

Solvent Effect on the Dynamics of Radical Ion Pair Separation

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Picosecond absorption spectroscopy has been employed in the study of the solvent dynamics of 1,2,4,5-tetracyanobenzene/biphenyl derivative radical ion pairs, and the resulting rates of radical ion pair separation are faster in acetonitrile than in dichloromethane. In an effort to account quantitatively for such solvent effect on the rate of radical ion pair separation, an equation for the rate of radical ion pair separation is introduced, in which the rate depends exponentially on the electrostatic interaction energy in the radical ion pair. In our analysis of the types of electrostatic interaction energy, the electrostatic energy based on the conducting spheres in dielectric continuum was chosen, and the rate equation employing this electrostatic energy provided information on the distance of radical ion pair separation and solvation energy of the radical ion pair, thereby providing quantitative explanation for the observed solvent effect on the rate of radical ion pair separation.

key words: picosecond, charge transfer complex, solution dynamics, radical ion pair, electrostatic energy, solvation energy

INTRODUCTION

The solution dynamics of photogenerated radical ion pairs includes the process of electron transfer and the process of radical ion pair separation. In our previous investigation [1] into the solution dynamics of photogenerated radical ion pairs of 1,2,4,5-tetracyanobenzene(TCB)/biphenyl derivatives, we paid our attention to the process of electron transfer, and showed that the rates of back electron transfer correlated with the Gibbs free energy changes according to the Marcus equation [2], and that the solvent effect on the rate of electron transfer was attributed to the changes in the reorganization energies.

In this study, we focus on the process of radical ion pair separation, the other part of the solution dynamics of photogenerated radical ion pairs. The solvent effect on the rate of electron transfer was manifested in such a way that the rates of electron transfer were higher in acetonitrile than in dichloromethane [1]. Similar to this, the rates of radical ion pair separation were higher in acetonitrile than in dichloromethane [3]. For example, the rate of separation of radical ion pair of TCB/biphenyl was *ca.* 17 times faster in acetonitrile than in dichloromethane.

Factors affecting the rate of radical ion pair separation are mutual diffusion coefficient and the electrostatic energy of the radical ion pair. If we express the mutual diffusion coefficient of the radical ion pair by the sum of the diffusion coefficients of the electron donor and acceptor molecules

[4,5], and use Stokes-Einstein equation for the diffusion coefficient, the increase in the mutual diffusion coefficient of the radical ion pair from dichloromethane to acetonitrile is by a factor of *ca.* 1.24. Hence, the contribution of diffusion coefficient to the observed solvent effect on the rate of radical ion pair separation is minor in comparison to the electrostatic energy.

In order to account for the contribution of the electrostatic energy to the observed solvent effect, we have introduced an equation for the rate of radical ion pair separation in terms of the mutual diffusion coefficient, Onsager distance, the distance of radical ion pair separation, and the electrostatic energy. For the electrostatic energy, we have used the usual Coulomb interaction energy, the electrostatic energy by Tachiya [6], and the electrostatic energy by Suppan [7], and the resulting rates of radical ion pair separation will be compared with the experimental data. In the process, we expect not only to estimate the distance of radical ion pair separation, but also to test the validity of the types of the electrostatic energy used.

MATERIALS AND METHODS

The picosecond transient absorption experiment has been described elsewhere [8]. Our sample includes 1:1 charge transfer complex (CTC) of TCB/biphenyl derivative in acetonitrile and in dichloromethane. TCB was purchased from Fluka, and biphenyl derivatives such as 2-methylbiphenyl, 4-methylbiphenyl, 2-fluorobiphenyl, and 4-fluorobiphenyl were purchased from Aldrich, and they were recrystallized prior to use. Acetonitrile and dichloromethane were purified and kept in Schlenk flasks under argon prior to use. The CTC's were

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excited by the third harmonic (355nm) of the fundamental output (1.06 μm , *ca.* 20 ps) of passively-actively mode locked Nd:YAG laser, and the transient absorption spectra of biphenyl cations were monitored as a function of time via Dual diode array detector and optical time delay. The samples were prepared to give an absorbance of *ca.* 0.55 at 355 nm, and were excited by a laser pulse of *ca.* 1 mJ.

RESULTS AND DISCUSSION

The transient absorption signals of biphenyl and biphenyl derivative cations were analyzed according to a scheme, in which photogenerated radical ion pairs either decay to the ground state CTC via back electron transfer or become free ions via diffusive separation [9], and the resulting rates of radical ion pair separation (k_2 's) are presented in Table 1. As shown in Table 1, the k_2 values in acetonitrile are larger than those in dichloromethane by more than an order of magnitude.

Table 1. The rates of ion pair separation $k_2(\times 10^{-8})$ in CH_3CN and CH_2Cl_2 .
Acceptor: TCB

Donor	$k_2(\times 10^{-8})$ (s^{-1})	
	CH_3CN	CH_2Cl_2
biphenyl	184	10.68
2-methylbiphenyl	236.4	5.38
4-methylbiphenyl	172.8	11.2
2-fluorobiphenyl	163.6	8.64
4-fluorobiphenyl	193.2	14.59

According to Inada et al. [10], the rate of ion pair separation is expressed as

$$k_2 = Dr_c / [r_q^3 \{ \exp(r/r_q) - 1 \}] \quad (1)$$

where D is the diffusion coefficient, r_c is the Onsager distance (15.6 \AA in acetonitrile and 62 \AA in dichloromethane), r_q is the effective quenching distance, and

$$r_c = e^2/(\epsilon\kappa T) \quad (2)$$

where e is the electric charge of the ion, ϵ is the dielectric constant of the solvent, κ is the Boltzmann constant, and T is the temperature in Kelvin.

For the diffusion coefficient, we used the Stokes-Einstein equation

$$D = \kappa T/(6\pi\eta r) \quad (3)$$

where η is the viscosity of the solvent, and van der Waals radius is used for r .

The molecular volumes and their radii calculated using the

Table 2. Molecular volumes (V_m) and radii r .

Molecule	V_m (\AA^3)	r (\AA)
TCB	156.8	3.35
biphenyl	150.2	3.30
2-methylbiphenyl	167.6	3.42
4-methylbiphenyl	167.6	3.42
2-fluorobiphenyl	154.8	3.33
4-fluorobiphenyl	154.8	3.33

van der Waals increments method [11] are listed in Table 2.

Our scheme for the radical ion pair dynamics is based on the contact ion pair, and the distance of radical ion pair separation for the contact ion pair is the sum of the radii of the donor and acceptor molecules. Since the distance of radical ion pair separation in the contact ion pair is expected to be considerably smaller than the Onsager distance, Eq.(1) can be written as follows, if we use the distance of radical ion pair separation (r) in place of the effective quenching distance (r_q).

$$k_2 = (Dr_c / r^3) \exp(-e^2/(\epsilon r)) / \kappa T \quad (4)$$

Equation (4) is in the form of Arrhenius equation, and the energy term in the exponent corresponds to the Coulomb attraction energy between the ions of opposite charges.

Now, we may express the rate of radical ion pair separation as follows.

$$k_2 = (Dr_c / r^3) \exp(C(r) / (\kappa T)) \quad (5)$$

where $C(r)$ is the electrostatic energy between the ions separated by a distance of r .

In this study, we have considered three types of the electrostatic energy. The first type is the usual Coulomb attraction energy

$$C(r) = -e^2 / (\epsilon r) \quad (6)$$

The second type is derived by Tachiya [6] by way of treating the two ions as conducting spheres in dielectric continuum, and it will be referred to as the electrostatic energy by Tachiya.

$$C(r) = -e^2/(\epsilon r) + 0.5e^2 (1-1/\epsilon)(f(r, d) + f(r, a)) \quad (7)$$

where $f(r, a) = \{0.5r/(r^2 - a^2)\} [a/r - 0.5(1 - a^2/r^2) \ln\{(r+a)/(r-a)\}]$ (8)

and $f(r, d) = \{0.5r/(r^2 - d^2)\} [d/r - 0.5(1 - d^2/r^2) \ln\{(r+d)/(r-d)\}]$ (9)

and a and d are the radii of the spherical ions.

The third type is derived by Suppan [7].

$$C(r) = -e^2 [a/(r^2\epsilon_1) + \{1/(r\epsilon)\}(1 - a/r)] \quad (10)$$

where ϵ_1 is the dielectric constant of the solute.

Equation (10), which will be referred to as the electrostatic

energy by Suppan, is based on the effective dielectric constant as follows.

$$1/\epsilon = (1/r)\{2a/\epsilon_1 + (r - 2a)/\epsilon\} \quad (11)$$

Equation (11) results from the consideration that the ion pair and the intervening solvent form a system of capacitors connected in series, and thus, $2a$ corresponds to the thickness of the capacitor formed by the two ions of the same radii a , and $(r - 2a)$ corresponds to the thickness of the capacitor formed by the intervening solvent.

At 25°C, Eqs. (6), (7), and (10) were each plugged into Eq. (5), and the resulting equations were fitted to the experimental values in Table 1 using r as the only adjustable parameter. The results showed that the rates of radical ion pair separation calculated with Eq. (7) were only reasonable, and, therefore, further optimization was carried out with the electrostatic energy by Tachiya. The final results are given in Tables 3 and 4, and we can see that the experimental values of k_2 are reproduced using Eq. (7) in Eq. (5), and that the optimized distance of radical ion pair separation agrees well with the sum of the van der Waals radii for each radical ion pair. Quantitatively, the values of r are longer by *ca.* 16.8 % ,in average, in acetonitrile, but shorter by *ca.* 2.6 % ,in average, in dichloromethane than the sum of the van der Waals radii. Between the values of r in the two solvents, the distance of radical ion pair separation in acetonitrile is

Table 3. The rates of ion pair separation based on electrostatic energy by Tachiya and optimized distance of ion pair separation in acetonitrile. Acceptor: TCB

Donor	r (Å)	Electrostatic energy $C(r)$ (eV)	$k_2(\times 10^{-8})$	
			Coulomb	Suppan
biphenyl	7.81	0.0096	184.07	
2-methylbiphenyl	7.73	0.0158	236.57	
4-methylbiphenyl	7.94	0.0097	172.75	
2-fluorobiphenyl	7.91	0.0077	163.55	
4-fluorobiphenyl	7.79	0.0108	193.12	

Table 4. The rates of ion pair separation based on electrostatic energy by Tachiya and optimized distance of ion pair separation in dichloromethane. Acceptor: TCB

Donor	r (Å)	Electrostatic energy $C(r)$ (eV)	$k_2(\times 10^{-8})$	
			Coulomb	Suppan
biphenyl	6.37	- 0.1094	10.604	
2-methylbiphenyl	6.74	- 0.1220	5.376	
4-methylbiphenyl	6.46	- 0.1064	11.196	
2-fluorobiphenyl	6.46	- 0.1134	8.648	
4-fluorobiphenyl	6.30	- 0.1019	14.614	

ca. 1.37 Å longer in average than in dichloromethane.

In view of an estimation of the separation distance for the solvent separated ion pair at *ca.* 7 ~ 8 Å by Knibbe *et al.* [12], our radical ion pair may correspond to either the solvent separated radical ion pair or the contact radical ion pair; however, this issue cannot be resolved at this time.

In acetonitrile, the electrostatic energies by Suppan and Coulomb in Table 5 are all attractive, and the former is *ca.* 9 times bigger than the latter. On the other hand, the electrostatic energy by Tachiya in Table 3 is repulsive, while approaching zero. In dichloromethane, the values of $C(r)$ in Tables 4 and 6 show that the electrostatic energies by Suppan, by Coulomb, and by Tachiya are in the order of decreasing magnitude, and they are all attractive.

The order of magnitude in the values of $C(r)$ shows correlation with that in the values of k_2 , and such a correlation is merely a reflection that the stronger the attractive energy in the radical ion pair, the slower the rate of radical ion pair separation becomes. In Tables 5 and 6, the attractive electrostatic energy by Suppan is so strong that the corresponding values of k_2 are essentially negligible in either solvent. Also, the Coulomb attraction energy is still strong enough to give k_2 values much less than the experimental values in either

Table 5. The rates of ion pair separation based on electrostatic energy by Coulomb and by Suppan in acetonitrile^a.

Donor	Electrostatic energy $C(r)$ (eV)		$k_2(\times 10^{-8})$	
	Coulomb	Suppan	Coulomb	Suppan
biphenyl	-0.0492	-0.4307	18.63	6.59×10^{-6}
2-methylbiphenyl	-0.0497	-0.4527	18.49	2.83×10^{-6}
4-methylbiphenyl	-0.0484	-0.4308	17.97	6.13×10^{-6}
2-fluorobiphenyl	-0.0486	-0.4235	18.28	8.35×10^{-6}
4-fluorobiphenyl	-0.0493	-0.4353	18.58	5.50×10^{-6}

^aDistances of ion pair separation in Table 3 are used.

Table 6. The rates of ion pair separation based on electrostatic energy by Coulomb and by Suppan in dichloromethane^a.

Donor	Electrostatic energy $C(r)$ (eV)		$k_2(\times 10^{-8})$	
	Coulomb	Suppan	Coulomb	Suppan
biphenyl	-0.2493	-0.7250	0.0457	4.13×10^{-10}
2-methylbiphenyl	-0.2353	-0.6746	0.0651	2.43×10^{-9}
4-methylbiphenyl	-0.2455	-0.7235	0.0498	4.10×10^{-10}
2-fluorobiphenyl	-0.2455	-0.7112	0.0503	6.70×10^{-10}
4-fluorobiphenyl	-0.2520	-0.7426	0.0423	5.50×10^{-10}

^aDistances of ion pair separation in Table 4 are used.

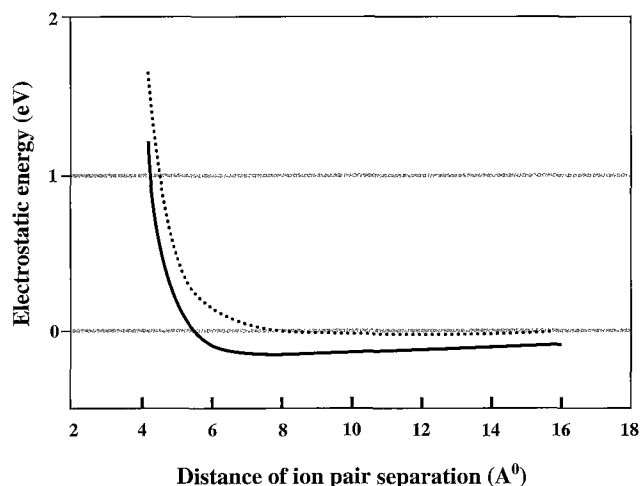


Figure 1. Electrostatic energy by Tachiya as a function of distance of ion pair separation for TCB/biphenyl radical ion pair. (solid line: dichloromethane, dotted line: acetonitrile).

solvent. Typical electrostatic energy plots according to Eq. (7) in acetonitrile and in dichloromethane are presented in Fig. 1 for the radical ion pair of TCB/biphenyl. The repulsive electrostatic energy in acetonitrile (dotted line) becomes attractive beyond 8.2 \AA , and the electrostatic energy remains attractive beyond 5.5 \AA in dichloromethane (solid line). Comparison between the values of $C(r)$ by Eq. (7) in acetonitrile and those in dichloromethane clearly shows the following: the electrostatic energy between the ions in the radical ion pair is repulsive but close to zero in acetonitrile, but the same energy in dichloromethane is attractive and quite appreciable, thereby providing an explanation why the values of k_2 in acetonitrile are more than an order of magnitude larger than in dichloromethane, i.e., the solvent effect on the rate of radical ion pair separation.

In terms of solvation, higher solvation and thus higher stabilization of radical ion pair is expected in a solvent of higher polarity [13]. The expression for the solvation energy $S(r)$ of radical ion pair separated by a distance r is given as follows.

$$S(r) = -C(r) - \frac{e^2}{r} + (0.5e^2/d)(1-1/\epsilon) + (0.5e^2/a)(1-1/\epsilon) \quad (12)$$

Table 7. Solvation energy of ion pair.

Donor	Solvation energy (eV)	
	CH ₃ CN	CH ₂ Cl ₂
biphenyl	2.36	1.70
2-methylbiphenyl	2.26	1.77
4-methylbiphenyl	2.32	1.66
2-fluorobiphenyl	2.37	1.72
4-fluorobiphenyl	2.34	1.65

where the third and the fourth terms on the right hand side are solvation energies of the isolated ions, and the second term is the Coulomb energy between the two bare ions.

The solvation energy calculated by Eq. (12) are given in Table 7, and the solvation energy of radical ion pair is larger in acetonitrile than in dichloromethane. It is interesting to point out that high stabilization of radical ion pair in acetonitrile has an effect of making the electrostatic energy slightly repulsive in the contact ion pair.

CONCLUSION

Introduced is an equation for the rate of radical ion pair separation as a function of the electrostatic energy between the solvated ions in the ion pair, and this equation has been shown to reproduce experimental rates when the electrostatic energy by Tachiya is used for the electrostatic energy term. Other electrostatic energy expressions considered including the Coulomb interaction energy and one by Suppan overestimate the electrostatic interaction energy, and have resulted in much underestimated rates for the radical ion pair separation. To be more specific, the Coulomb interaction energy and the electrostatic energy by Suppan do not account for the solvation energy of the ion pair properly.

From the plots of the electrostatic energy as a function of distance of radical ion pair separation in both acetonitrile and dichloromethane, we have demonstrated the differences in the electrostatic energy between these solvents quantitatively. In particular, the behavior of the electrostatic energy curve in acetonitrile is interesting, since it is repulsive in the range of separation distance for the contact radical ion pair, but almost zero in the range of separation distance for the solvent separated ion pair.

An explanation for the observed differences in the electrostatic energy between these solvents is provided by higher solvation energy of the ion pair in acetonitrile than in dichloromethane. Due to high solvation energy, high stabilization of the radical ion pair is expected in acetonitrile, and such stabilization is shown to cause the electrostatic energy between the solvated ions in the radical ion pair to be even repulsive, although the magnitude of repulsion is very small in this case. On the other hand, stabilization of the radical ion pair is less and the corresponding electrostatic attraction energy is larger in magnitude in dichloromethane. Accordingly, reduced electrostatic attraction in a polar solvent such as acetonitrile is expected to contribute to the fast rate of radical ion pair separation, and the validity of such radical ion pair dynamics has been demonstrated quantitatively in our analysis.

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