

STUDY OF CONTACT ION PAIR DYNAMICS IN VIEW OF THE MOLECULAR SHAPES

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Abstract - Dynamics of contact ion-pair between 1,2,4,5-tetracyanobenzene anion and cation of biphenyl derivatives was investigated on the picosecond time scale. Solvent effect on the electron transfer was observed and electron transfer rates were examined using Marcus equation which contains distance dependence of the electron transfer rate in the frequency factor, along with the consideration of molecular shape. From the discussion based on disk model for molecular shape, contribution of interring torsional motion of biphenyl to the inner-sphere reorganization energy is strongly suggested, which leads to the physical explanation for the observed solvent effect on the rate of electron transfer.

INTRODUCTION

Ultrafast investigation of ion-pair dynamics provides an unique opportunity to directly study electron transfer reactions that are so important both in chemistry and biology. Despite much work on the ion-pair dynamics, discussions on the variation in the ion-pair dynamics with changes in solvent have not dealt with the physical description of the process.

In an attempt to provide more insight into the subject, picosecond experiment was performed on the charge-transfer complex where biphenyl or biphenyl derivative is a donor and 1,2,4,5-tetracyanobenzene (TCNB) is an acceptor. Biphenyl is one of the widely used photosensitizers in the photochemical electron transfer reactions, and it readily forms charge-transfer complex with TCNB in common organic solvents such as acetonitrile and dichloromethane. Direct monitoring of biphenyl(derivative) cation on the picosecond time scale provided transient absorption spectra, from which electron transfer rates were obtained.

Marcus equation¹, in which the frequency factor decreases exponentially with separation distance in the ion-pair, was used for the best fit, and solvent reorganization energy based on both sphere-shaped and disk-shaped donor and acceptor was considered² in view of the best fit results on the frequency of nuclear motion, ion-pair separation, and reorganization energy in acetonitrile and dichloromethane. Using the solvent reorganization energy based on disk model, an explanation is provided for the variation in ion-pair dynamics with changes in solvent.

MATERIALS AND METHODS

Materials. 1,2,4,5-tetracyanobenzene was prepared in the laboratory and biphenyl, 2-methylbiphenyl, and 4-methylbiphenyl were commercially obtained from Aldrich, and they were recrystallized prior to use. Acetonitrile and dichloromethane were repurified and kept in Schlenk flasks under argon prior to use.

Experimental methods. The picosecond transient absorption experiment has been described elsewhere³. The 1:1 biphenyl (derivative) complexes with TCNB in acetonitrile and dichloromethane, respectively, were excited by the third harmonic (355 nm, 1 mJ) of the fundamental output (1.06 μm , ca 20 ps) of passively-actively mode locked Nd:YAG laser (Continuum 501C), and the transient absorption spectra of donor cation were monitored as a function of time via Dual diode array detector system (Princeton Instruments ST-120). The sample was probed by two continuum probe beams, one passing through the excited region of the sample and the other unexcited, and this arrangement made possible the measurement of absorbance changes in a single experiment. The continuum (400 – 800 nm) was generated by the fundamental output of Nd:YAG laser in a 50:50 mixture of H₂O and D₂O, and it was sent to bifurcated optical fiber bundles to obtain two continuum probes. The variable time delay between the pump pulse and the probe was achieved by optical delay line. The sample was prepared to give absorbance of ca 0.55 at 355 nm, which was checked by UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Following picosecond laser excitation, transient absorption spectra for the cations were obtained at various time intervals, in both acetonitrile and dichloromethane,

up to 4 nanosecond or longer. The absorbance maxima of the cations are given in Table 1 and the transient absorption signals of these cations are shown in Fig. 1 – 6. In the Figures, the dot symbol is used for the experimental data and the curve represents the best fit to the corresponding data. As can be seen in the Figures, solvent effect on the decay dynamics of cation is quite

Table 1. Absorption maxima of radical cations

cation	Absorption maximum(nm)	
	dichloromethane	acetonitrile
biphenyl	681.4	671.7
2-methylbiphenyl	737.5	620
4-methylbiphenyl	686.4	677

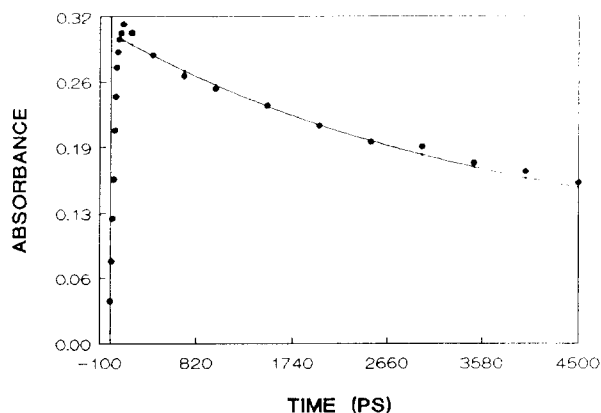


Figure 1. Transient absorption signal of biphenyl cation in dichloromethane

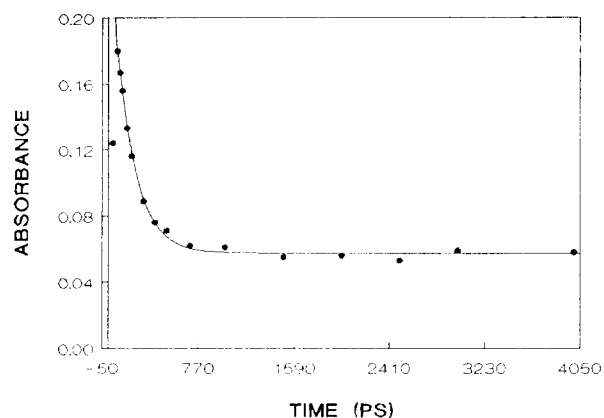


Figure 4. Transient absorption signal of 2-methyl biphenyl cation in acetonitrile

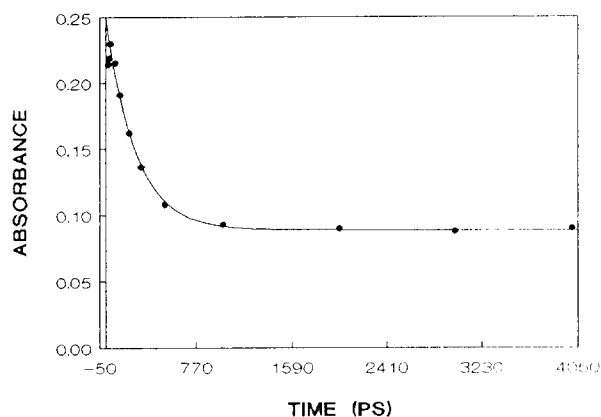


Figure 2. Transient absorption signal of biphenyl cation in acetonitrile

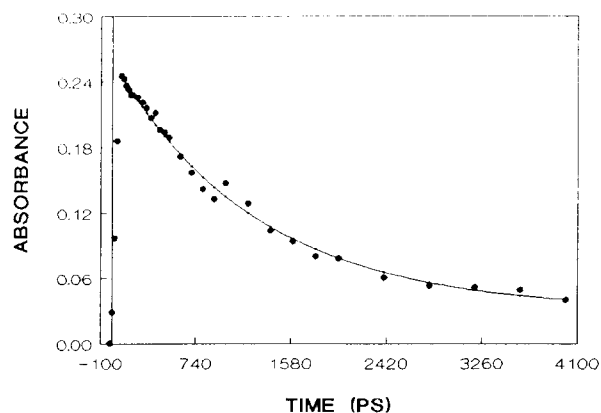


Figure 5. Transient absorption signal of 4-methyl biphenyl cation in dichloromethane

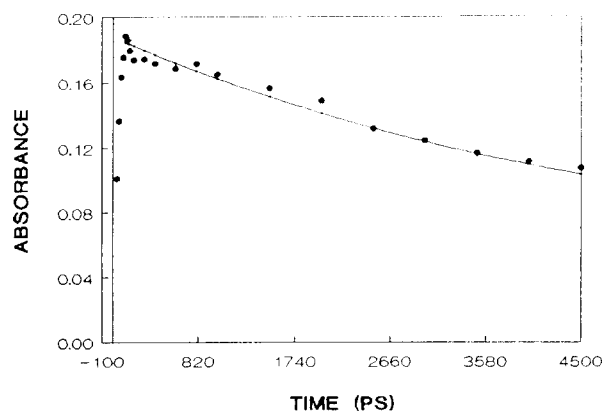


Figure 3. Transient absorption signal of 2-methyl biphenyl cation in dichloromethane

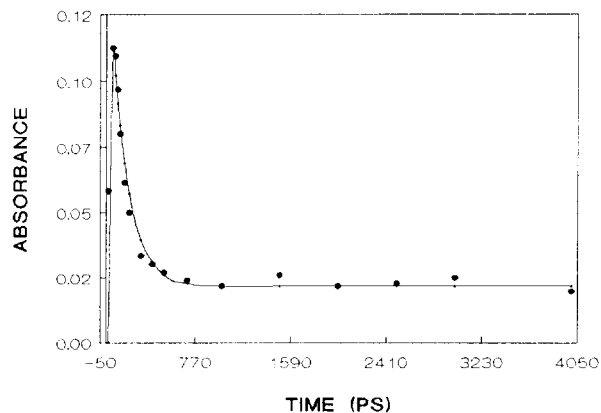
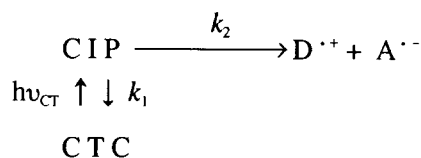


Figure 6. Transient absorption signal of 2-methyl biphenyl cation in acetonitrile

pronounced. In acetonitrile, the transient signal has a fast decaying initial component followed by essentially constant value extending to 4 nanosecond or longer. On the other hand, in dichloromethane, decay of transient signal is noticeably slower and continues up to 4 nanosecond or longer.

The dynamics of contact ion pair (CIP) following picosecond excitation of the charge transfer complex of biphenyl(derivative) and TCNB can be examined with respect to the following scheme⁴.



According to this scheme, the time-dependent concentration of the biphenyl(derivative) cation is

$$[\text{D}^{\cdot+}](t) = C \{ (1 - R) \exp(- (k_1 + k_2) t) + R \} \quad (1)$$

where k_1 is the rate of back electron transfer, k_2 is the rate of separation to form free ions, C is a constant reflecting the concentration at $t = 0$, and $R = k_2 / (k_1 + k_2)$ is called the residual. The transient absorption $A(t)$ is obtained by convolution of $[\text{D}^{\cdot+}](t)$ with the Instrument function $I(\tau)$.

$$A(t) = \int_{-\infty}^t I(\tau) [\text{D}^{\cdot+}](t - \tau) d\tau \quad (2)$$

where Gaussian pulse of 20 ps (FWHM) was used as the instrument function for the current experiment. The values of k_1 and k_2 in Eq. (1) were obtained as a result of optimum procedure to yield minimum deviations between the calculated and experimental data, and they are given in Table 2, together with the free energy changes in acetonitrile. The corresponding free energy changes in dichloromethane were determined from the following Eq.⁵.

$$\Delta G^0(\text{kcal/mole}) = \Delta G^0_{37.5} - (e^2/2)(1/r_D + 1/r_A)(1/37.5 - 1/\epsilon_s) + (e^2/R_{DA})(1/37.5 - 1/\epsilon_s) \quad (3)$$

where ΔG^0 is the free energy change in the solvent, $\Delta G^0_{37.5}$ is the free energy change in acetonitrile, r_D and r_A are the radii of the donor and the acceptor, respectively, ϵ_s is the dielectric constant of the solvent, and R_{DA} is the distance of ion-pair separation. The Marcus plot in Fig. 7 shows a behavior in the Marcus inverted region, and observed solvent effect agrees with the inverted region behavior that increasing the solvent polarity increases the electron transfer rates. This study employed a series of donors including biphenyl, 2-methylbiphenyl, and 4-methylbiphenyl, and the contact ion-pairs of these donor cations and TCNB anion were assumed to have the same frequency of nuclear motion, ion-pair separation, and reorganization energy, which are the factors, determining the rate of electron transfer. In view of the assumptions

Table 2. The rates of $k_1(\times 10^{-8})$ and $k_2(\times 10^{-8})$ in the Contact Ion-Pair. Acceptor: 1,2,4,5-tetracyanobenzene.^{a)}

donor	dichloromethane			acetonitrile			$-\Delta G^{0b}$
	k_1	k_2	$R(A_0)$	k_1	k_2	$R(A_0)$	
biphenyl	22.7	10.68	0.32	300	184	0.38	54.88
2-methylbiphenyl	18	5.38	0.23	480	236.4	0.33	56.27
4-methylbiphenyl	82	11.2	0.12	650	172.8	0.21	51.65
9,10-dihydrophenanthrene	86	8.5	0.09	800	212.7	0.21	49.58
fluorene	110	28	0.20				

^{a)} $k_1 = k_{\text{bet}}$ and $k_2 = k_d$

^{b)} kcal/mole

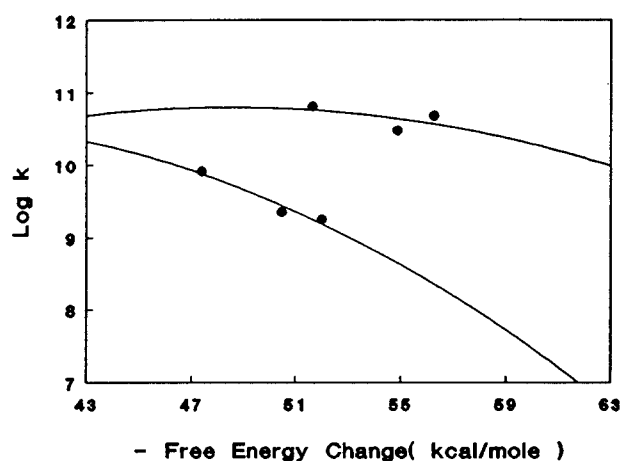


Figure 7. Marcus plot of TCNB/biphenyl derivatives in different solvents

made on these factors, following Marcus equation⁷ was used to fit picosecond kinetics data in Table 2.

$$k_{\text{bet}} = A e^{-\beta(R-R_0)} \exp\left\{-\frac{(\Delta G^0 + \lambda)^2}{4RT\lambda}\right\} \quad (4)$$

where A refers to the frequency for motion of nuclei along the reaction coordinate in the range between 10^{12} and 10^{14} s⁻¹, β is a parameter whose value is 1.2 Å⁻¹ in biphenyl donor-acceptor system, R is the distance of separation in ion-pair, and R_0 ($= 3$ Å) is the value of R allowing for the extension of the Π -electronic orbitals beyond the carbon nuclei, ΔG^0 is the free energy change of electron transfer reaction, λ is the reorganization energy, R is gas constant, and T is the temperature in kelvin.

The reorganization energy obtained from the best fit was further examined with respect to the outer-sphere reorganization energy (λ_s). Under the assumption that the donor-acceptor molecules are spherical, Eq. (5) based on the sphere model⁷ can be used to calculate the outer-sphere reorganization energy, and the best fit results including the outer-sphere reorganization energy based on the sphere model are given in Table 3, where the same van der Waals radii are used for donor-acceptor molecules. However, aromatic compounds such as TCNB, biphenyl, and biphenyl derivatives are more

Table 3. The best fit result and the outer-sphere reorganization energy based on sphere model($r = 3.37 \text{ \AA}$)

vibrational frequency of nuclear motion(s^{-1})	dichloromethane				acetonitrile			
	$R(A_{\nu})$	λ	λ_s	$\Delta\lambda$	$R(A_{\nu})$	λ	λ_s	$\Delta\lambda$
10^{12}	5.64	35.51	15.81	19.70	5.30	48.46	20.19	28.27
10^{13}	7.56	35.51	21.79	13.72	7.22	48.46	29.60	18.86
10^{14}	9.48	35.51	25.36	10.15	9.14	48.46	35.06	13.40

Table 4. The best fit result and the inner-sphere reorganization energy based on disk model($a = 3.89 \text{ \AA}$, $c = 1.685 \text{ \AA}$)

vibrational frequency of nuclear motion(s^{-1})	dichloromethane			acetonitrile		
	$R(A_{\nu})$	λ	λ_s	$R(A_{\nu})$	λ	λ_s
10^{12}	5.64	35.51	-8.96	5.30	48.46	-24.95
10^{13}	7.56	35.51	31.06	7.22	48.46	35.19
10^{14}	9.48	35.51	59.98	9.14	48.46	78.30

appropriately approximated as disk, since biphenyl in anion, cation, or excited state has planar structure.⁶ Thus, Eq. (6) based on disk model² was used and the best fit results including the solvent reorganization energy based on disk model are presented in Table 4. In determining the radius of the disk, van der Waals radius of carbon⁷ was used for the thickness of the disk, and the same volume was applied to both molecular models.

$$\lambda_s = e^2/2 (1/n^2 - 1/\epsilon_s) (1/a + 1/b - 2/R) \quad (5)$$

where a and b are the radii of the spheres corresponding to donor and acceptor molecules, and R is the distance of ion-pair separation.

$$\lambda_s = e^2/4 (1/n^2 - 1/\epsilon_s) [(2/c - 2c/(R^2 - c^2) - 4/(R+2c) + 1/a (\tan^{-1}((R+c)/a) - \tan^{-1}((R-c)/a) + 2 \tan^{-1}(c/a)) - 2 \int_{0.5R-c}^{0.5R+c} 2 a^2 / ((f(x)(f(x) + a^2 - x^2 + 0.25 R^2)) dx] \quad (6)$$

where a is the radius and $2c$ is the thickness of the disk, and R is the distance of ion-pair separation, and $f(x) = [a^4 + 2 (x^2 + 0.25 R^2) a^2 + (x^2 - 0.25 R^2)^2]^{0.5}$. As can be seen in Tables 3 and 4, ion-pairs tend to be less separated in acetonitrile than in dichloromethane, and the distance of ion-pair separation shows positive correlation with the frequencies of nuclear motion in both sphere and disk models. Using sphere model, the difference between the reorganization energy and the outer-sphere reorganization energy could be identified as the inner-sphere reorganization in a series of frequencies of nuclear motion considered; however, when disk model was employed, physically meaningful result was obtained only for the frequency of 10^{13} s^{-1} , and the values of $\Delta\lambda$ between the reorganization energy (λ) and the outer-sphere reorganization energy (λ_s) were 4.45 kcal/mole and

13.27 kcal/mole in dichloromethane and acetonitrile, respectively. According to Miller *et al.*⁸, the solvent reorganization energy consists of the reorganization energy for high frequency molecular vibrations (λ_s) and that due to low frequency modes (λ_i), and the latter is composed of the solvent reorganization energy (λ_s) and the reorganization energy for low frequency internal motions (λ_{ij}) such as torsional motion.^{9,10} Their investigation⁸ into the effect of the inter-ring torsional motion of biphenyl on the intramolecular electron transfer rates shows that torsional reorganization energy for biphenyl in 2-methyl tetrahydrofuran is $0.13 \pm 0.03 \text{ eV}$. In view of this finding by Miller *et al.*⁸, it is suggested that the difference of 4.45 kcal/mole (0.19 eV) between the reorganization energy and the outer-sphere reorganization energy in dichloromethane corresponds to the torsional vibrations of biphenyl. The value of $\Delta\lambda$ in acetonitrile is 13.27 kcal/mole (0.58 eV), which is about 3 times the torsional reorganization energy of biphenyl in dichloromethane. Considering that the viscosity of acetonitrile is about twice that of dichloromethane, and the low frequency torsional reorganization energy is independent of the distance of ion-pair separation⁸, the torsional reorganization energy of biphenyl in acetonitrile is expected to be less than the value in dichloromethane, and therefore, more than 2/3 of $\Delta\lambda$ in acetonitrile is expected to be the reorganization for high frequency molecular vibrations.

CONCLUSION

In the contact ion-pair between 1,2,4,5-tetracyanobenzene anion and cation of biphenyl, 2-methylbiphenyl, or 4-methylbiphenyl, electron transfer occurs in the Marcus inverted region in both acetonitrile and dichloromethane, and the rate of electron transfer is higher in acetonitrile. Based on the analysis presented in this work, an explanation is given as to the increase in the reorganization energy in acetonitrile. According to this picture, ion-pair separation is shorter in acetonitrile, giving rise to a factor of 1.5 increase in the rate of electron transfer in this solvent. In acetonitrile, the outer-sphere reorganization energy is larger, and both high frequency molecular vibrations and low frequency torsional vibrations of biphenyl contribute to the inner-sphere reorganization energy, whereas only torsional vibrations of biphenyl accounts for the inner-sphere reorganization energy in dichloromethane, and, therefore, the rate of electron transfer in acetonitrile is higher than in dichloromethane. In the process, it is shown that inter-ring torsional motion of biphenyl has an effect on the intermolecular electron transfer as is the case for the intramolecular electron transfer⁸, and this effect is to increase the rate of electron transfer in the Marcus inverted region.

REFERENCES

1. Marcus, R. A. and N. Sutin (1985) Electron transfers in chemistry and biology. *Biochimica et Biophysica Acta* **811**, 265-322.
2. Kato, T. and M. Tachiya (1995) Effect of the molecular shapes of donor and the acceptor on electron transfer rates. *Chem. Phys. Letters*. **241**, 463-468.
3. Han, C. (1995) Picosecond ion-pair dynamics following CT excitation of EDA complexes of tetranitromethane with anthracene. *Proc. 3rd Symp. on Laser Spectroscopy*, **4**, 202-212.
4. O'Driscoll, E., J. D. Simon and K. S. Peters (1990) Solvent effects on the energetics of intermolecular charge-transfer reactions. *J. Am. Chem. Soc.* **112**, 7091-7098.
5. Kavarnos, G. (1993) *Fundamentals of Photoinduced Electron Transfer*, pp. 349-350. VCH, New York.
6. Courtneidge, J. L., A. G. Davies, T. Clark and D. Wilhelm (1984) The electron spin resonance spectrum of the biphenyl radical cation. *J. Chem. Soc. Perkin Trans. II*. 1197-1200.
7. Bondi, A. (1964) Van der Waals volumes and radii. *J. Phys. Chem.* **68**, 441-451.
8. Miller, J. R., B. P. Paulson, R. Bal and G. L. Closs (1995) Torsional low-frequency reorganization energy of biphenyl anion in electron transfer. *J. Phys. Chem.* **99**, 6923-6925.
9. Siewert, S. and L. H. Spangler (1995) Substituent effects on torsional barriers: *p*-methoxy- and *p*-methoxy-*p'*-methyl-*trans*-stilbene. *J. Phys. Chem.* **99**, 9316-9324.
10. Rucker, R. L., B. J. Schwartz, M. A. El-Bayoumi and C. B. Harris (1995) Ultrafast dynamics of sterically hindered tetraphenylmethylbutadiene in liquids. *Chem. Phys. Letters*. **235**, 471-478.