Bond-Coupled Electron Transfer Processes: A New Strategy for High-Efficiency Photoinduced Electron Transfer Reactions

S. B. Karki,[†] J. P. Dinnocenzo,*,[†] S. Farid,*,[‡]
J. L. Goodman,*,[†] I. R. Gould,*,[‡] and T. A. Zona[†]

*Center for Photoinduced Charge Transfer
University of Rochester, Rochester, New York 14627-0219
Department of Chemistry, University of Rochester
Rochester, New York 14627-0216
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650-2109*

Received July 5, 1996

Return electron transfer (RET) processes in photoinduced electron transfer reactions are typically viewed as undesirable energy-wasting steps. Indeed, a considerable amount of work has been directed toward strategies to increase the efficiencies of photoinduced electron transfers by decreasing the rate of RET, or increasing the rates of useful competing processes such as ion pair separation or follow-up ion radical reactions.[1] An alternative approach would be to have RET itself do useful work. This approach is illustrated in Figure 1 for reaction between an excited-state electron acceptor (A*) and an electron donor (X−Y). RET in the geminate ion radical pair can occur as normal to form A and X−Y. Alternatively, if the energy of the ion radical pair is greater than the X−Y bond dissociation energy, electron transfer can instead occur to produce a pair of radicals, X• and Y•. This latter process corresponds to a dissociative return electron transfer (DRET).

For efficient DRET, it seems likely that a triplet ion radical pair would be more useful than a singlet pair, since RET to give ground state A and X−Y is formally spin-forbidden in the triplet manifold and because the (X•/•Y) triplet state can be dissociative. In a singlet pair, RET and DRET occur as a result of partitioning after the spin-allowed electron transfer, and the nondissociative path is expected to be favored. Several examples of chemical reactions via triplet ion radical pairs have been described in the literature.[2] Of particular interest is work on the photosensitized *cis-/trans* isomerization of 1,2-diphenylcyclopropane (DPC), which suggested that it might involve DRET.[3,4]

The electron transfer photosensitized isomerization of DPC was first investigated by Wong and Arnold.[3] On the basis of CIDNP experiments, they proposed a mechanism involving ring-opening of DPC•+ to a 1,3-cation radical, followed by RET to a triplet 1,3-biradical, with subsequent intersystem crossing and ring-closure. On the basis of additional CIDNP experiments, Schilling and Roth showed that *configurationally stable cis-* and *trans*-DPC cation radicals are involved in these reactions and that the isomerization involves return electron transfer in the triplet ion radical pair leading to formation of the triplet biradical.[4] Biradical formation could occur by RET leading to a locally excited triplet DPC, which subsequently undergoes bond breaking to form the triplet biradical. Alternatively, the biradical could be the direct product of RET (i.e., it is formed by a DRET process.) These two fundamentally different
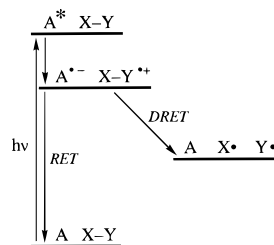

Figure 1. Schematic presentation of dissociative return electron transfer (DRET) in a photochemically generated ion radical pair, as an alternate path to the conventional return electron transfer (RET).

mechanisms cannot be distinguished using CIDNP.[5] Here we (1) provide direct identification of the intermediates involved in the electron transfer photosensitized isomerization of DPC, (2) demonstrate that the isomerization occurs by DRET with several triplet sensitizers (eq 1), and (3) show that bond fragmentation can occur with 100% quantum efficiency.
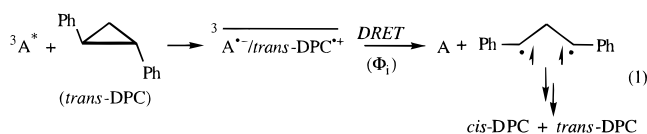
All of the experiments were performed in chloroform, to prevent separation of the ion radical pair.[6] Irradiation of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (313 nm) in the presence of *cis-* or *trans*-DPC leads to efficient isomerization.[7,8] When the experiment is started with either isomer, a (42:58) ± 2 *cis-/trans* photostationary state is attained, implying a common intermediate. Correcting the isomerization quantum yields measured for either isomer by the photostationary ratio gives a quantum yield for formation of the intermediate (Φ_i) of essentially unity (0.95 ± 0.05).[9]

Picosecond transient absorption spectroscopy (355 nm) of BTDA and *trans*-DPC (1.0 M) indicated a transient species which decayed with a lifetime <100 ps. The transient spectrum of this species, shown in Figure 2, agrees well with the spectral sum of independently generated BTDA•− and *trans*-DPC•+.[10] These data indicate that ³BTDA* and *trans*-DPC react to form a *short-lived* BTDA•−/*trans*-DPC•+ triplet ion radical pair.[11]

The product of this fast-decaying ion radical pair was investigated by two different techniques. Time-resolved photoacoustic calorimetry[12] showed that, after an initial rapid heat deposition due to reaction of ³BTDA* with *trans*-DPC followed by decay of the ion radical pair, an intermediate was formed with an energy of 29 ± 1 kcal/mol above the ground state reactants (BTDA + *trans*-DPC) and a lifetime of 14 ± 2 ns. The energy and lifetime of this intermediate are in good agreement with that expected for triplet 1,3-diphenyltrimeth-

† University of Rochester.
‡ Eastman Kodak Company.
(1) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.
(2) For example, see: (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 4303. (b) Roth, H. D.; Schilling, M. L. M.; Jones, G. *J. Am. Chem. Soc.* **1981**, *103*, 1246.
(3) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101.
(4) (a) Schilling, M. L. M.; Roth, H. D. *J. Am. Chem. Soc.* **1980**, *102*, 7956. (b) Schilling, M. L. M.; Roth, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 7210.

(5) This is especially true when the activation barrier for bond cleavage is low.
(6) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.
(7) The energy of the triplet BTDA (66 kcal/mol, 2.86 eV)[7a] is greater than that of the ion radical pair BTDA•−/DPC•+ in chloroform (2.75 eV), estimated as the oxidation potential of *trans*-DPC (1.62 V vs SCE)[7b] minus the reduction potential of BTDA (−0.82 V vs SCE)[7c] in acetonitrile, plus 0.2 eV to account for the differential solvation of the ion radical pair in chloroform vs in acetonitrile.[6] (a) Loutfy, R. O.; Winnik, M. A. *J. Phys. Chem.* **1978**, *82*, 1304. (b) Lingenfelter, T. L.; Simpson, T. R.; Dinnocenzo, J. P. Manuscript in preparation. (c) Pykhtina, E. V.; Glukhoedov, N. P.; Karkash, I. E.; Pravednikov, A. N. *Zh. Fiz. Khim.* **1978**, *52*, 1217.
(8) The steady-state irradiations were carried out in argon-purged chloroform at 313 nm (BTDA and TCB) or 365 nm (quinones) with 0.01 M DPC, unless stated otherwise, and to ≤10% conversion of DPC.
(9) The Φ_i was calculated from the isomerization quantum yields according to $\Phi_{c \to t}/f_t$ and $\Phi_{t \to c}/f_c$, where $\Phi_{c \to t}$ and $\Phi_{t \to c}$ are the quantum yields for *cis* → *trans* and *trans* → *cis* isomerization and f_c and f_t are the photostationary state fractions of *cis*-DPC and *trans*-DPC, respectively.
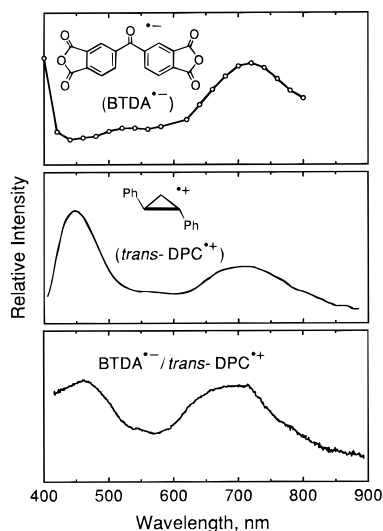
Figure 2. Transient spectra for BTDA$^{\bullet-}$, *trans*-DPC$^{\bullet+}$, and from the reaction of *trans*-DPC with ^{3}BTDA*.

ylene biradical.[13,14] This assignment was supported by nanosecond transient absorption experiments in which a species with an absorption maximum at ca. 320 nm and a lifetime of 15 ± 2 ns was detected. Similar absorption maxima and lifetimes have been reported for several related biradicals.[14]

Triplet-sensitized steady-state experiments support the assignment of the triplet 1,3-diphenyltrimethylene biradical as the common intermediate in the DPC isomerization reactions. The biradical was independently generated by the deazetization of *cis*- and *trans*-3,5-diphenyl-1-pyrazoline[15] using Michler's ketone in chloroform as the sensitizer.[16] The resulting ratio of *cis-/trans*-DPC was ($39:61 \pm 2$) from both pyrazoline isomers, in reasonable agreement with that obtained in the electron transfer sensitized reaction with ^{3}BTDA*.

The mechanism of conversion of the BTDA$^{\bullet-}$/DPC$^{\bullet+}$ triplet ion radical pair to the triplet 1,3-biradical was next investigated. The cation radicals of *cis*-DPC$^{\bullet+}$ and *trans*-DPC$^{\bullet+}$ were generated independently in nanosecond transient absorption experiments[17] and showed distinct absorption spectra. As expected from the earlier observations of Schilling and Roth,[4] no interconversion of the *cis* and *trans* cation radicals was observed over a time scale greater than 10 μs, whereas the lifetime of the BTDA$^{\bullet-}$/DPC$^{\bullet+}$ triplet ion radical pair is <100

ps with either *cis*- or *trans*-DPC. These data demonstrate that the triplet ion radical pair is converted quantitatively into the triplet 1,3-biradical and exclude, at least in this case, an isomerization mechanism involving a ring-opened cation radical.

As described above, the other possible isomerization mechanism involves formation of a locally excited triplet state of DPC. The energy of the BTDA$^{\bullet-}$/*trans*-DPC$^{\bullet+}$ triplet ion radical pair ($E_{IRP} \approx 61$ kcal/mol)[7] is sufficiently similar to a reported value for the energy of the DPC triplet (≥ 60 kcal/mol)[18] that this mechanism cannot be excluded on energetic grounds. To further test this mechanism, triplet electron transfer sensitizers that would give lower E_{IRP} were examined. Both *cis*- and *trans*-DPC were efficiently isomerized by 365 nm irradiation of 2,6-dichloro-, 2,5-dichloro-, or tetrachloro-1,4-benzoquinone.[8] In each case the *cis-/trans*-DPC photostationary state ratio was ca. 45:55, consistent with reaction via the triplet 1,3-biradical. Quantum yields for formation of the intermediate biradical calculated as described above were 0.67, 0.74, and 0.60, respectively.[19] Transient absorption and time-resolved photoacoustic experiments performed on these systems indicated formation of ion radical pairs which decayed in <10 ns. These lifetimes taken together with E_{IRP} of 42−46 kcal/mol[20] exclude the formation of the DPC triplet state.

The mechanism outlined in eq 1 is in good agreement with the data presented above, namely, *very fast decay* of an initially formed triplet ion radical pair to *efficiently* form a triplet biradical even when the energy stored in the pair is much lower than that required to form triplet DPC. These observations, coupled with the lack of interconversion of the *cis* and *trans* cation radicals on time scales orders of magnitude longer than the lifetime of the ion radical pair, provide strong support for the proposed dissociative return electron transfer (DRET).

Finally, 1,2,4,5-tetracyanobenzene (TCB) was used as an electron transfer photosensitizer to assess the importance of the spin state in determining the efficiency of the DRET process.[20] The reaction at high *cis*-DPC concentration (0.1 M), where mostly the singlet excited TCB is intercepted, showed that the singlet ion radical pair does not lead to any significant isomerization.[21] At low *cis*-DPC concentration, however, where the reaction proceeds mostly via interception of triplet TCB, the measured $\Phi_{c \to t}$ showed again that the triplet ion radical pair leads to the biradical formation with essentially unit efficiency.[22]

In summary, evidence is presented for dissociative return electron transfer as an alternative path for normally unproductive return electron transfer.[23] The DRET reaction may be part of a more general class of reactions—bond-coupled electron transfer processes—in which electron transfer can occur in conjunction with breaking and/or making chemical bonds.

(10) BTDA$^{\bullet-}$ was generated by reaction of ^{3}BTDA* with benzyltrimethylsilane, whose cation radical undergoes rapid desilylation under the reaction conditions.[10a,b] *trans*-DPC$^{\bullet+}$ was generated by photolysis of *N*-methylquinolinium hexafluorophosphate using toluene (2 M) as a co-sensitizer in the presence of *trans*-DPC (0.02 M) and oxygen to destroy the *N*-methylquinolinium radical.[10b] (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (b) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. Submitted.

(11) Irradiation of BTDA in the absence of *trans*-DPC leads to ^{3}BTDA*, the absorption spectrum of which agrees with that previously reported (Kuhlmann, R.; Schnabel, W. *Angew. Makromol. Chem.* **1977**, *57*, 195).

(12) (a) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 1381. (b) Goodman, J. L. In *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Blackie: New York, 1996; Vol. 4, Chapter 5.

(13) We presume that the energy of the triplet biradical relative to *trans*-DPC is slightly lower than the activation enthalpy for isomerization of DPC, 33−34 kcal/mol (Rodewald, L. B.; DePuy, C. H. *Tetrahedron Lett.* **1964**, 2951. Crawford, R. J.; Lynch, T. R. *Can. J. Chem.* **1968**, *46*, 1457).

(14) (a) Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797. (b) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549. (c) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

(15) Schneider, M.; Strohäcker, H. *Tetrahedron* **1976**, *32*, 619.

(16) (a) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. (b) DeBoer, C. D. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1966.

(17) *cis*-DPC$^{\bullet+}$ was generated in the same manner as *trans*-DPC$^{\bullet+}$.[10]

(18) Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584.

(19) The isomerization quantum yield in acetonitrile using tetrachlorobenzoquinone as the sensitizer was significantly lower than that in chloroform, consistent with the previous report of Schilling and Roth.[4] The quantum yield is difficult to interpret in this case because separation or other processes might occur in the geminate ion radical pair.

(20) The ion radical pair energies (E_{IRP}) were calculated as in ref 6, with the following reduction potentials for 2,6- and 2,5-dichlorobenzoquinone (-0.18 V),[20a] tetrachlorobenzoquinone (0.01 V),[20a] and TCB (-0.65 V).[20b] (a) Peover, M. E. *J. Chem. Soc.* **1962**, 4540. (b) Mattes, S.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.

(21) Essentially all of the observed isomerization ($\Phi_{c \to t} = 0.023 \pm 0.003$) occurs through interception of a small amount of TCB triplet formed under the reaction conditions.

(22) At [*cis*-DPC] of 0.005 M in chloroform: $\Phi_{c \to t} = 0.42 \pm 0.05$, the *cis-/trans* photostationary state was (42:58) $\pm$ 2, and the fraction of intercepted ^{1}TCB* = 0.04. For TCB in chloroform, Φ_{isc} is 0.740 ± 0.02.

(23) For a preliminary discussion of singlet DRET, see: Zona, T. A. Ph.D. Dissertation, University of Rochester, Rochester, NY, 1996.