

# A Quantitative Relationship between Radiative and Nonradiative Electron Transfer in Radical-Ion Pairs

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One consequence of recent progress in our understanding of electron-transfer reactions is a revival of interest in relating reaction rates to spectroscopic measurements and, in particular, to radiative electron-transfer processes.<sup>1</sup> Here we describe such a relationship for electron transfer in the contact radical-ion pairs (CRIP) formed by excitation of the charge-transfer (CT) complex of 1,2,4,5-tetracyanobenzene (TCB) as the acceptor (A) and hexamethylbenzene (HMB) as the donor (D). The absolute rate constants for nonradiative return electron transfer in these systems can be predicted from analyses of CRIP emission data.

Nonadiabatic theories for electron transfer give the rate as a function of an electronic coupling matrix element ( $V$ ), the reaction free energy  $\Delta G_{\text{et}}$ , a reorganization energy ( $\lambda_s$ ), associated with low-frequency (mainly solvent) modes, and (in the simplest case) a single averaged high-frequency (skeletal) mode ( $\nu_s$ ) with reorganization energy  $\lambda_v$ .<sup>2</sup> When the nonradiative return electron transfer occurs in the Marcus "inverted region", a corresponding radiative return electron transfer process (CT emission) is also possible.<sup>3</sup> The reorganization parameters  $\lambda_s$ ,  $\lambda_v$ , and  $\nu_s$  that define the dependence of the nonradiative rate on  $\Delta G_{\text{et}}$  also determine the spectral distribution of the emission.<sup>3,4</sup> Thus, an analysis of such emission spectra can provide estimates for the reorganization parameters. Furthermore, when the CT absorption that corresponds to the emission can be observed,  $\Delta G_{\text{et}}$  can be obtained as

**Table I.** Calculated and Measured Rate Constants for Nonradiative Return Electron Transfer in the Contact Radical Ion Pairs of Tetracyanobenzene and Hexamethylbenzene in Different Solvents

solvent	$E_{\text{mid}}^a$ (eV)	$-\Delta G_{\text{et}}^b$ (eV)	$\lambda_s^b$ (eV)	$(k_{\text{et}})_{\text{calcd}}^c$ (10 <sup>7</sup> s <sup>-1</sup> )	$(k_{\text{et}})_{\text{measd}}^d$ (10 <sup>7</sup> s <sup>-1</sup> )
c-C <sub>6</sub> H <sub>12</sub>	2.59	2.57	0.14	0.64	ca. 1.7
CCl <sub>4</sub>	2.52	2.50	0.16	2.1	3.8
C <sub>6</sub> F <sub>6</sub>	2.50	2.48	0.26	11	19
ClCH=CCl <sub>2</sub>	2.43	2.52	0.35	26	35
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO	2.47	2.46	0.36	56	130
CHCl <sub>3</sub>	2.34	2.43	0.44	220	200
CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	2.46	2.47	0.43	130	310
ClCH <sub>2</sub> CH <sub>2</sub> Cl	2.35	2.45	0.53	540	770

<sup>a</sup> Energies of the crossing points of the reduced CT absorption and emission spectra.<sup>9</sup> <sup>b</sup> Obtained from fitting the emission spectra. Fixed values were used for  $\lambda_v$  and  $\nu_s$  of 0.31 eV and 1400 cm<sup>-1</sup>, respectively (see text). On the basis of the range of parameters which give acceptable fits to the spectra, the uncertainty in the reorganization parameters results in a corresponding uncertainty of ca. 20% in the calculated rates. <sup>c</sup> Calculated using the values given here and an electronic coupling matrix element of 860 cm<sup>-1</sup> (see also ref 5). <sup>d</sup> Measured values from time-resolved emission experiments as described in the text. Experimental errors are estimated to be  $\pm 5\%$ .

the energy of the 0,0 vibrational component.<sup>3</sup> Finally, a value for the electronic coupling matrix element  $V$  can also be estimated from CT emission data, using eq 1, in which  $k_f$  is the radiative rate constant,  $n$  the solvent refractive index,  $\nu_{\text{av}}$  the average CRIP emission frequency, and  $\Delta\mu$  the magnitude of the difference in dipole moment between the pure A<sup>-</sup>D<sup>+</sup> and pure neutral AD states.<sup>5</sup>

$$k_f = \frac{64\pi^4}{3h^3c^3} n^3 \nu_{\text{av}} (V\Delta\mu)^2 \quad (1)$$

Irradiation into the CT band of the TCB/HMB complex produces TCB<sup>-</sup>/HMB<sup>+</sup> CRIP.<sup>6,7</sup> CRIP emission spectra were obtained in solvents of varying polarity (Table I).<sup>8,9</sup> With increasing polarity the apparent Stokes shifts increase and the absorption and emission spectra broaden, indicating an increase in reorganization energy.<sup>3,4</sup> The measured CT emission and absorption spectra<sup>9</sup> exhibit an approximate mirror image relationship. For these systems the emitting CT state may be different from the state formed upon excitation,<sup>8a-c</sup> and so the crossing points of the reduced emission and absorption spectra (suitably normalized),  $E_{\text{mid}}$ , were taken as starting estimates rather than actual values for the  $-\Delta G_{\text{et}}$ . The emission spectra were fitted using a variant of eq 6 of ref 4 (described in supplementary material) by fixing  $\lambda_v$  and  $\nu_s$  at 0.31 eV and 1400 cm<sup>-1</sup>, respectively,

(5)  $\nu_{\text{av}}$  is given by  $(\int I_{\lambda} \nu^{-2} d\nu) / (\int I_{\lambda} \nu^{-3} d\nu)$ , where  $I_{\lambda}$  is the observed emission intensity per unit wavelength and  $\nu$  is the frequency. An estimate of 15 D is taken for  $\Delta\mu$ . An uncertainty of 10% in this estimate corresponds to an uncertainty of a factor of ca. 1.2 in the calculated rate constants. Equation 1 will be discussed further in a full paper (Chem. Phys., to be submitted).

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(9) The reduced emission spectrum, obtained as a plot of the reduced emission intensity ( $I_{\lambda} \nu^{-3}$ ) versus  $\nu$ , accounts for the dependence of the Franck-Condon factors on  $\nu$  and converts the emission intensity per unit wavelength to intensity per unit frequency. The corresponding reduced intensity for the absorption spectra is  $\epsilon \nu$ . Further details are given in the supplementary material.

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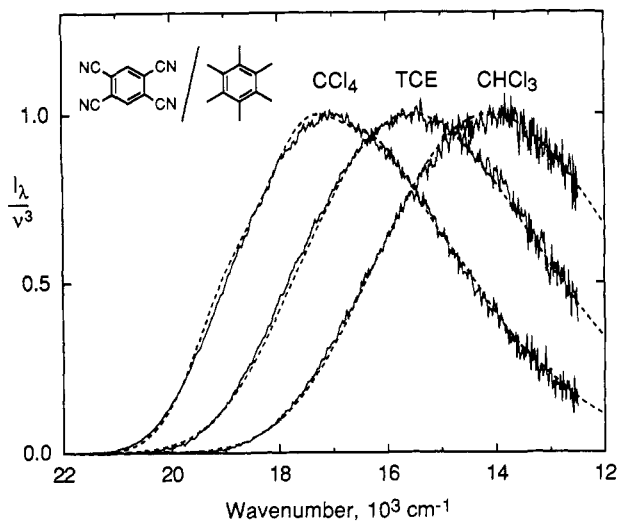
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**Figure 1.** Reduced and normalized emission spectra<sup>9</sup> for the excited CT complexes of 1,2,4,5-tetracyanobenzene/hexamethylbenzene in carbon tetrachloride ( $\text{CCl}_4$ ), trichloroethylene (TCE), and chloroform ( $\text{CHCl}_3$ ) solvents at room temperature (solid curves). The dashed curves are fits calculated as described in the text, using values of 0.31 eV and  $1400\text{ cm}^{-1}$  for  $\lambda_s$  and  $\nu_s$ , respectively, and the values for  $\lambda_s$  and  $-\Delta G_{\text{et}}$  given in Table I (see text for definition of parameters).

and adjusting  $-\Delta G_{\text{et}}$  and  $\lambda_s$  (Figure 1).<sup>10</sup> The  $-\Delta G_{\text{et}}$  values that gave the best fits were only slightly different from the  $E_{\text{mid}}$  values (Table I).

CRIP radiative rate constants were determined in carbon tetrachloride, diethyl carbonate, and chloroform as  $\Phi_f/\tau$ , in which  $\Phi_f$  is the emission quantum yield and  $\tau$  is the lifetime.<sup>11</sup> Estimates

(10) Estimates for the reorganization parameters could, in principle, be obtained by fitting both the CT absorption and emission spectra. The emission process is more closely related to CRIP nonradiative return electron transfer, however, especially for the present systems in which a different CRIP may be formed by CT absorption.

(11) Emission lifetimes were measured using time-correlated single photon counting as described previously,<sup>10</sup> typically exciting at 378 nm with detection at 650–750 nm.

for  $V$  of 880, 890, and  $800\text{ cm}^{-1}$  were thus obtained using eq 1. An average of  $860\text{ cm}^{-1}$  was adopted for all of the solvents. Values for the nonradiative rates ( $k_{\text{et}}^{\text{calcd}}$ ) were calculated using this value for  $V$  and the parameters used to fit the spectra, using eq 5 of ref 4 (see supplementary material). Nonradiative return electron-transfer rate constants ( $k_{\text{et}}^{\text{measd}}$ ) were measured as  $(\tau^{-1} - k_f)$  when emission was significant (cyclohexane and carbon tetrachloride,  $\Phi_f \approx 0.1$  and  $0.07$ , respectively) and as  $\tau^{-1}$  otherwise ( $\Phi_f \lesssim 0.01$  in the other solvents).<sup>12</sup>

The measured and predicted  $k_{\text{et}}$  (Table I) agree remarkably well over a rate range of almost 3 orders of magnitude. The results further underscore the close relation between radiative and nonradiative electron-transfer processes<sup>1,3,4,13</sup> and support the use of the nonadiabatic model used here, even though high frequency modes<sup>1m</sup> are modeled using a simplified single frequency treatment. The model appears to be particularly useful in predicting absolute rate constants in CRIP systems. We are now studying systems in which A and D are varied, to determine the influences of molecular structure on the reorganization parameters.

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**Supplementary Material Available:** Method for correcting the measured CT emission spectra for the various dependencies on emission frequency, equations used to calculate the reduced CT emission spectra, and equations for the corresponding reduced CT absorption spectra (3 pages). Ordering information is given on any current masthead page.

(12) (a) Intersystem crossing is energetically unfavorable for these complexes.<sup>8a</sup> Solvation to form a solvent-separated radical ion pair is intrinsically unlikely in low-polarity solvents<sup>12b,c</sup> and unlikely here also in the higher polarity solvents due to the high rates of return electron transfer. Product formation is not efficient in the TCB/HMB CRIP.<sup>12d</sup> (b) Weller, A. *Pure Appl. Chem.* **1982**, *54*, 1885. (c) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. (d) Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207.

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