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Absolute Energies of Interconverting Contact and Solvent-Separated Radical−Ion Pairs

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The primary intermediates in photoinduced electron transfer reactions between an electron acceptor (A) and a donor (D) in solution are the contact radical−ion pair (CRIP) and the solvent-separated radical−ion pair (SSRIP).[1] Recent experiments have provided a reasonable understanding of the dynamics of these intermediates;[2] however, very little is known about their absolute energies.[3,4] Usually, the free energies of formation of radical−ion pairs from the neutral acceptor and donor, in a solvent of dielectric constant ϵ, are calculated using eq 1.[5] Here, E_D^{ox}

$$\Delta G_{RIP} = (E_D^{\ ox} - E_A^{\ red}) + \Delta_{RIP} \qquad (1)$$

and E_A^{red} are the donor and acceptor oxidation and reduction potentials, which are measured in a polar solvent such as acetonitrile.[5] For a CRIP, the quantity Δ_{RIP} in eq 1 can be estimated using an Onsager dipole model as shown in eq 2, where μ is the CRIP dipole moment and ρ is the equivalent sphere radius.[5] For a SSRIP, Δ_{RIP} is usually estimated using a Born approach, eq 3, where r is the average radius of the radical ions, R_{DA} is their separation distance, and ϵ' is the dielectric constant of the solvent in which the redox potentials are measured.[5]

$$\Delta_{CRIP} = \text{const} - (\mu^2/\rho^3)(\epsilon - 1)/(2\epsilon + 1) \qquad (2)$$

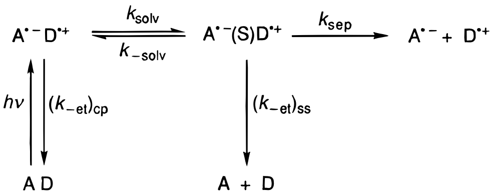
$$\Delta_{SSRIP} = (e_0^{\ 2}/\epsilon)(r^{-1} - R_{DA}^{\ \ -1}) - (e_0^{\ 2}/\epsilon')(r^{-1}) \qquad (3)$$

Table 1. Rate Constants for Interconversion of CRIP and SSRIP at 22 °C and the Difference in their Free Energies in Solvents of Varying Dielectric Constant

solvent	ϵ	k_{solv}[a] (10^9 s^{-1})	k_{-solv}[a] (10^9 s^{-1})	$\Delta G_{SSRIP} - \Delta G_{CRIP}$[b] (meV)
CH_3CCl_3	7.2	0.2	1.85	57
$CH_3CH(Cl)CH_2Cl$	8.3	0.29	1.77	46
CH_2Cl_2	8.9	0.34	1.65	40
$ClCH_2CH_2Cl$	10.3	0.64	0.91	9
$Cl(CH_2)_3Cl$	10.6	0.65	0.98	10
$CH_3(CH_2)_3CN$	20.2	2.6	0.7	−33
$CH_3(CH_2)_2CN$	24.6	3.4	0.9	−34

[a] Estimated error is ±20%. [b] Determined from the equilibrium constant, $K_{eq} = k_{solv}/k_{-solv}$, and by substitution in $K_{eq} = \exp\{-(\Delta G_{SSRIP} - \Delta G_{CRIP})/RT\}$; estimated error is ±10 meV.

Scheme 1



The methods for estimating Δ_{RIP} indicated in eqs 2 and 3 involve a number of implicit assumptions, and the uncertainties in the calculated energies are not known. Here we report the first systematic experimental determination of the relative and the absolute free energies for a series of CRIPs and SSRIPs in solvents of varying polarity and compare the data with the predictions of eqs 2 and 3.

Excitation of a ground state CT complex (AD) yields a CRIP ($A^{\bullet -}D^{\bullet +}$), which can form a SSRIP ($A^{\bullet -}$ (S)$D^{\bullet +}$) according to the mechanism shown in Scheme 1.[1c,2a] Interconversion of the radical−ion pairs can readily be detected as a double-exponential decay in a time-resolved CRIP emission experiment.[2a,6] By the combination of emission data and complementary data from time-resolved absorption experiments, all five rate constants of Scheme 1 can be determined, as described in a previous publication.[2a] Importantly, for the present purposes, the equilibrium constant for radical−ion pair interconversion ($K_{eq} = k_{solv}/k_{-solv}$) can be obtained, and thus the difference in the free energies of the CRIP and SSRIP can be calculated.

Experiments were performed using 1,2,4,5-tetracyanobenzene (TCB) as the electron acceptor and *p*-xylene (*p*-Xy) as the donor.[7] For this system, radical−ion pair interconversion is observed in solvents with dielectric constants ranging from 7 to 25. In solvents with lower ϵ, K_{eq} is less than 0.1, $(k_{-et})_{cp}$ is much larger than k_{solv} (Scheme 1), and the SSRIP is not formed to any appreciable extent within the lifetime of the CRIP. In solvents with ϵ higher than 30, the CRIP emission for the TCB/*p*-Xy pair is too weak to be reliably analyzed. The free energy differences between the radical-ion pairs derived from the K_{eq} are summarized as a function of ϵ in Table 1.

Absolute values for ΔG_{CRIP} can, in principle, be obtained from analyses of CT absorption and emission spectra, although very little experimental data has actually been reported.[3,4] We have carried out such measurements for CT complexes with over 20 different acceptor/donor/solvent combinations, with solvent dielectric constants ranging from 2 (cyclohexane) to 36 (acetonitrile).[8] Δ_{CRIP} values were determined as $\Delta G_{CRIP} - (E_D^{\ ox} - E_A^{\ red})$, as indicated in eq 1.[9−11] A plot of Δ_{CRIP} vs the Onsager dielectric function $(\epsilon - 1)/(2\epsilon + 1)$ is reasonably linear (plot not shown).[12] As shown in Figure 1, a plot of the Δ_{CRIP} vs $1/\epsilon$

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(6) (a) In a related experiment,[6b] interconversion was observed between two charge-separated states in a rigidly linked trichromophoric molecule using time-resolved emission spectroscopy. (b) Willemse, R. J.; Verhoeven, J. W.; Brouwer, A. M. *J. Phys. Chem.* **1995**, *99*, 5753.

(7) The experimental details for the time-resolved experiments have been described previously.[2a]

(8) For CT spectra, the spectroscopic energies obtained in this way correspond to free energies, rather than enthalpies.[4] Experimental details are provided as supporting information.

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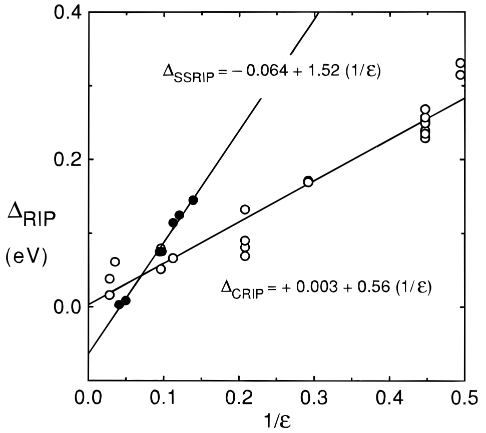

Figure 1. Difference between the free energies of formation of contact and solvent-separated radical−ion pairs and the electrochemical redox energies,[11] Δ_{RIP}, vs the reciprocal of solvent dielectric constant (in debyes).

is also quite linear.[13] This is because the Onsager function is approximately linear with $1/\epsilon$ for the range of ϵ used in this work. One advantage of this plot is that it provides a very simple relationship for the dependence of Δ_{CRIP} on ϵ. Although the CRIPs studied here have different acceptors and donors, the relatively low scatter in the data suggests that the variations in parameters such as molecular size and dipole moment are sufficiently small that a general relationship is obtained. From the dependence of Δ_{CRIP} on dielectric constant (Figure 1) and the free energy differences given in Table 1, ΔG_{SSRIP} for the TCB/*p*-Xy pair, and thus Δ_{SSRIP}, was obtained as a function of dielectric constant. A plot of Δ_{SSRIP} vs $1/\epsilon$ is linear as indicated in Figure 1.

The Δ_{RIP} values for both CRIP and SSRIP are plotted in Figure 2 as a function of ϵ. Clearly, the Δ_{SSRIP} values are more sensitive to solvent polarity than are the Δ_{CRIP} values, which is understandable since the SSRIPs are more highly solvated than the CRIPs.[2f] Figure 2 shows that in solvents with dielectric constant lower than 7, Δ_{SSRIP} is so much larger than Δ_{CRIP} that K_{eq} is <0.1. Under these conditions, appreciable formation of the SSRIP does not occur within the CRIP lifetime, and the SSRIP does not play an important role in the radical−ion pair dynamics. With increasing solvent polarity, Δ_{SSRIP} decreases more rapidly than does Δ_{CRIP}, so that population of the SSRIP becomes observable at $\epsilon \cong 7$. The energies of the two radical−ion pairs become approximately equal ($\Delta_{CRIP} \cong \Delta_{SSRIP}$, $K_{eq} \cong 1$) when the dielectric constant reaches ca. 13.

Qualitatively, the dependence of free energy on dielectric constant for the two radical−ion pairs shown in Figure 2 agrees remarkably well with predictions based on eqs 2 and 3.[5,14] There are, however, some quantitative differences. For example, using the parameters given in ref 5, the predicted intercept of the plot of Δ_{CRIP} vs $1/\epsilon$ is 0.15 eV compared to the measured value of near zero, although the predicted slope (0.47 eV) is only slightly smaller than the measured value (0.56 eV). According to the Born model, the slope of the plot for the SSRIP in Figure 1 is equal to $e_0^2(r^{-1} - R_{DA}^{-1})$. The measured slope is 1.52 eV, compared to the value of 2.6 eV which is calculated using eq 3 with conventional values for r and R_{DA} of 3 and 6.5 Å, respectively.[5] One consequence of these differences is that the SSRIP would be predicted to be ca. 220 meV lower in energy than the CRIP in acetonitrile, whereas the observed difference is only ca. 40 meV.

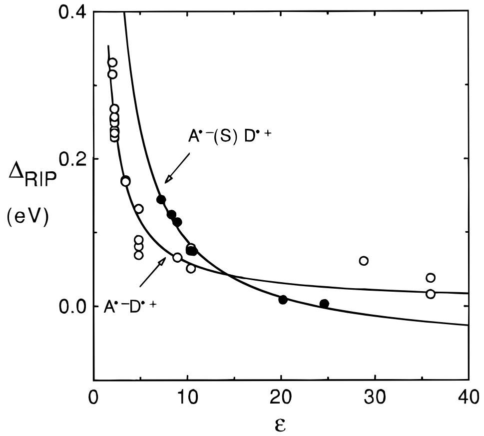

Figure 2. Difference between the free energies of formation of contact and solvent-separated radical−ion pairs and the electrochemical redox energies,[11] Δ_{RIP}, vs solvent dielectric constant (in debyes).

In summary, the free energies of formation for a variety of CRIPs, ΔG_{CRIP}, can be calculated using the empirical eq 4. The corresponding free energies for the SSRIP of the TCB/*p*-Xy pair, and possibly others, can be calculated using eq 5. Importantly, these equations use readily accessible electrochemical data and might apply to a variety of other systems where ΔG_{SSRIP} and ΔG_{CRIP} cannot be measured experimentally.

$$\Delta G_{CRIP} = (E_D^{ox} - E_A^{red}) + \Delta_{CRIP} \tag{4}$$

where $\Delta_{CRIP} = 0.56\ \text{eV}(1/\epsilon) + 0.003\ \text{eV}$

$$\Delta G_{SSRIP} = (E_D^{ox} - E_A^{red}) + \Delta_{SSRIP} \tag{5}$$

where $\Delta_{SSRIP} = 1.52\ \text{eV}(1/\epsilon) - 0.064\ \text{eV}$

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Supporting Information Available: Experimental details of the determination of the free energies of formation of contact ion-radical pairs from analyses of charge-transfer spectra; table including ΔG_{CRIP} values and electrochemical redox data (3 pages). Ordering information is given on any current masthead page.

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(9) The stabilization energy of the CT complex with respect to the separated donor and acceptor should also be subtracted from the Δ_{CRIP} values; however, these are not accurately known for all of the A/D/solvent combinations studied and are usually small anyway ($\leq$50 meV) and were, therefore, ignored.

(10) By comparison of Δ_{CRIP} instead of ΔG_{CRIP}, solvent effects on radical−ion pair energies can be directly compared for A/D pairs with different redox energies.

(11) (a) The donor and acceptor redox potentials used here are measured as described in ref 11b and are summarized in the supporting information. (b) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(12) (a) The slope of this plot is −0.94 eV, which according to eq 2 is equivalent to μ^2/ρ^3. Assuming a dipole moment of 14 ± 1 D,[3a] the equivalent sphere cavity radius is thus 5.9 ± 0.3 Å. From exciplex emission data, Weller et al.[12b] obtained a value of 0.75 for μ^2/ρ^3, which for $\mu = 14 \pm 1$ would correspond to a ρ of 6.4 ± 0.3 Å. (b) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.

(13) The correlation coefficient of the plot vs $(\epsilon - 1)/(2\epsilon + 1)$ is actually smaller than that of the plot vs $(1/\epsilon)$.

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