The formation of *trans*-piperylene was monitored by gas chromatography and prevented from going past 5% *trans*-piperylene in order to avoid back-isomerization.

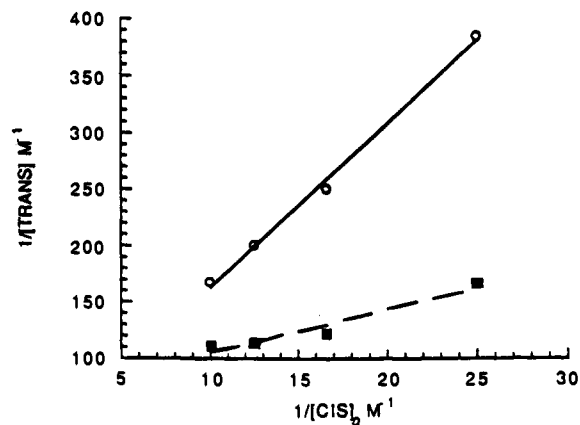(14) Turro, N. J. *Modern Molecular Photochemistry*; University School Books: Mill Valley, CA, 1991; p 314.