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# Role of Solvent Dynamics in the Charge Recombination of a Donor/Acceptor Pair

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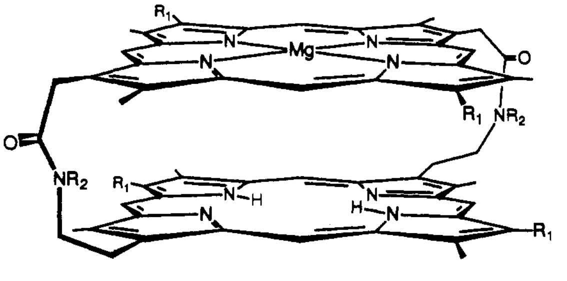
The rates of photoinduced charge separation (CS) or charge recombination (CR) between donor/acceptor sites in naturally occurring systems and biomimetic inorganic and organic compounds can be strongly influenced by the environment.[1] Ultrafast kinetics studies have shown that the CS and CR rates may be limited by solvent motion owing to strong dielectric coupling between the developing (or in the case of charge recombination, disappearing) charge-separated state of the chromophore and solvent dipoles.[2] These dynamic medium effects are most evident for electron-transfer events that are activationless or nearly activationless; in this case the ET rate directly reflects the time scale of solvent motion.[3] We now report the solvent dependence for the electron-transfer kinetics of the cofacial diporphyrin shown, designated as $Mg-H_2$ ($R_1$ = *n*-octyl, $R_2$ = *n*-butyl), and we show that the highly exothermic CR rate between the photogenerated $Mg^+-H_2^-$ acceptor/donor pair is governed by solvent dynamics even when the observed electron-transfer rate is slow with respect to the solvent motion.



**Mg—H₂**

The picosecond transient absorption kinetics of $Mg-H_2$ was monitored in acetone (Ac), dichloromethane (DCM), dimethylformamide (DMF), and methyl, ethyl, *n*-propyl, and *n*-butyl acetates (ROAc with R = Me, Et, Pr, and Bu, respectively). Population of the $^1(\pi\pi^*)$ excited state of $Mg-H_2$ results in the rapid ($k_{CS} > 2 \times 10^{11}$ s$^{-1}$) production of the $Mg^+-H_2^-$ charge-separated state,[4] which is characterized by prominent absorptions for the $Mg^+$ porphyrin cation subunit at 665 nm and free base anion at 645 nm, as Netzel and co-workers have shown.[5] The disappearance of the $Mg^+-H_2^-$ charge-separated intermediate obeys first-order kinetics, and a similar rate constant is obtained for the decrease in the ground-state bleaching of the Soret band at 405 nm, thereby confirming CR. The rate constant of CR is markedly solvent dependent, but lacks any consistent correlation with solvent polarity ($k_{CR} = 28 \times 10^8$ s$^{-1}$ for DCM to $k_{CR} = 5.8 \times 10^8$ s$^{-1}$ in PrOAc; see Figure 1). The slowness of CR as compared to CS in this system has been attributed to CR electron transfer occurring in the Marcus inverted regime.[5] Interestingly, the CR rates do not follow a simple dependence on the driving force for electron transfer. In such a case, DMF should most strongly solvate a CS state, and hence CR will be least exothermic in this solvent; inverted regime arguments would predict the rate to be fastest in this solvent,[6] but it is not. Conversely, the CR rate in DCM, which will not stabilize the $Mg^+-H_2^-$ charge-separated state as well as DMF, is fastest, whereas energetic considerations would predict this rate to be slow in the inverted region.

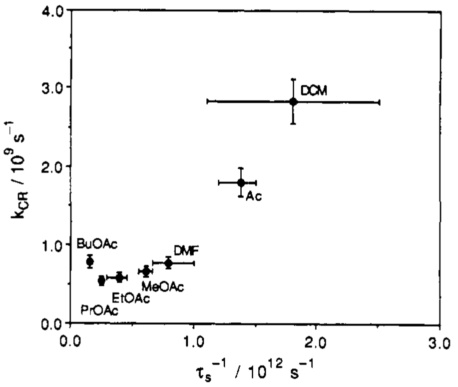


**Figure 1.** Plot of the CR rate constants of $Mg^+-H_2^-$ in dichloromethane (DCM), acetone (Ac), dimethylformamide (DMF), and methyl, ethyl, propyl, and butyl acetates (MeOAc, EtOAc, PrOAc, BuOAc, respectively) vs the reciprocal of the solvent microscopic relaxation time.

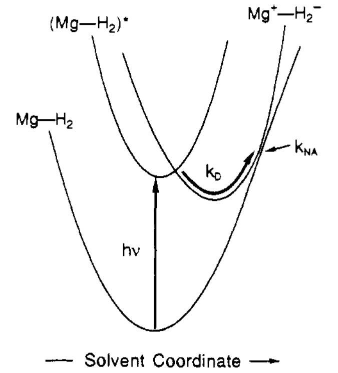


**Figure 2.** Reaction surface diagram for $Mg^+-H_2^-$ formed by photoinduced electron transfer of the $^1(\pi\pi^*)$ excited state of $Mg-H_2$. Diffusional motion governed by the solvent dynamics within the $Mg^+-H_2^-$ well is represented by the rate constant $k_D$. The nonadiabatic electron-transfer rate for bringing the charge-separated complex to its neutral ground state is denoted by $k_{NA}$.

In contrast to these conventional Marcus predictions,[7] the CR rates correlate with the inverse of the solvent relaxation times. Figure 1 shows the dependence of the $Mg^+-H_2^-$ CR rate constant on the reciprocal of the microscopic solvent relaxation time $\tau_s$.

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(4) The picosecond transient absorption apparatus consists of a Coherent Antares (76-s) mode-locked Nd:YAG laser ($\lambda_{exc}$ = 532 nm, 80 ps, 76 MHz), a cavity-dumped, synchronously-pumped R6G dye laser (Coherent 702, 20 nJ/pulse, 1 MHz), and an excimer-pumped (XeCl, Lambda Physik EMG 102), four-stage pulsed dye amplifier (Lambda Physik FL 2003). Output pulses ($\lambda_{exc}$ = 588 nm, Fwhm = 3 ps, 300 μJ/pulse, 50 Hz) from the dye amplifier are 60/40 split for sample excitation and continuum generation (saturated $ZnCl_2/H_2O$ solution), respectively. Absorption changes are measured with a dual diode array detector (PI DDA-512) which is retrofitted to a single monochromator (ISA HR-320, 300 gr/mm grating).

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(7) A similar solvent-dependent trend of the rate constant arises from contributions of the reorganization energy to the electron-transfer activation barrier in the inverted region. The observed rate constant for CR should be fastest in the most polar solvents (i.e., those solvents with the greatest reorganization energies) and become slower with decreasing polarity (Cukier, R. I.; Nocera, D. G. *J. Chem. Phys.*, submitted for publication).

0002-7863/92/1514-3564$03.00/0

Multicomponent relaxation times have been reported for some solvents, and it has been suggested that the fastest components best correlate to the electron-transfer event.[3c] We have included in Figure 1 the entire range of the most reliable $\tau_s$ values measured by ultrafast spectroscopy for each solvent.[2a,8] Despite the large error limits on $1/\tau_s$, a nearly linear dependence of $k_{CR}$ on $1/\tau_s$ is apparent, even though the rate constant of CR is much slower than the time scale of solvent motion.

This observation is consistent with theoretical predictions for electron-transfer processes influenced by solvent dynamics,[2a,b] which is schematically represented in Figure 2. The motion in the CS well is characterized by a rate constant $k_D$, and the crossing motion between the surfaces is characterized by $k_{NA}$. The overall electron-transfer rate for CR is given as[9-11]

$$k_{CR} = \frac{k_{NA}k_D}{k_{NA} + k_D} \qquad (1)$$

where $k_{NA}$ is given by a standard Marcus expression,

$$k_{NA} = |V|^2\left(\frac{\pi\hbar^2}{E_r k_B T}\right) \exp[-U(x^*)/k_B T] \qquad (2)$$

$U(x^*) = (E_r - \Delta E)^2/4E_r$, where $E_r$ is the reorganization energy and $\Delta E$ is the driving force. In the case where the electron transfer occurs at a localized crossing point,[10] $k_D$ becomes[11]

$$k_D = \frac{1}{\tau_s}\left(\frac{U(x^*)}{\pi k_B T}\right)^{1/2} \exp[-U(x^*)/k_B T] \qquad (3)$$

It is important to note that the well dynamics under discussion refer to that of solvent polarization coordinate, as characterized by $\tau_s$. The acceptor/donor pair is assumed to be kept at a fixed distance and, as such, is not involved in the reaction coordinate. From eq 1, if the rate constant for well dynamics is large relative to the rate constant for surface crossing (i.e., $k_D \gg k_{NA}$), then the well population is equilibrated and the conventional nonadiabatic rate expression is obtained (i.e., $k_{CR} = k_{NA}$). On the other hand, if the well motion is sufficiently slow, a dependence on well dynamics will be obtained (i.e., for $k_{NA} \gg k_D$, $k_{CR} = k_D$). In this case, $k_{CR}$ should depend intimately on the microscopic solvation time of the solvent. As observed in Figure 1 and predicted by eq 3, $k_{CR}$ should vary linearly with the inverse of the solvent relaxation time.[12] Slow electron-transfer rates can exhibit a dependence on fast solvent motions because $k_D$ is characterized by an activated process. Thus, the intrinsic well dynamics may be fast, but as illustrated in Figure 2, the rate constant describing the motion within the well is retarded because the system must reach a point high on the potential energy surface. Therefore, the solvent effectively "gates" the overall reaction of the CS state at a localized crossing.

Our observations further emphasize the important role that solvent can play in governing the rates of electron transfer in biological and chemical charge separating networks. In a static sense, the importance of solvent in mediating CS and CR kinetics by affecting the activation energy of electron transfer has recently been stressed.[13] Yet as we have shown here, the dynamics of solvation may dominate the reactivity of charge-separated states, even when the overall rate for the electron-transfer reaction is slow.

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(12) Solvent-dependent contributions to $k_D$ can also arise via the activation free energy Boltzmann factor in addition to $1/\tau_s$. However, electrochemical studies performed on the corresponding monomeric forms of Mg(II) and free base octaethylporphyrins show only small changes (~0.05 V) in the appropriate charge-separated redox potentials over the range of solvents reported. These observations are further supported by the electrochemistry reported for the cofacial Mg–$H_2$ system in a limited solvent series (see ref 5). Nevertheless, in the inverted region, the Boltzmann factor should cause deviations from linearity, which may explain the slight nonlinearity of the data in Figure 1.

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# Highly Chemo- and Stereoselective Cyclopolymerization of 2-Methyl-1,5-hexadiene: Chain Transfer via $\beta$-$CH_3$ Elimination

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Homogeneous cyclopolymerization of nonconjugated dienes yields an array of structurally diverse cyclopolymers. We have previously reported the diastereo- and enantioselective cyclopolymerization of 1,5-hexadiene to give stereoregular poly(methylene-1,3-cyclopentanes).[1] For the homogeneous polymerization systems,[2] the selectivity for cyclization is dependent on a number of factors,[1c] but generally exceeds 95% for hexadiene. This remarkable selectivity prompted us to investigate the cyclopolymerization of unsymmetrical dienes, where one terminus of the diene contains a sterically hindered olefin subunit.[3] Herein we report the unprecedented chemo- and stereoselective cyclopolymerization of 2-methyl-1,5-hexadiene to give *trans*-poly(methylene-1,3-(1-methylcyclopentane)) (PMMCP).

Homogeneous Ziegler–Natta catalysts derived from $Cp_2^*ZrMe_2$/MAO (Cp* = pentamethylcyclopentadienyl, MAO = methylaluminoxane) or from $[Cp_2^*ZrMe]^+X^-$ cations (X = $B(C_6F_5)_4$ or $CH_3B(C_6F_5)_3$)[4-8] are active for the cyclo-

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