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Communications to the Editor

Dynamics of Interconversion of Contact and Solvent-Separated Radical-Ion Pairs

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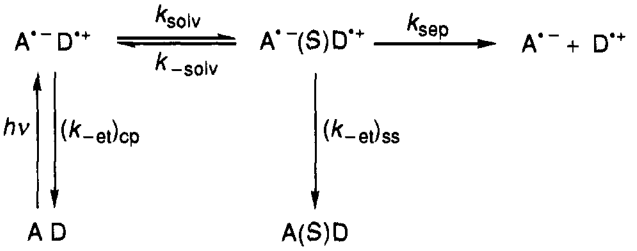
The important intermediates in photoinduced bimolecular electron transfer reactions in solution are the contact radical-ion pair (CRIP, $A^{\bullet-}D^{\bullet+}$) and the solvent-separated radical-ion pair (SSRIP, $A^{\bullet-}(S)D^{\bullet+}$).[1,2] Their role in the photochemistry of ground state charge-transfer (CT) acceptor (A)/donor (D) complexes, as an example, is illustrated in Scheme 1. Excitation of the AD complex gives a CRIP that may undergo solvation to form a SSRIP (k_{solv}) or return electron transfer to the ground state $(k_{-et})_{cp}$. Within the SSRIP, return electron transfer $(k_{-et})_{ss}$, further separation (k_{sep}) to form free (fully separated) radical ions (FRI, $A^{\bullet-} + D^{\bullet+}$), and feedback (desolvation) to the CRIP (k_{-solv}) may occur. Previous studies of radical-ion-pair dynamics have relied mainly on time-resolved absorption spectroscopy.[3] However, the CRIP, SSRIP and FRI can all potentially contribute to the transient absorption signals,[3] and the complete dynamics of the interconverting radical-ion pairs cannot be determined.[3g,i4] Here we describe an approach that allows *all* of the rate constants shown in Scheme 1 to be determined, including the rates of interconversion of the CRIP and SSRIP (k_{solv}, k_{-solv}), thus establishing their relative energies.

Excitation of a CT complex usually results in a transient absorption decay due to reactions of the CRIP and the SSRIP and a relatively long-lived "residual" absorption due to the FRI.[3] The absorption decay may be resolved into two exponential components, depending upon the relative magnitudes of the appropriate rate constants (Scheme 1). In principle, four independent experimental parameters are available from such experiments, i.e., two time constants (λ_1 and λ_2), the ratio of their preexponential factors (R_{abs}), and the quantum yield for formation of free radical ions (Φ_{ions}). However, accurate determination of four independent experimental parameters from picosecond time-resolved absorption measurements is difficult.[3d,g,i,j,5] Furthermore, at least one additional experimental parameter is required to determine the five rate constants shown in Scheme 1.

Scheme 1. Dynamics of Primary Intermediates in Photoinduced Electron-Transfer Reactions in Solution



Weak CT emission may be observed upon excitation of CT complexes due to radiative return electron transfer from the CRIP.[6] A time-resolved CT emission experiment gives the concentration of *only* the CRIP as a function of time. If significant feedback from the SSRIP to the CRIP occurs (k_{-solv}), the emission decay will be a double exponential with the same time constants as the absorption decay. In fact, the occurrence of feedback from the SSRIP to the CRIP can only be established positively by observing double-exponential kinetic behavior for the CRIP in an emission experiment. The quality of time-resolved single photon counting emission experiments is usually very high, allowing double-exponential analysis to be performed with reasonable accuracy. The ratio of preexponential factors will be different for the emission and the absorption experiments (R_{em} and R_{abs}), reflecting the fact that different concentrations of transient species are monitored in each. Thus, the combined data from *both* experiments can provide five independent experimental parameters and all of the rate constants of Scheme 1 can be determined.[7]

The acceptor used in this study was 1,2,4,5-tetracyanobenzene (TCB), which forms CT complexes with the methylated benzene donors summarized in Table 1.[6] Experiments were performed in argon-purged 1,2-dichloroethane at room temperature.[8] Both the time-resolved emission and absorption decays were observed to be nonexponential, confirming that feedback from the SSRIP to the CRIP must occur. From the combined experimental data were determined the rate constants shown in Table 1.[9,10]

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(1) (a) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129. (b) Mataga, N. In *Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena*; Mataga, N., Okada, T., Masuhara, H., Eds.; North-Holland: Amsterdam, 1992; p 3. (c) Gould, I. R.; Young, R. H.; Farid, S. In *Photochemical Processes in Organized Molecular Systems*; Honda, K., Ed.; Elsevier: Amsterdam, 1991; p 19.

(2) For aromatic acceptors and donors, the CRIP presumably adopt a fixed "sandwich" configuration, with a center-to-center distance of ca. 3.5 Å. The structure of the SSRIP is more dynamic, and it is usually assumed that the ions are separated by, on average, a single layer of solvent molecules, with a separation distance of ca. 7 Å.[1a]

(3) See, for example: (a) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. (b) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071. (c) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. (d) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 7534. (e) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1956. (f) Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 4491. (g) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1992**, *96*, 8941. (h) Asahi, T.; Ohkohchi, M.; Mataga, N. *J. Phys. Chem.* **1993**, *97*, 13132. (i) Peters, K. S.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 3643. (j) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401.

(4) For interconverting contact and solvent-separated *ion pairs*, where return electron transfer does not occur, the equilibrium constant can be obtained using absorption spectroscopy alone, as reported in ref 3j.

(5) Recent data from Peters et al. represents an exception in this regard.[3g,i,j]

(6) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(7) $(k_{-et})_{cp}$ represents all of the decay processes of the CRIP, i.e., return electron transfer, emission, and intersystem crossing. However, the latter two processes contribute less than 5% to $(k_{-et})_{cp}$ in the present systems[6] (and so are not included in Scheme 1), which is thus essentially the return electron transfer rate constant.

(8) (a) The TCB concentration was 0.015 M, and the donor concentrations varied between 0.01 and 0.03 M. No significant self-quenching was observed in this concentration range. The transient absorptions were monitored at 468 nm (excitation at 355 nm), and the emissions were monitored between 700 and 800 nm (excitation at 380 nm). For these systems, a very fast relaxation from an initially formed CRIP to a more stable CRIP occurs within ca. 10–30 ps.[8b] This relaxation was observed in both the absorption and emission experiments. Data points corresponding to this process were not included in the kinetic analyses. (b) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5834.

(9) The kinetic data were analyzed as a sum of two exponentials.[10] According to Scheme 1, the time dependencies of the normalized concentrations of the ion pairs and the free radical ions are as follows: [CRIP] = $1/(\lambda_2 - \lambda_1)\{(\lambda_2 - Y)\exp(-\lambda_2 t) + (Y - \lambda_1)\exp(-\lambda_1 t)\}$; [SSRIP] = $k_{solv}/(\lambda_2 - \lambda_1)\{-\exp(-\lambda_2 t) + \exp(-\lambda_1 t)\}$; [FRI] = $k_{solv}k_{sep}/(\lambda_2 - \lambda_1)\{\exp(-$

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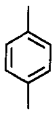
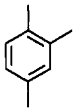
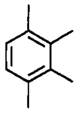
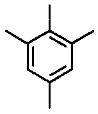
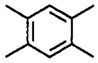
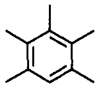
Table 1. Rate Constants for Return Electron Transfer, Solvation, and Separation for CRIP and SSRIP of TCB with Alkylbenzene Donors in 1,2-Dichloroethane at Room Temperature

donor	$(k_{-et})_{cp}$[a] (10^9 s^{-1})	$(k_{-et})_{ss}$[b] (10^9 s^{-1})	k_{solv}[b] (10^9 s^{-1})	k_{-solv}[b] (10^9 s^{-1})	k_{sep}[c] (10^9 s^{-1})
	1.10	0.76	0.64	0.91	0.36
	2.07	0.67	0.64	1.02	0.40
	2.90	1.63	1.04	0.81	0.37
	3.19	1.68	1.27	0.98	0.36
	3.99	1.71	1.10	1.00	0.52
	5.60	1.86	0.70	0.83	0.44

[a] Estimated error is ±0.2. [b] Estimated error is ±0.4. [c] Estimated error is ±0.1.

Reasonable trends are observed in each of the rate constants for the different donors, which provides strong support for the experimental method. The rate constants for the CRIP and SSRIP solvation and desolvation processes vary somewhat for the different radical-ion pairs (k_{solv}, ca. 0.6−1.3 × 10^9 s^{-1}, k_{-solv}, ca. 0.8−1.0 × 10^9 s^{-1}), but exhibit no particular trends. Importantly, the equilibrium constants obtained for the radical-ion pair interconversions are close to unity (ca. 0.6−1.3). Therefore, the energies of the CRIP and the SSRIP are essentially identical. The solvation of the CRIP to the SSRIP (and the separation of the SSRIP to free radical ions) is associated with an energy increase due to decreased Coulombic stabilization, which is compensated by an energy decrease due to increased solvent stabilization, especially in polar solvents.[11] With increasing solvent polarity, the change in Coulombic stabilization becomes smaller than the change in solvent stabilization. Thus, although the energy of the SSRIP is much larger than that of the CRIP in nonpolar solvents,[12] this energy difference is expected to decrease with increasing solvent polarity. Using a semiempirical approach, Weller predicted that the energies of the CRIP and the SSRIP should, in fact, become equal in solvents with dielectric constant around 7.[12] The dielectric constant of dichloroethane (10.4) is slightly larger than this value.

The rate constants for separation of the SSRIP into free radical ions (k_{sep}) are fairly constant at ca. 4 × 10^8 s^{-1} and are not much smaller than the values reported for separation of the same SSRIP in acetonitrile, ca. 2 × 10^9 s^{-1}.[3d] This suggests that the energy difference between the SSRIP and the FRI is not very different for these two solvents.

The rate constants for return electron transfer in the CRIP ($(k_{-et})_{cp}$) increase with decreasing oxidation potential of the donor due to the Marcus inverted region effect.[6,13a] A much smaller dependence is observed for the SSRIP ($(k_{-et})_{ss}$). This is expected, however, since the solvent reorganization energy should be larger for electron transfer in the SSRIP compared to the CRIP,[14] and consequently the data for the former will be closer to the maximum of the Marcus curve.[13b] It is interesting that the $(k_{-et})_{ss}$ are only somewhat smaller than the $(k_{-et})_{cp}$, despite the fact that the electronic coupling in the CRIP is almost certainly much higher than in the SSRIP.[14] However, the rate constants for electron-transfer reactions in the inverted region increase with increasing reorganization energy. Presumably in the range of free energies for the present systems, the effect of the difference in the reorganization energies for the two pairs almost cancels the effect of the difference in the electronic coupling.

The method described here for determining the rate constants of Scheme 1 and thus the relative energies of the CRIP and the SSRIP is strongly supported by the observation that reasonable trends are observed for the rate constants for the different systems. We are in the process of extending the measurements to determine the influence of solvent polarity and temperature on the relative energies of the radical-ion pairs.

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$\lambda_2 t)/\lambda_2 - \exp(-\lambda_1 t)/\lambda_1\} + k_{solv}k_{sep}/\lambda_2\lambda_1$. The time constants λ_1 and λ_2 were determined from the CRIP *emission* decays, together with the ratio of the preexponential factors (R_{em}). From these parameters were obtained values for X and Y (defined as ($k_{solv} + (k_{-et})_{cp}$) and ($k_{-solv} + (k_{-et})_{ss} + k_{sep}$), respectively) and the product ($k_{solv}k_{-solv}$) using $X = (\lambda_1 + R_{em}\lambda_2)/(1 + R_{em})$, $Y = \lambda_1 + \lambda_2 - X$, and $k_{solv}k_{-solv} = XY - \lambda_1\lambda_2$. Using λ_1 and λ_2 from the emission data as fixed parameters, values for k_{solv} and k_{sep} were then determined as the only variable parameters from best fits to the *absorption* decays. The remaining rate constants were obtained by substitution. Uncertainty values for the rate constants based on the results of repeated measurements are included in Table 1.

(10) In addition to the two main exponential decay components, an additional small (<1%) long-lived component (ca. 2 ns) is observed in the emission experiments. If more than one type of SSRIP is involved in the overall dynamics, for example with more than one solvent molecule separating the radical ions, then more complex or even time-dependent kinetic behavior would be expected. The additional small decay component might indicate that this is the case. However, it is difficult to determine whether the long-lived emission is a consequence of this effect or is simply due to a small amount of impurity. The fact that the data can be described quite accurately as a sum of two exponentials suggests that the SSRIP mainly react in one preferred conformation or separation distance. The possible role of time-dependent kinetics for the SSRIP will be discussed further in a full publication.

(11) (a) The energy of the singlet SSRIP is also lower than that of the singlet CRIP due to smaller electron exchange interactions.[11b] (b) Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982.

(12) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93.

(13) (a) The dependence of $(k_{-et})_{cp}$ on reaction free energy is smaller than expected from conventional electron transfer theory because the reorganization energy decreases with decreasing driving force.[6] (b) A change in reorganization energy with driving force may also be a contributing factor to the small dependence of $(k_{-et})_{ss}$ on driving force.

(14) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.