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Interaction between 1,1′-Biacenaphthene-2,2′-diyl and Dibromomethane. Decay Kinetics in Mixed Solvents

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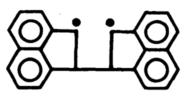
Interaction of the triplet biradical, 1,1′-biacenaphthene-2,2′-diyl (BR) with dibromomethane has been examined by means of transient absorption measurements and kinetic analysis. The absorption spectrum of BR in CH_2Br_2 shows a red shift compared with those in other solvents with various polarities. The spectral result indicates that the red shift is not due to effect of solvent polarity but due to existence of weak electronic interaction acting directly between BR and CH_2Br_2. The nonlinear dependence of decay rates of BR upon $[CH_2Br_2]$ is interpreted in terms of a simple kinetic model of solvation based on solvent replacement between cage and bulk.

In a previous paper, it was reported that BR interacts with halogenated compounds to cause intersystem crossing (ISC) through spin-orbit (SO) interaction enhanced by heavy atoms, prior to chemical reactions.[1] At the same time, a complex formation between BR and the quencher C_2H_5I was suggested from a result of only kinetic analysis for decay rates of BR as a function of $[C_2H_5I]$. However, no spectroscopic evidence for the complex formation was obtained, because the intensity of BR absorption became too weak to observe the spectrum of the complex with increasing the quencher concentration. For the type II biradicals, on the other hand, it has been considered that a complex formation does not contribute to the enhancement of ISC induced by di-*t*-butyl nitroxide or oxygen through spin-spin interaction.[2] BR has two aromatic rings which are apt to form electron donor-acceptor (EDA) complexes with several quenchers. Therefore, in order to elucidate the decay behavior of BR, it will be important to examine whether direct electronic interaction concerns the biradical decay or not.



BR

In this paper we examine in detail the interaction between BR and CH_2Br_2 in the wide range of $[CH_2Br_2]$, since the decay time of BR lies in a measurable time range of our experimental apparatus even in neat solvent of CH_2Br_2. Results give spectral evidence for the existence of an electronic interaction different from solvent polarity effect. In addition, a simple solvation model is proposed for interpreting the decay rates as a function of $[CH_2Br_2]$.

Experimental

The transient absorption spectra were observed by means of a 347 nm ruby-laser photolysis at room temperature.[3] For kinetic analysis, the decay times of BR were measured at several temperatures controlled by circulating thermostated water into a cell holder.

trans-Dimer of acenaphthylene (t-D) as a source material of BR was synthesized and purified by the same methods as described before.[3] Commercially available dibromomethane (Wako, GR grade) was taken out from an ampoule and immediately used without further purification. Zone-refined benzophenone (BP) was used as a triplet sensitizer. The concentrations of t-D and BP were both *ca.* 4×10^{-3} M (1 M=1 mol dm^{-3}). All solutions were degassed by the freeze-pump-thaw method.

Results and Discussion

Figure 1 shows time-resolved absorption spectra obtained for the BP–t-D system in several solvents, where the absorbances in the wavelength region ≤400 nm observed at the earlier time after excitation are omitted for simplicity. The initially observed absorptions at 530 nm and around 450 nm are due to ^{3}BP and ^{3}t-D, respectively.[3] After disappearance of ^{3}BP and ^{3}t-D, BR exhibits characteristic absorption bands at 379±1 nm in toluene (dielectric constant at 20 °C: ε=2.38), pyridine (ε=13.23), chlorobenzene (ε=5.71), and dichloromethane (ε=9.14) as well as in benzene (ε=2.28), dichloromethane, and 1,4-dioxane (ε=2.29) reported previously.[1,3] Although no spectra are given here, BR also shows the absorption maxima at 379±1 nm both in 1,2-dichloroethane (ε=10.66) and bromobenzene (ε=5.39). In dibromomethane solvent (ε=7.04), however, the absorption of BR is red-shifted by *ca.* 5 nm (Fig. 1(5)). Then, it is clear that the red shift is not due to the effect of solvent polarity but due to a weak electronic interaction between BR and CH_2Br_2. An origin of the interaction is probably charge-transfer (CT) interaction as in the systems of anthracene–CCl_4 and *etc.*[4] The quenching of BR by CH_2Br_2 in both CH_2Cl_2 and C_6H_6 were followed by lifetime measurements at 380 nm over the wide range of $[CH_2Br_2]$. Figure 2 shows the Stern-Volmer plots in C_6H_6. Each quenching curve bends downward similar to that by C_2H_5I in C_6H_6 but the deviation from a straight line is remarkable only in much higher concentration region for the quencher CH_2Br_2 than for C_2H_5I. In the present case, therefore, an influence of change of medium properties by the addition of CH_2Br_2 could not be neglected for analyzing the quenching curve. Then, it is supposed that a complex formation is unrealistic, although the curvatures fit fairly well to Eq. 4 in Ref. 1 based on the complex formation mechanism. In order to obtain a more precise information about this circumstance, highly resolved absorption spectra around 380 nm were measured in mixed solvents of CH_2Cl_2 plus CH_2Br_2 and C_6H_6 plus CH_2Br_2 as well as in CH_2Cl_2, C_6H_6, and CH_2Br_2. The results are given in Fig. 3. The spectrum of BR shows gradual red-shift with increasing $[CH_2Br_2]$ in each solvent system (CH_2Cl_2 or C_6H_6). But, no spectrum with two absorption peaks indicating firmly the simultaneous existence of both free and complexed BR was observed in the mixed solvents of any composition of CH_2Br_2 so far as we examined (at 3, 5, and 10 M of CH_2Br_2). Hence, it seems plausible to consider that the red shift and nonlinear quenching curves are due to a

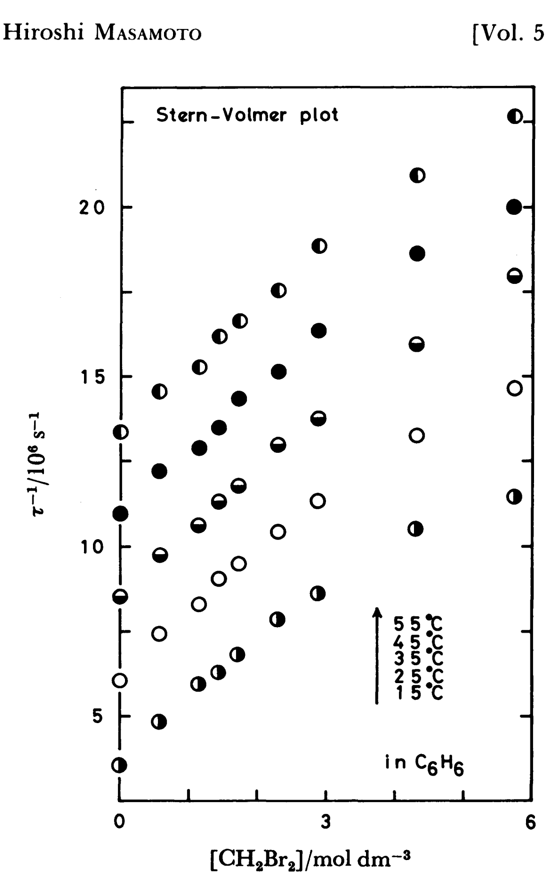


Fig. 2. Stern-Volmer plots for the CH_2Br_2/C_6H_6 system observed at several temperatures. The origin of ordinate is shifted upward by 2.5 each in the order of measurements at 15, 25, 35, 45, and 55 °C.

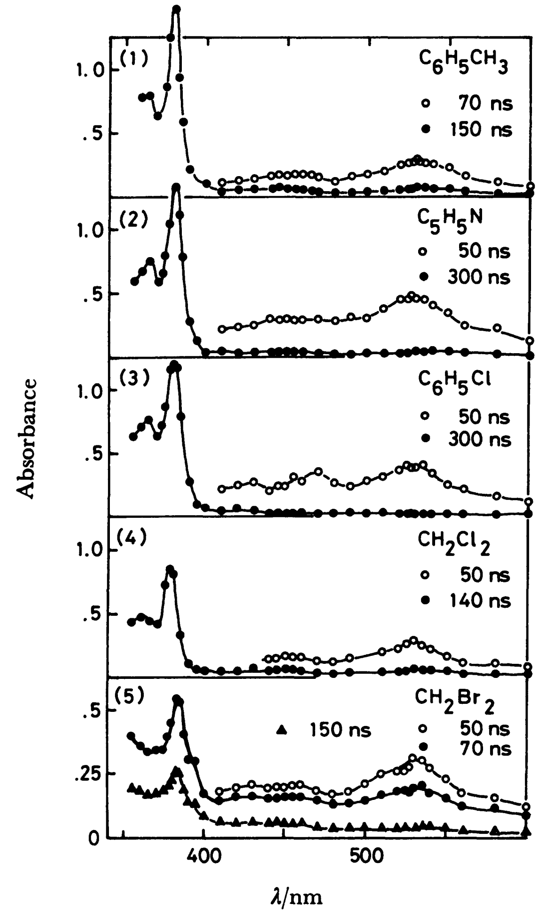


Fig. 1. Transient absorption spectra obtained in the solvents; (1) toluene, (2) pyridine, (3) chlorobenzene, (4) dichloromethane, and (5) dibromomethane. Delay times after the start of laser excitation are indicated in the figure.

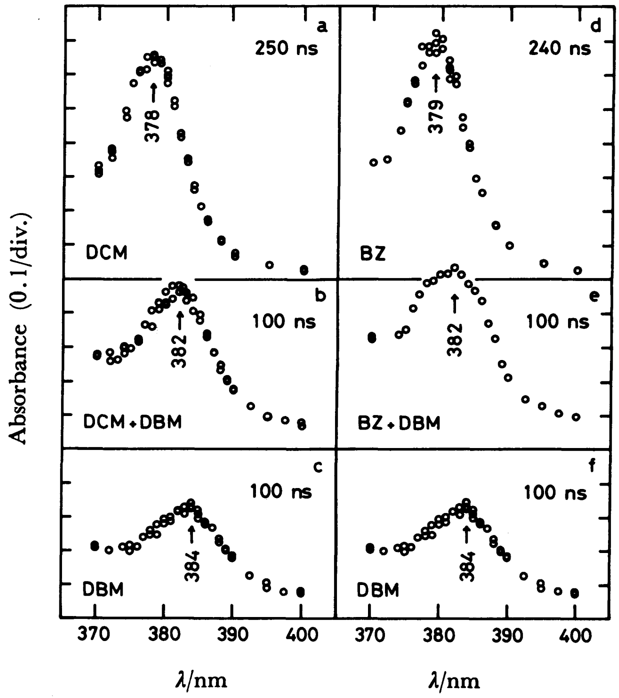


Fig. 3. Absorbance spectra of BR in (a) CH_2Cl_2, (b) $CH_2Cl_2+(10\ M)\ CH_2Br_2$, (c) CH_2Br_2, (d) C_6H_6, (e) $C_6H_6+(10\ M)\ CH_2Br_2$, and (f) CH_2Br_2: DCM = CH_2Cl_2, BZ = C_6H_6, DBM = CH_2Br_2. Delay times after the start of laser excitation are indicated in the figure.

continuous change of properties of medium surrounding BR but not due to formation of a complex with fixed geometry and stoichiometry.

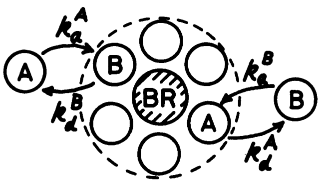
Then, we employ a simple solvation model developed below for analyzing the decay behavior of BR in the mixed solvents. We assume the following conditions in the model: (i) The decay rate constant of BR (τ^{-1}) is determined by the composition of a solvent cage surrounding BR, as expressed by Eq. 1.

$$\tau^{-1} = \theta_A \tau_A^{-1} + \theta_B \tau_B^{-1} \tag{1}$$

where τ_A and τ_B are the lifetimes of BR in neat solvent A and B, respectively and θ_A and θ_B denote the mole fractions of component solvents A and B, respectively, in the solvent cage. Namely, Eq. 1 indicates the additivity between τ_A^{-1} and τ_B^{-1}. (ii) The solvent composition of the cage is proportional to that of the bulk solution in an equilibrium state of solvation;

$$\theta_A/\theta_B = K(\chi_A/\chi_B), \tag{2}$$

where χ_A and χ_B are the mole fractions of A and B, respectively, in the bulk solution and K is the proportionality constant. Equation 2 can be derived by assuming a solvent replacement between one component molecule (A or B) in the solvent cage and another component one (B or A) in the bulk. This situation is schematically shown as follows:



where k_a^i and k_d^i are the rate constants of solvation (or association) to BR and escape (or dissociation) from the cage, respectively, for *i*-th component molecule. When the equilibrium as to the solvent replacement is attained, the rate of solvation will be equal to the rate of escape for each component under the given conditions; *i.e.*, $k_a^A\theta_B[A]=k_d^A\theta_A[B]$ or $k_d^B\theta_B[A]=k_a^B\theta_A[B]$. These two equations are rearranged to Eq. 3;

$$\frac{\theta_A}{\theta_B} = \frac{k_a^A}{k_d^A}\cdot\frac{\chi_A}{\chi_B} = \frac{k_d^B}{k_a^B}\cdot\frac{\chi_A}{\chi_B}. \tag{3}$$

Therefore, K in Eq. 2 is equal to k_a^A/k_d^A or k_d^B/k_a^B. By combining Eq. 1 with Eq. 2 using the relations $\theta_A+\theta_B=1$ and $\chi_A+\chi_B=1$, one can obtain Eq. 4,

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{K\chi_A}{1+(K-1)\chi_A}\left(\frac{1}{\tau_A}-\frac{1}{\tau_B}\right). \tag{4}$$

Equation 4 shows that τ^{-1} is a nonlinear function of χ_A, involving only one unknown parameter K if τ_A and τ_B values are known. Rearrangement of Eq. 4 yields the following linear expressions with respect to $X(\equiv\chi_A/\chi_B)$, which are mathematically equivalent to one another.

$$(\tau^{-1}-\tau_B^{-1})^{-1} = (\tau_A^{-1}-\tau_B^{-1})^{-1}\{1+(KX)^{-1}\} \tag{5}$$

$$X^{-1}(\tau^{-1}-\tau_B^{-1}) = K(\tau_A^{-1}-\tau^{-1}) \tag{6}$$

$$X(\tau^{-1}-\tau_B^{-1})^{-1} = (\tau_A^{-1}-\tau_B^{-1})^{-1}(X+K^{-1}) \tag{7}$$

Equation 5 is identical in form to those derived by Ketelaar *et al.* for analyzing EDA complex formation5) and by Ware *et al.* for exciplex formation.6) Equation 6 is formally identical to those employed by Foster *et al.* for EDA complex systems7) and by Rayner and Wyatt for an acid-base equilibrium in the excited state.8) Equation 7 has also the same form as that described by Scott for EDA complexes.9) These equations are very useful, since they do not need the knowledge about τ_A value.

Here, we analyze the decay times of BR using Eqs. 5, 6, and 7, because we can estimate the lifetime of BR in neat CH_2Br_2 simultaneously with K.10) It was found that the observed lifetimes (τ) in the solvent systems of CH_2Br_2 (component A)/C_6H_6 (component B) and CH_2Br_2 (A)/CH_2Cl_2 (B) follow the relations, Eqs. 5, 6, and 7 with correlation factors better than those in the complex formation model. The results obtained for the CH_2Br_2/C_6H_6 mixture are shown in Fig. 4. By using the method of weighted least square,11) each K and τ_A values obtained from these plots are, as a matter of course, in agreement with one another. Table 1 lists the parameter values obtained at several temperatures. According to the van't Hoff equation, the temperature dependence of K yields ΔH (−6.4±1.1 kJ mol^{-1}) and ΔS (−14±4 J mol^{-1} K^{-1}) for the solvation of CH_2Br_2 in the place of C_6H_6. In the CH_2Br_2 (A)/CH_2Cl_2 (B) mixture, K and τ_A values were also estimated to be 2.5±0.2 and 70±6 ns respectively at 20 °C.

The estimated τ_A values for both solvent systems agree with each other and are in fair agreement with the observed τ_A (84±3 ns at 25 °C).12) Therefore, the kinetic model used here is consistent. The small values of ΔH and ΔS seem to support that this model is more appropriate than the (1:1) complex forma-

TABLE 1. K AND τ_A (in ns) VALUES IN THE $CH_2Br_2(A)/C_6H_6(B)$ SYSTEM AT SEVERAL TEMPERATURES (t in °C)

t	K	τ_A
15	2.6±0.3	71± 8
25	2.6±0.5	64±10
35	2.2±0.5	62±11
45	2.0±0.5	60±10
55	1.9±0.5	58±13

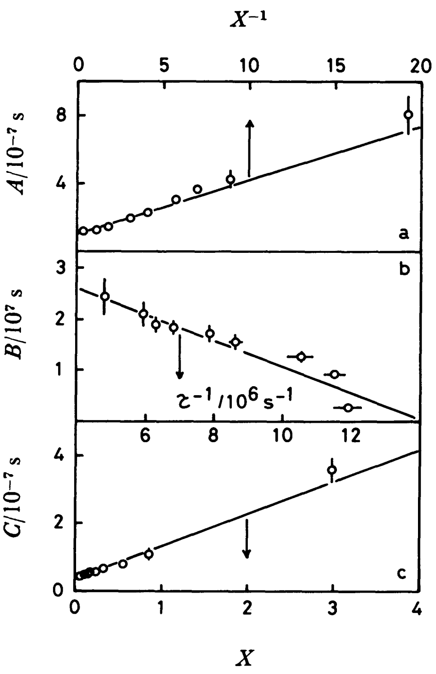


Fig. 4. Plots of the relations corresponding to Eqs. 5, 6, and 7 for the CH_2Br_2/C_6H_6 system at 15 °C. The abbreviated functions in the ordinate:
(a) $A=(\tau^{-1}-\tau_0^{-1})^{-1}$; (b) $B=X^{-1}(\tau^{-1}-\tau_0^{-1})$;
(c) $C=X(\tau^{-1}-\tau_0^{-1})^{-1}$.

tion model which, in most cases, accompanies rather large values of ΔH(*ca.* 20 kJ mol^{-1}) and ΔS(*ca.* 40 J K^{-1} mol^{-1}).[7] It is then implied that BR is likely to be solvated by CH_2Br_2 approximately 2.5 times stronger than by C_6H_6 or CH_2Cl_2, since K is *ca.* 2.5 in both solvent systems at ordinary temperatures. A different approach to solvation has been done for fluorescence frequency shift and quenching in mixed solvents by Lippert and Moll[13] and Kokubun[14] based on the Langmuir adsorption isotherm. They derived a kinetic equation which has also the same form as the present Eq. 5, if ψ or [Q] in their expression is replaced by X.

It should be noted further that a change in hydrodynamic properties of solvent mixtures is not negligible when the viscosity and molecular volume of A are largely different from those of B. If K is replaced by $(\eta_A V_A/\eta_B V_B)\exp\gamma_A$, Eq. 4 becomes identical to the expression derived by Stevens *et al.* based on the cage displacement model.[15] Here, η_i and V_i are the viscosity coefficient and the molecular volume of i-th component solvent, respectively, and γ_A is the index of preferential solvation of A in place of B. In the present cases, $\eta_A V_A/\eta_B V_B=1.26$ for $A=CH_2Br_2$ and $B=C_6H_6$ at 25 °C and $\eta_A V_A/\eta_B V_B=2.53$ for $A=CH_2Br_2$ and $B=CH_2Cl_2$ at 20 °C. By using these values, $\gamma_A=0.72$ for the CH_2Br_2/C_6H_6 system and $\gamma_A=-0.011$ for the CH_2Br_2/CH_2Cl_2 system are obtained. Accordingly, the preferential solvation by CH_2Br_2 should be taken into account for the BR quenching in the CH_2Br_2/C_6H_6 system and need not almost completely for that in the CH_2Br_2/CH_2Cl_2 system, in addition to the change of hydrodynamic properties.

As for BR decay, an important fact is that there exists the direct electronic interaction between BR and CH_2Br_2, which is able to cause the red shift of the BR spectrum but not so strong as a complex formation is confirmed spectroscopically. In conclusion, it is considered that the BR quenching is enhanced by SO interaction[1] perturbed by the weak electronic interaction, probably CT interaction, between BR and CH_2Br_2 in the solvent cage.

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10) This analysis allows us to compare the estimated τ_A value with the observed one. Analysis by Eq. 4 was not chosen for fear that the observed lifetime τ_A in CH_2Br_2 might involve the contribution of the decay time of precursor ^{3}t-D.

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