

Charge Recombination in Cyclophane-Derived, Intimate Radical Ion Pairs

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Rates of charge recombination (CR) within photogenerated radical ion pairs (RIPs) have been derived for several systems in which the exergonicity (ΔG°) was varied by changing one of the reactants.¹⁻³ Two types of RIP need be considered; namely, intimate ion pairs and solvent-separated ion pairs.⁴ These species differ primarily by the degree of electronic coupling (V) between the reactants. This may lead, in turn, to different energy gap dependences for the CR processes.⁵ Indeed, CR within weakly-coupled RIPs may be explained satisfactorily in terms of current nonadiabatic electron-transfer theory,¹⁻³ whereas CR within intimate RIPs appears not to exhibit the same bell-shaped energy gap dependence.⁵ Proper evaluation of these systems has been hampered, however, by lack of structural information and clear definition of V and ΔG° . We now report the rates of CR within intimate RIPs of well-defined structure and for which both V and ΔG° can be readily quantified. These species are generated by pulsed laser excitation of charge-transfer complexes formed by inclusion of an electron donor into the central cavity of a cyclophane-derived electron acceptor.⁶ X-ray crystallographic studies⁷ have shown that the reactants are held within van der Waals contact with the mutual π -systems being almost coplanar (Figure 1).

The cyclophane-derived electron acceptor⁶ is rigid with a central cavity that accommodates many 1,4-disubstituted benzene derivatives. Insertion of a donor is accompanied by appearance of a Gaussian-shaped absorption band, for which the peak maximum (λ_{\max}) depends on the ionization potential of the donor. The derived association constants (K), molar extinction coefficients at the absorption maximum (ϵ_{\max}), and λ_{\max} values are provided in Table I for a range of donors in acetonitrile solution. The

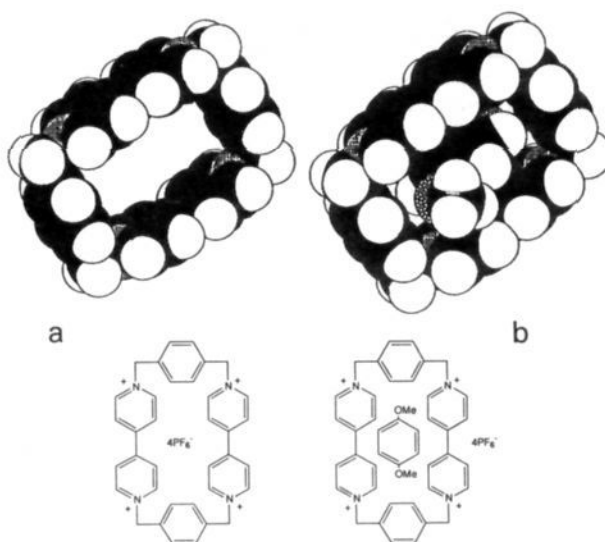


Figure 1. Structure of (a) the cyclophane-derived electron acceptor and (b) its inclusion complex with 1,4-dimethoxybenzene.

Table I. Parameters Measured for the Charge-Transfer Complexes Formed between the Cyclophane-Derived Electron Acceptor and Various Donors in Acetonitrile Solution

donor	K (M^{-1})	ϵ_{\max}^k ($M^{-1} \text{ cm}^{-1}$)	V^k (cm^{-1})	λ_{\max}^l (nm)	τ_{cr}^k (ps)	$k_{\text{cr}}^k/10^9$ (s^{-1})	$k_{\text{id}}^k/10^8$ (s^{-1})	$-\Delta G^\circ$ ^m (eV)
TMPD ^a	42	710	1800	820	4.0	248		1.06
PD ^b	112	712	1570	655	4.4	230		1.22
MTOL ^c	15	780	1660	601	7.0	145		1.62
BHQ ^d	18	620	1670	473	18.0	56		2.06
MEOPH ^e	24	480	1410	469	15.4	65		2.12
DMB ^f	18	420	1300	475	21.7	46		2.25
xylene	16	665		355	105	9.3	2.0	2.93
tBBENZ ^g	5	1040		333	121	7.3	10.0	3.08
FTOL ^h	10	900		320	156	6.0	4.0	3.15
toluene	16	1675		319	170	5.5	4.0	3.17
DCB ⁱ	3	395		312	185	5.1	3.0	>3.2
benzene	17	1295		290	294	2.6	8.0	>3.2

^a (*N,N,N',N'*-Tetramethyl-1,4-diamino)benzene. ^b 1,4-Diaminobenzene. ^c (*N,N*-Dimethylamino)toluene. ^d 1,4-Benzohydroquinone. ^e 4-Methoxyphenol. ^f 1,4-Dimethoxybenzene. ^g *tert*-Butylbenzene. ^h 4-Fluorotoluene. ⁱ 1,4-Dichlorobenzene. ^j $\pm 2 M^{-1}$. ^k $\pm 10\%$. ^l $\pm 2 \text{ nm}$. ^m $\pm 0.05 \text{ eV}$.

absorption bands are ascribed to charge-transfer interactions between the reactants within the confines of an inclusion complex (Figure 1). As such, the magnitudes of V and ΔG° can be derived⁸ by fitting the charge-transfer absorption band to a Gaussian profile (Table I). The average value of $V = 1570 \pm 250 \text{ cm}^{-1}$ indicates strong coupling between the reactants, due to their close proximity, while ΔG° can be varied over a wide range⁹ without significant change in structure.

Excitation of each charge-transfer complex with an ultrashort laser pulse resulted in immediate formation of a transient absorption spectrum that closely resembled that characterized for the *N,N'*-dimethyl-4,4'-bipyridinium π -radical cation.¹⁰ Thus, excitation causes rapid charge transfer from included donor to cyclophane-derived acceptor. The transient species decayed by first-order kinetics, for which the derived lifetimes (τ_{cr}) show a

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(9) Calculated according to: $\Delta G^\circ = -F[E_D^\circ - E_A^\circ + E_c]$ where E_D° and E_A° refer, respectively, to the one-electron redox potentials for oxidation of the donor and reduction of the acceptor. In acetonitrile solution, E_A° was measured to be -0.53 V vs SCE for the cyclophane containing an included molecule of 1,4-dimethoxybenzene. Values for E_D° were measured for the various donors in acetonitrile solution. The Coulombic term E_c was calculated to be 0.34 eV .

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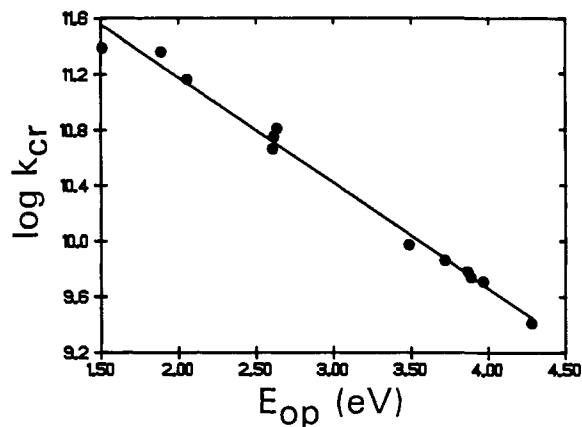


Figure 2. Correlation between the rate constant for charge recombination (k_{cr}) and the energy of the charge-transfer absorption maximum (E_{op}) for the various donors in acetonitrile solution.

weak dependence on ΔG° (Table I). In most cases, the transient absorption signal decayed to the prepulse base line due to rapid charge recombination within an initially-formed RIP. For $\tau_{cr} > 100$ ps, however, the decay profile was biphasic, with the longer-lived species surviving for several tens of microseconds. The two transients exhibited identical absorption spectra, but the longer-lived species decayed by second-order kinetics with an average bimolecular rate constant of $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. It is attributed, therefore, to separated radical ions formed by ejection of the oxidized donor from the cyclophane. For these systems, rates of CR (k_{cr}) and ionic dissociation (k_{id}) were calculated from the decay profiles (Table I).

The rates of CR decrease with increasing energy of the absorption maximum ($E_{op} = hc/\lambda_{max}$), as shown in Figure 2, and can be expressed in the following form:

$$k_{cr} = A \exp[\delta E_{op}] \quad (1)$$

This behavior is analogous to that of internal conversion within

polyatomic molecules and infers that deactivation of the RIP may be considered in terms of an activationless process in which leakage of energy from the upper to lower states occurs by a vibronic mechanism.¹¹ The extremely small δ value ($\delta = 1.75 \text{ eV}^{-1}$) suggests that only modest nuclear displacement accompanies CR, whilst the derived A value ($A = 5 \times 10^{12} \text{ s}^{-1}$) suggests a relatively low value for the nuclear momentum matrix element which couples vibrational modes between initial and final states.¹² The rates of CR can also be expressed in terms of ΔG° , but it is not evident at this stage that varying ΔG° over such a wide range does not cause systematic changes in reorganization energies, electron/vibronic coupling terms, and/or electronic/vibronic matrix coupling elements. Thus, the apparent shallow energy gap dependence¹³ may be coincidental and not genuinely reflective of a compact RIP. We expect to explore the validity of this sentiment in detail using structurally-related RIPs.

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Supplementary Material Available: Descriptions of the methods used to derive association constants, molar extinction coefficients, absorption maxima, and electronic coupling elements and of the experimental setup used for the transient absorption studies; figures showing the CT absorption band varying with increasing 1,4-dimethoxybenzene concentration, the best-fit Gaussian profile of the same CT band, and transient absorption measurements of toluene and 1,4-diaminobenzene in acetonitrile (8 pages). Ordering information is given on any current masthead page.

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