The Journal of Physical Chemistry A

VOLUME 102, NUMBER 25, JUNE 18, 1998

ARTICLES

Exothermic Triplet−Triplet Excitation Transfer in Solution under High Pressure

Masami Okamoto

Faculty of Engineering and Design, Kyoto Institute of Technology Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received: January 16, 1998; In Final Form: April 8, 1998

The rate constants, k_q, for the exothermic energy transfer from the triplet states of benzophenone (^{3}BZP*) and triphenylene (^{3}TPh*) to naphthalene (N), and also from the singlet sate of triphenylene (^{1}TPh*) to benzophenone (BZP), were measured in polar and nonpolar solvents as a function of pressure at 25 °C. For all the systems of the donor−acceptor pairs, the plots of k_q against $1/\eta$ showed downward curvature. For ^{3}BZP*/N in acetonitrile, methanol, and *n*-hexane, the plots of ln k_q against ln η were linear with the slopes larger than −1, while for ^{3}BZP*/N in toluene and for ^{1}TPh*/BZP in *n*-hexane they showed downward curvature. However, the plots of $1/k_q$ against η were linear with positive intercepts for all the systems examined. It was also found that the plot of $1/k_q$ against η/T, in which k_q was measured for ^{3}BZP*/N as a function of temperature and pressure in *n*-hexane, is linear. These results were interpreted by the energy transfer mechanism via the formation of an encounter complex between the donor and acceptor molecules, and it was concluded that the exothermic energy transfer examined in the present study is not fully diffusion-controlled but competes with a diffusion process that is expressed by a modified Debye equation. The bimolecular rate constants for the energy transfer, k_{bim} ($=k_{diff}k_{et}/k_{-diff}$), were in the range of $(1-10) \times 10^{10}$ M^{-1} s^{-1} depending on solvent. The pressure dependence of k_{et} is discussed from the experimental fact that k_{bim} is independent of solvent viscosity changed by varying pressure and temperature in all the systems examined.

Introduction

Because of photochemical and photobiological importance, the bimolecular exothermic triplet−triplet excitation transfer has been extensively studied. The exothermic energy transfer process, which is due to an electron exchange mechanism developed by Dexter, is often believed to occur upon every encounter between a donor molecule (^{3}D*) in the electronically excited triplet state and an acceptor molecule (A) in the ground state.[1]

$$^3\mathrm{D}^* + \mathrm{A} \xrightarrow{k_q} \mathrm{D} + {}^3\mathrm{A}^*$$

When the solute molecules move in a continuum medium with viscosity η (P unit), the diffusion-controlled rate constant, k_{diff} (M^{-1} s^{-1}), is expressed by

$$k_{diff} = 8RT/\alpha\eta \tag{1}$$

where α is 3000 and 2000 for the stick and slip boundary limits, respectively.[2] The conclusion that the exothermic triplet−triplet energy transfer is diffusion-controlled ($k_q \sim k_{diff}$) is mainly due to the $1/\eta$ dependence of k_q upon changing temperature or solvent.[3]

The deviation of k_q from eq 1, which is observed in alcohol and viscous hydrocarbon solvents, has been often attributed to the viscosity dependence of the diffusion coefficient in solution, and modified empirical equations were proposed.[4]

On the other hand, Wagner and Kochevar suggested that energy transfer competes with diffusion apart of the encounter pairs in the quenching of the triplet state of valerophenone by 2,5,-dimethyl-2,4-hexadiene by the stationary-state measurements.[5] The same conclusion was reported on the basis of the

S1089-5639(98)00806-8 CCC: $15.00

TABLE 1: Energies of the Lowest Singlet, S_1, and Triplet, T_1, States and van der Waals Radii, r_w, of Solutes

donor/acceptor	S_1,[a] kJ mol^{-1}	T_1,[a] kJ mol^{-1}	r_w,[b] nm
naphthalene (N)	385	277	0.309
benzophenone (BZP)	314	289	0.345
triphenylene (TPh)	347	280	0.365

[a] Reference 8. [b] Estimated values according to the method by Bondi.[9]

evidence obtained from the quenching of thermally produced acetone triplets by acceptors.[6] Subsequently, the rate constants for the quenching of singlet and triplet states of aromatic molecules by a series of azo compounds with varying steric properties were measured, and the significance of the contribution of steric hindrance to these collisional exothermic energy transfer processes was pointed out.[7] This is another suggestion that the rate constant for exothermic energy transfer by the exchange mechanism is comparable to that for diffusional separation of encounter pairs in solution, and further the significance of the steric hindrance implies that the observed rate processes for the energy transfer involve the distance dependence between the donor and acceptor pairs in solvent cage as well as those for translational diffusion.

Application of high pressure is a useful technique for the study of bimolecular diffusion-controlled reactions since the viscosity of the solvent can be changed without varying solvent and temperature. In this paper, the rate constants for exothermic energy transfer from the triplet states of benzophenone and triphenylene to naphthalene, where the lowest triplet states of the donors are $^3n\pi^*$ and $^3\pi\pi^*$, respectively, are measured as a function of pressure up to 400 MPa in order to provide some insight into the mechanism, and the contribution of diffusion to the energy transfer is investigated from the pressure-induced solvent viscosity dependence. One of the aims of the present work is to attempt the separation of the observed rate constants into contributions of translational diffusion and energy transfer processes. Therefore, rate constants are also measured for energy transfer from the singlet state of triphenylene to benzophenone, whose system might be expected to show similar viscosity dependence to the triplet−triplet energy transfer for diffusion processes but a different energy transfer rate. The energies for the lowest singlet and triplet states of donors and acceptors[8] examined in the present work are listed in Table 1, together with values of their van der Waals radii.[9]

Experimental Section

Benzophenone (Wako Pure Chemical Industries Ltd.) and triphenylene (Tokyo Kasei Kogyo Co., Ltd.) of guaranteed grade were recrystallized three times from benzene and ethanol, respectively. Zone-refined naphthalene (Tokyo Kasei Kogyo Co., Ltd.) was used as received. Acetonitrile, methanol, toluene, and *n*-hexane of spectroscopic grade (Dojin Pure Chemicals Co.) were used as received.

Transient absorption measurements at high pressure were performed by using an 8-ns pulse from a nitrogen laser (337.1 nm) for excitation and a xenon analyzing flash lamp positioned at right angles to the direction of the excitation pulse. The analyzing light intensities were monitored by a Hamamatsu R928 photomultiplier through a Ritsu MC-25N monochromator and the signal was digitized by using a Hewlett-Packard 54510A digitizing oscilloscope. Fluorescence decay curve measurements at high pressure were performed at right angles by using a 0.3-ns pulse from a PRA LN103 nitrogen laser for excitation. The fluorescence intensities were measured with a Hamamatsu R1635-02 photomultiplier through a Ritsu MC-25NP monochromator and the resulting signal was digitized by using a LeCroy 9362 digitizing oscilloscope. All data were analyzed by using a NEC microcomputer interfaced to the digitizers. Details about the associated high-pressure techniques have been described elsewhere.[10,11]

Concentrations of benzophenone and triphenylene for transient absorption measurements were adjusted to give ca. 0.8 absorbance (1 cm cell) at 337.1 nm, and that of triphenylene for fluorescence decay measurements was adjusted to give less than 0.1 absorbance at the maximum absorption wavelength in order to minimize self-absorption effects. Sample solutions were deoxygenated by bubbling nitrogen gas under a nitrogen atmosphere. Changes in concentration of the acceptor due to bubbling were corrected for by weighing the sample solution. The increase in concentration due to the application of high pressure was corrected for by using the compressibility of solvent.[12−15]

Temperature was controlled within 0.2 °C. Pressure was measured with a calibrated manganin wire or with a Minebea STD-5000K strain gauge.

Results

Rate Constants for Energy Transfer from the Benzophenone Triplet to Naphthalene. Energy transfer from benzophenone triplets (^{3}BZP*) to naphthalene (N) to yield naphthalene triplets (^{3}N*) in solvent RH is expressed by[16]

$$\mathrm{BZP} \xrightarrow{h\nu} {}^1\mathrm{BZP}^* \rightarrow {}^3\mathrm{BZP}^*$$

$$ {}^3\mathrm{BZP}^* + \mathrm{RH} \xrightarrow{k_r} \text{ketyl radical} + \mathrm{R} \tag{1}$$

$$ {}^3\mathrm{BZP}^* + \mathrm{N} \xrightarrow{k_q} \mathrm{BZP} + {}^3\mathrm{N}^* \tag{2}$$

According to this scheme, the time dependence of the observed absorbance at time t, $A(t)$, is given by

$$A(t) = A(\infty) + \{A(0) - A(\infty)\} \exp(-k_{obs}t) \tag{3}$$

where

$$k_{obs} = k_r[\mathrm{RH}] + k_q[\mathrm{N}] \tag{4}$$

In eqs 3 and 4, $A(0)$ and $A(\infty)$ are the initial and residual absorbances, respectively, and [N] and [RH] are the concentrations of N and RH, respectively. The decay curves of ^{3}BZP* obtained at 530 nm were analyzed satisfactorily by eq 3 in the experimental conditions examined. To confirm the kinetic scheme (eqs 1 and 2) further, $A(t)$ at 415 nm due mainly to ^{3}N* was also measured at 0.1 MPa and analyzed by eq 3, and it was found that the values of k_{obs} agreed within 5% with those observed at 530 nm. Figure 1 shows typical examples of plots of k_{obs} against [N]. Rate constants, k_q, for energy transfer were obtained from the least-squares slopes, and those for hydrogen abstraction, k_r, were determined from the intercepts of the least-squares plots and [RH] at each pressure. The pressure dependence values of k_r obtained in toluene, methanol, and *n*-hexane are in good agreement with those of our previous work.[11] The values for k_q in toluene, methanol, and acetonitrile at 25 °C and in *n*-hexane at 15, 25, and 35 °C are listed in Tables 2 and 3, respectively, together with those of solvent viscosity.[12−15]

Rate Constants for Energy Transfer from Triphenylene Triplet to Naphthalene. The rise time of the absorbance at 415 nm was measured as a function of the concentration of N

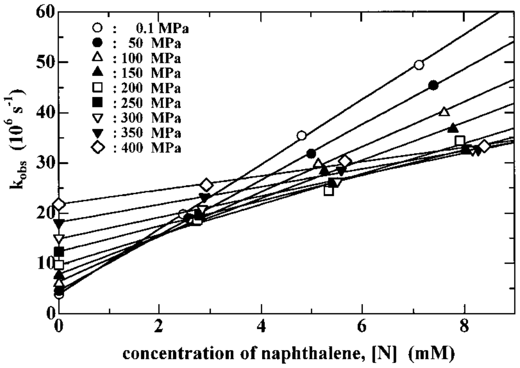

Figure 1. Plots of k_{obs} against the concentration of naphthalene, [N], in toluene at 25 °C.

in *n*-hexane for pressures up to 400 MPa:

$$^3\text{TPh}^* + \text{N} \xrightarrow{k_q} \text{TPh} + {}^3\text{N}^* \tag{5}$$

Values of k_{obs} were determined by curve-fitting to eq 3 in which eq 4 is replaced by the equation $k_{obs} = k_q[\text{N}]$, although the transient absorption spectra of ^{3}TPh* and ^{3}N* are partially overlapping.[16,17] Plots of k_{obs} against six concentrations of N show good linearity through the origin at each pressure. The rate constants, k_q, were determined from the least-squares slopes of the plots. The values of k_q are listed in Table 4.

Rate Constants for Energy Transfer from Triphenylene Singlet to Benzophenone. The fluorescence decay curves of triphenylene (TPh) were measured as a function of [BZP] in *n*-hexane for pressures up to 400 MPa at 25 °C and were found to be monoexponential for the experimental conditions examined. The singlet lifetime, τ_0, of TPh in the absence of BZP is almost independent of pressure (ca. 36 ns). The quenching constants, k_q, were determined from the least-squares slopes of the plots of $1/\tau$ against four concentrations of BZP according to

$$1/\tau - 1/\tau_0 = k_q[\text{BZP}] \tag{6}$$

where τ is the lifetime at a specific concentration of [BZP]. The values of k_q are listed in Table 4, together with those of the ^{3}TPh*/N system in *n*-hexane at 25 °C.

Discussion

As seen in Tables 2−4, the rate constants, k_q, for energy transfer decrease strongly with increasing pressure in all solvents examined. The apparent activation volumes, $\Delta V_q^{\ddagger}$, evaluated by eq 7 are listed in Table 5, together with those of the solvent viscosity.

$$\left(\frac{\partial \ln k_q}{\partial P}\right)_T = -\frac{\Delta V_q^{\ddagger}}{RT} \tag{7}$$

It can be seen in Table 5 that the value of $\Delta V_q^{\ddagger}$ does not depend on solvent polarity, but seems to correlate with those for solvent viscosity, $\Delta V_\eta^{\ddagger}$. The observation suggests that the energy transfer is qualitatively diffusion-controlled, in agreement with conclusions reported by earlier workers.[3] However, it is noted from the data listed in Tables 2 and 3 that the values of k_q are significantly smaller than those of k_{diff} calculated with the use of eq 1 ($\alpha = 2000$ or 3000) in solvents examined, especially at lower pressures. Similar results were found for the ^{3}TPh*/N and ^{1}TPh*/BZP systems (Table 4). These results imply that the energy transfer processes are not fully diffusion-controlled or that the solvent viscosity dependence of k_{diff} is not correctly described by eq 1, as pointed out by earlier workers.[4]

Diffusion-Controlled Quenching. The rate constant, k_{diff}, for bimolecular diffusion-controlled reaction between the electronically excited state of the donor, D*, and the ground state of the acceptor, A, is given by eq 8 in a solvent with the relative diffusion coefficient, $D_{D^*A}(=D_{D^*} + D_A)$, when the transient terms can be neglected:[2]

$$k_{diff} = 4\pi r_{D^*A} D_{D^*A} N_A / 10^3 \tag{8}$$

where r_{D^*A} and N_A are the encounter distance and Avogadro's number, respectively. The solvent viscosity dependence of D_i (i = D* or A) is expressed by the Einstein relation (eq 9) using the friction coefficient, ζ_i, between the solvent and the solute molecule, i:

$$D_i = k_B T / \zeta_i \tag{9}$$

where k_B is the Boltzmann constant. Since the hydrodynamic friction, ζ_i^H, is given by $\zeta_i^H = f_i \pi \eta r_i$ (Stokes' law), we can obtain the Stokes−Einstein (SE) equation (eq 10) by combining with eq 9:

$$D_i^{SE} = k_B T / f_i \pi \eta r_i \tag{10}$$

where r_i is the radius of the spherical solute molecules and $f_i = 6$ and 4 for the stick and slip boundary limits, respectively. However, the breakdown of the SE equation has been often observed for diffusion in solution, and the corrections were attempted. Among them, an empirical equation proposed by Spernol and Wirtz[4] has been applied successfully to the diffusion-controlled radical self-termination reactions[18] and exothermic triplet excitation transfer.[1c,3c] According to this approach, the diffusion coefficient, D_i^{SW}, is expressed by introducing a microfriction factor, f_i^{SW}, as a correction factor:

$$D_i^{SW} = k_B T / 6\pi f_i^{SW} \eta r_i \tag{11}$$

where

$$f_i^{SW} = (0.16 + 0.4 r_i/r_S)(0.9 + 0.4 T_S^r - 0.25 T_i^r) \tag{12}$$

In eq 12, the first parenthetical quantity depends only on the solute-to-solvent size ratio, (r_i/r_S). The second parenthetical quantity involves the reduced temperatures, T_S^r and T_i^r, of solvent and solute, respectively, which can be calculated by using the melting point, T_{mp}, and boiling point, T_{bp}, of the solvent or solute at the experimental temperature, T, according to

$$T_{i(S)}^{\ r} = [T - T_{mp(S)}]/[T_{bp(S)} - T_{mp(S)}] \tag{13}$$

From eqs 8 and 11, the diffusion-controlled rate constant, k_{diff}, by Spernol and Wirtz approximation is given by

$$k_{diff} = \frac{2RTr_{D^*A}}{3000\eta}\left(\frac{1}{f_{D^*}^{\ SW} r_{D^*}} + \frac{1}{f_A^{\ SW} r_A}\right) \tag{14}$$

Comparing with eq 1, α^{SW} is given by

$$\alpha^{SW} = \frac{1.2 \times 10^3}{r_{D^*A}}\left(\frac{1}{f_{D^*}^{\ SW} r_{D^*}} + \frac{1}{f_A^{\ SW} r_A}\right)^{-1} \tag{15}$$

TABLE 2: Solvent Viscosity, η, and Rate Constants, k_q, for the ^{3}BZP*/N System in Toluene, Methanol, and Acetonitrile at 25 °C

	toluene		methanol		acetonitrile	
pressure, MPa	η, 10^{-2} P	k_q, 10^9 M^{-1} s^{-1}	η, 10^{-2} P	k_q, /10^9 M^{-1} s^{-1}	η, 10^{-2} P	k_q, 10^9 M^{-1} s^{-1}
0.1	0.556	6.44 ± 0.07	0.543	8.97 ± 0.05	0.343	9.84 ± 0.18
50	0.785	5.50 ± 0.04	0.669	7.33 ± 0.09	0.454	8.40 ± 0.29
100	1.063	4.47 ± 0.09	0.794	6.66 ± 0.08	0.560	8.01 ± 0.24
150	1.400	3.77 ± 0.10	0.917	5.43 ± 0.13	0.658	7.06 ± 0.08
200	1.814	3.10 ± 0.04	1.041	5.40 ± 0.10	0.750	6.19 ± 0.21
250	2.333	2.53 ± 0.02	1.164	4.53 ± 0.07	0.849	5.49 ± 0.15
300	2.996	2.13 ± 0.05	1.287	3.95 ± 0.09	0.974	5.22 ± 0.07
350	3.849	1.76 ± 0.06				
400	4.939	1.41 ± 0.07				

TABLE 3: Solvent Viscosity, η, and Rate Constants, k_q, for the ^{3}BZP*/N System at 15, 25, and 35 °C in *n*-Hexane

	15 °C		25 °C		35 °C	
pressure, MPa	η, 10^{-2} P	k_q, 10^9 M^{-1} s^{-1}	η, 10^{-2} P	k_q, 10^9 M^{-1} s^{-1}	η, 10^{-2} P	k_q, 10^9 M^{-1} s^{-1}
0.1	0.325	9.64 ± 0.22	0.294	10.4 ± 0.2	0.267	10.7 ± 0.4
50	0.523	7.81 ± 0.16	0.472	7.47 ± 0.45	0.429	9.19 ± 0.35
100	0.716	6.24 ± 0.24	0.650	5.79 ± 0.52	0.594	7.29 ± 0.31
150	0.940	5.27 ± 0.17	0.849	5.24 ± 0.15	0.772	5.91 ± 0.33
200	1.180	3.93 ± 0.22	1.063	4.33 ± 0.29	0.964	5.70 ± 0.16
250	1.463	3.60 ± 0.10	1.310	3.77 ± 0.45	1.181	5.05 ± 0.14
300	1.810	3.14 ± 0.17	1.610	2.92 ± 0.46	1.443	4.45 ± 0.30
350	2.203	2.61 ± 0.05	1.948	2.72 ± 0.45	1.736	3.33 ± 0.15
400	2.687	1.75 ± 0.11	2.368	2.69 ± 0.23	2.104	2.89 ± 0.19

TABLE 4: Rate Constants, k_q, for the ^{3}TPh*/N and ^{1}TPh*/BZP Systems in *n*-Hexane at 25 °C

	k_q, 10^9 M^{-1} s^{-1}	
pressure, MPa	^{3}TPh*/N	^{1}TPh*/BZP
0.1	10.1 ± 0.5	15.4 ± 0.2
50	7.14 ± 0.23	11.9 ± 0.3
100	5.99 ± 0.16	9.23 ± 0.20
150	5.05 ± 0.12	7.57 ± 0.20
200	4.60 ± 0.23	6.39 ± 0.20
250	3.99 ± 0.20	5.21 ± 0.06
300	3.62 ± 0.19	4.34 ± 0.07
350	2.89 ± 0.15	3.69 ± 0.10
400	2.69 ± 0.17	3.08 ± 0.08

The $1/\eta$ dependence of the diffusion coefficient has often failed.[4c,19] This breakdown of the $1/\eta$ dependence is recognized as the deviation from the continuum model that arises as a result of short-range interactions between the solute and solvent molecules such as translational and rotational coupling. In such cases, the expression for ζ_i is phenomenologically given by

$$\zeta_i \propto \eta^{\gamma_i} \tag{16}$$

The viscosity exponent, γ_i, which is normally less than unity, depends on the solute size but is independent of solvent.[19] Assuming that $\gamma_{D^*} = \gamma_A$ ($= \gamma$) since their sizes are similar (Table 1), the diffusion-controlled rate constant, k_{diff}, is described by

$$k_{diff} = A\eta^{\gamma} \tag{17}$$

where A is assumed to be a constant that is invariant with η. In fact, eq 17 has been used to express the observed rate constants for chemical reactions that are influenced by solvent viscosity.[20]

Pressure and Pressure-Induced Viscosity Dependence of k_q. Energy transfer for the ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP systems with different quenching abilities was concluded to be qualitatively diffusion-controlled as mentioned above. In this section, the contribution of the diffusion to the energy transfer is discussed mainly from the pressure and pressure-induced viscosity dependence of k_q.

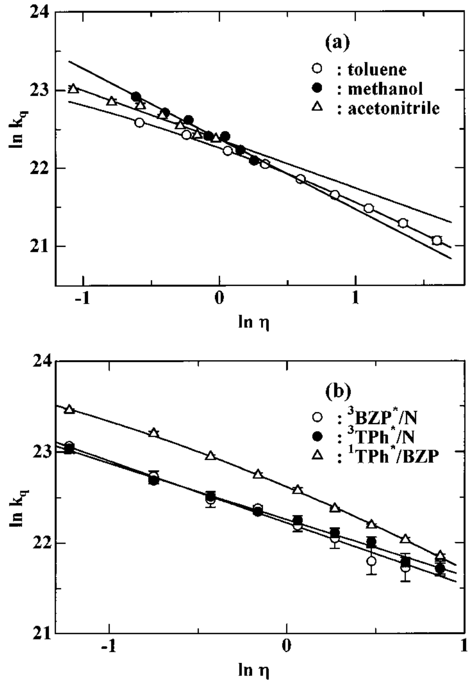

Figure 2. Plots of ln k_q against ln η (a) for ^{3}BZP*/N in three solvents and (b) for ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP in *n*-hexane at 25 °C.

Self-diffusion coefficients are inversely proportional to the pressure-induced solvent viscosity, η, for a number of liquids.[21] Even for methanol-*d*, this relationship seems roughly valid, although the value of f_i in eq 10 decreases slightly with increasing pressure.[22]

Dymond and Woolf [23] measured the diffusion coefficients, *D*, of benzene, toluene, and benzo[*a*]pyrene in *n*-hexane for pressures up to 384 MPa at 25 °C. Plots of their *D* values against $1/\eta$ (Table 3) give good linearity. Since the van der Waals radii of the solutes can be estimated to be 0.268, 0.287, and 0.374 nm for benzene, toluene, and benzo[*a*]pyrene,

TABLE 5: Activation Volumes for Solvent Viscosity, ΔV_η, and for k_q, $\Delta V_q^\ddagger$ of the ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP Systems at 25 °C and 0.1 MPa

solvent	$\Delta V_\eta^{\ddagger,a}$ cm^{3}mol^{-1}	$\Delta V_q^\ddagger$, cm^3 mol^{-1}			r_w,^{b} nm
		^{3}BZP*/N	^{3}TPh*/N	^{1}TPh*/BZP	
toluene	17.6	8.9 ± 0.3			0.287
methanol	11.4	7.6 ± 1.4			0.202
acetonitrile	16.1	5.9 ± 0.9			0.224
n-hexane	23.8	13.4 ± 1.2	10.9 ± 1.2	12.1 ± 0.4	0.301

[a] The values of $\Delta V_\eta^\ddagger$ were determined from $(\partial \ln \eta/\partial P)_T = \Delta V_\eta^\ddagger/RT$. [b] Estimated values according to the method by Bondi.[9]

TABLE 6: Values of α and the Bimolecular Rate Constant, $k_{bim}(=k_{diff}k_{et}/k_{-diff})$, for the ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP Systems in Various Solvents at 25 °C

solvent	α			$k_{bim}/10^{10}$ M^{-1} s^{-1}		
	^{3}BZP*/N	^{3}TPh*/N	^{1}TPh*/BZP	^{3}BZP*/N	^{3}TPh*/N	^{1}TPh*/BZP
toluene	2500 ± 30 (2110/1760)^b			1.1 ± 0.1		
methanol	3590 ± 200 (2850/2250)^b			9.4 ± 8.4		
acetonitrile	2970 ± 150 (2490/2100)^b			2.1 ± 0.3		
n-hexane	2840 ± 190^a (2110/1680)^b	2580 ± 100 (2250/1690)^b	2510 ± 20 (2440/1890)^b	1.4 ± 0.3^a	1.3 ± 0.2	3.9 ± 0.2

[a] Mean values of α and k_{bim} were determined to be 3100 ± 120 and (2.2 ± 0.4) × 10^{10} M^{-1} s^{-1}, respectively, from the data at 15, 25, and 35 °C for pressures up to 400 MPa (see text). [b] Values of α in parentheses represent α^{SW}(full)/α^{SW}(truncated) estimated by eq 15 (see text).

respectively,[9] the values of f_i in eq 10 from the least-squares slopes of the plots of D against $1/\eta$ were determined to be 2.99 ± 0.06, 3.04 ± 0.07, and 3.87 ± 0.11 for benzene, toluene, and benzo[*a*]pyrene in *n*-hexane, respectively. The value of f_i obtained is clearly smaller than that expected for the slip boundary limit ($f_i = 4$) for benzene and toluene but increases with increasing size of the solute. Such a size dependence of f_i has been often found in the measurements of the diffusion coefficient as a function of temperature at 0.1 MPa.[19] However, plots of k_q against $1/\eta$ for the data in Tables 2−4 show significant downward curvature for all the systems examined.

Another test for fully diffusion-controlled reaction is provided by the use of eq 17. The plots of ln k_q against ln η, which are shown in Figure 2, are almost linear for ^{3}BZP*/N in methanol (ln $A = 22.37 \pm 0.02$, $\gamma = 0.91 \pm 0.05$), acetonitrile (ln $A = 22.37 \pm 0.03$, $\gamma = 0.63 \pm 0.04$), and *n*-hexane (ln $A = 22.22 \pm 0.02$, $\gamma = 0.68 \pm 0.03$ at 25 °C) and for ^{3}TPh*/N in *n*-hexane (ln $A = 22.26 \pm 0.01$, $\gamma = 0.62 \pm 0.02$). However, as seen for ^{3}BZP*/N in toluene (Figure 2a) with larger pressure-induced viscosity dependence and also for ^{1}TPh*/BZP in *n*-hexane with higher k_q (Figure 2b), they show significant downward curvature. Consequently, these results, together with those described in the previous paragraph, suggest that the energy transfer for the systems of ^{3}BZP*/N in toluene and ^{1}TPh*/BZP in *n*-hexane is not fully diffusion-controlled.

In general, exothermic energy transfer from D* to A may occur via an encounter complex, ^{3}(DA)*, as follows:

$$^3\mathrm{D}^* + \mathrm{A} \underset{k_{-\mathrm{diff}}}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}} {}^3(\mathrm{DA})^* \xrightarrow{k_{\mathrm{et}}} \mathrm{D} + {}^3\mathrm{A}^* \tag{18}$$

According to eq 18, the observed rate constant, k_q, is given by

$$k_q = \frac{k_{diff}k_{et}}{k_{-diff} + k_{et}} \tag{19}$$

In eq 19, $k_q = k_{diff}$ if $k_{et} \gg k_{-diff}$ and $k_q = k_{diff}k_{et}/k_{-diff}$ if $k_{-diff} \gg k_{et}$; the energy transfer occurs upon every encounter for the former limiting case, whereas its efficiency is less than unity for the latter case.

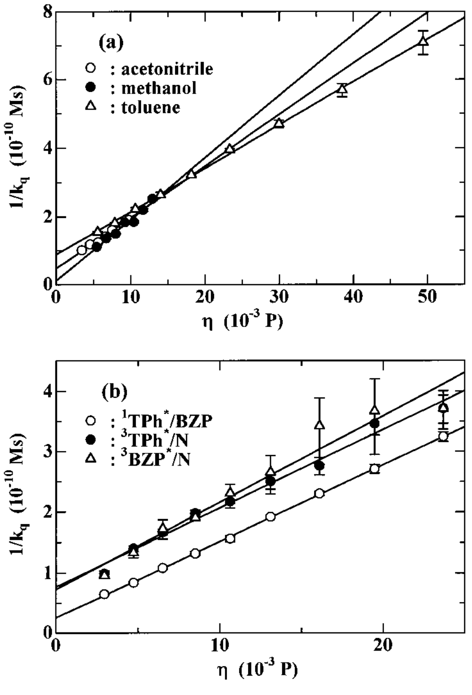

Figure 3. Plots of $1/k_q$ against η for (a) ^{3}BZP*/N in three solvents and (b) for ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP in *n*-hexane at 25 °C.

If k_{diff} is assumed to be expressed by a modified Debye equation (eq 1) since the diffusion coefficient is inversely proportional to the pressure-induced solvent viscosity as mentioned above, one may derive eq 20 from eqs 1 and 19:

$$\frac{1}{k_q} = \frac{k_{-diff}}{k_{diff}k_{et}} + \frac{\alpha}{8RT}\eta \tag{20}$$

Plots of $1/k_q$ against η are shown in Figure 3. As can be seen in these figures, the plots are linear in all systems examined. The values of the bimolecular rate constant for the energy transfer, $k_{bim}(=k_{diff}k_{et}/k_{-diff})$, and α determined by the least-squares plots are listed in Table 6, together with those of α^{SW} evaluated by eq 15.[24] The buildup and decay times of energy

TABLE 7: Values of Pressure Coefficients for the Bimolecular Rate Constant, $(\partial \ln k_{bim}/\partial P)_T$, and of $\Delta V_{et}^{\ddagger} - \Delta V_{-diff}$ for the ^{3}BZP*/N, ^{3}TPh*/N, and ^{1}TPh*/BZP Systems in Various Solvents at 25 °C

	^{3}BZP*/N		^{3}TPh*/N		^{1}TPh*/BZP	
solvent	$(\partial \ln k_{bim}/\partial P)_T$, 10^{-4} MPa^{-1}	$\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger}$, cm^3 mol^{-1}	$(\partial \ln k_{bim}/\partial P)_T$, 10^{-4} MPa^{-1}	$\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger}$, cm^3 mol^{-1}	$(\partial \ln k_{bim}/\partial P)_T$, 10^{-4} MPa^{-1}	$\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger}$, cm^3 mol^{-1}
toluene	-0.9 ± 1.4	-17.4 ± 0.4				
methanol	-7.5 ± 14.4	-9.5 ± 3.6				
acetonitrile	-0.4 ± 3.3	-16.0 ± 0.9				
n-hexane	-7.9 ± 3.0	-21.8 ± 0.8	-0.6 ± 3.1	-23.6 ± 0.8	1.0 ± 1.4	-23.5 ± 0.4

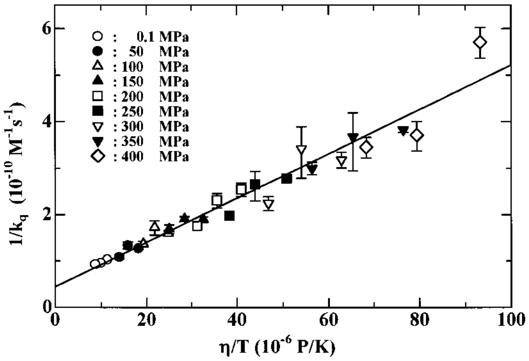

Figure 4. Plots of $1/k_q$ against η/T for ^{3}BZP*/N in three solvents at 15, 25, and 35 °C.

transfer from triplet benzophenone to 1-methylnaphthalene as solvent by picosecond laser photolysis were measured to be ca. 10 and 20 ps, respectively.[26] If we assume that the lifetimes in bulk quencher are given as the pseudo-first-order rate constant, the second-order rate constant for the energy transfer can be evaluated to be (0.7−1.4) × 10^{10} M^{-1} s^{-1} (molarity of 1-methylnaphthalene = 7.2 M), which are comparable to those of k_{bim} shown in Table 6.

It can be seen in Table 6 that the values of α are approximately in the range between the slip and stick boundary limits for ^{3}BZP*/N in five solvents and for ^{3}BZP*/N and ^{3}TPh*/N in hexane. We can also see in Table 6 that the solvent dependence of both α^{SW}(full) and α(truncated) estimated by eq 15 is similar to that of α determined experimentally, and we also see that α^{SW}(full) describes fairly well the rate constants for diffusion of interest (eqs 14 and 15). Further, as noted in Table 6, the value of k_{bim} for ^{1}TPh*/BZP in *n*-hexane is about 3 times larger than those for ^{3}BZP*/N and ^{3}TPh*/N; nevertheless, the values of α are almost independent of the donor−acceptor pairs. These results suggest that the bimolecular rate constant, k_{bim}, which is independent of solvent viscosity changed by the application of pressure, is comparable to k_{diff} (eq 20).[27]

This suggestion was tested experimentally by varying both temperature and pressure. Figure 4 shows the plots of $1/k_q$ against η/T for ^{3}BZP*/N in *n*-hexane at 15, 25, and 35 °C for pressures up to 400 MPa. As seen in Figure 4, the plot is linear, meaning that the intercept, $1/k_{bim}$, is independent of η/T. The mean values of α and k_{bim} obtained by the least-squares method were evaluated to be 3100 ± 120 and (2.2 ± 0.4) × 10^{10} M^{-1} s^{-1}, respectively (see Table 6). Therefore, it is concluded from the results that the observed rate constant, k_q, for energy transfer is described well by eq 20, in which the bimolecular rate constant, $k_{bim}(=k_{diff}k_{et}/k_{-diff})$, is independent of η/T.

Pressure Dependence of k_{et}. The rate constants, k_{diff} and k_{-diff}, depend undoubtedly on pressure and temperature. However, the bimolecular rate constant, k_{bim}, was found to be almost constant in the range of pressure and temperature examined. The pressure dependence of k_{bim}, $(\partial \ln k_{bim}/\partial P)_T$, was calculated from the least-squares slopes of the plots of $\ln (1/k_q - \alpha\eta/8RT)$ against pressure (Table 7). It can be seen in Table 7 that no pressure dependence of k_{bim} is observed within experimental errors. Since $(k_{diff}/k_{-diff})k_{et}$ is defined as k_{bim}, one may obtain

$$-RT(\partial \ln k_{bim}/\partial P)_T = \Delta V_{\eta}^{\ddagger} + \Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger} \quad (21)$$

where $\Delta V_{-diff}^{\ddagger}$ and $\Delta V_{et}^{\ddagger}$ are the activation volumes for k_{-diff} and k_{et}, respectively. By use of the data listed in Tables 5 and 7, the values of $\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger}$ were evaluated (Table 7). As seen in Table 7, $\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger} \sim -\Delta V_{\eta}$, since the left-hand side in eq 21 is nearly equal to zero.

The value of $k_{bim}(=k_{diff}k_{et}/k_{-diff})$ is the observed rate constant in the preequilibrium limit (see eq 19). Saltiel et al.[3c] have proposed from thermodynamic considerations that the equilibrium constant, K $(=k_{diff}/k_{-diff})$, is approximately equal to the inverse of the molarity of the solvent, [S], at 0.1 MPa. Hence, the value of K decreases slightly with increasing pressure, and the volume change for encounter complex formation, ΔV, is calculated to be zero since $RT(\partial \ln K/\partial P)_T = -\Delta V - RT\kappa$, where κ is the isothermal compressibility of the solvent, so that $\Delta V_{et}^{\ddagger} = 0$ (Table 7). Another estimation for the pressure dependence of K is given by the hard sphere theory, which has been applied successfully to many systems in liquid solution such as the complex formation between donor and acceptor.[28] According to this theory, ΔV is evaluated to be negative (ca. −7 ∼ −13 cm^3/mol for ^{3}BZP*/N depending on solvent).[29] Unfortunately, however, there is no direct evidence that would allow further discussion at present stage. The pressure dependence of the energy transfer rate constant in bulk quencher solution, which is in the picosecond time domain, may give us important information about this problem.

Summary

It has been demonstrated from the high-pressure study that exothermic energy transfers from ^{3}BZP* and ^{3}TPh* to N and also from ^{1}TPh* to BZP are not fully diffusion-controlled in solvents examined but compete with diffusional separation of encounter complex, which is expressed by a modified Debye equation (eq 1). The bimolecular rate constant for energy transfer, $k_{bim}(=k_{diff}k_{et}/k_{-diff})$, is found to be approximately constant for the range of pressure and temperature examined. It should be noted that the nonlinear plots between k_q and $1/\eta$ and between $\ln k_q$ and $\ln \eta$, and also the linear plots between $\ln k_q$ and $\ln \eta$ with the slopes larger than −1, are due to the contribution of bimolecular energy transfer rate processes to the diffusion.

Finally, exothermic energy transfer due to the exchange mechanism has been expected to depend on the spatial overlap of the orbitals of the donor and acceptor molecules as well as their collisional processes. However, it can be seen from the data of Table 7 that the values of $\Delta V_{et}^{\ddagger} - \Delta V_{-diff}^{\ddagger}$ show no difference in the electronic states of the donor−acceptor pairs for the ^{3}BZP*($^3n\pi^*$)/N($^1\pi\pi^*$), ^{3}TPh*($^3\pi\pi^*$)/N($^1\pi\pi^*$), and ^{1}TPh*($^1\pi\pi^*$)/BZP($^1n\pi^*$) systems in *n*-hexane within experimental errors. The reason is not known, but it seems likely that very rapid rate processes such as rotational diffusion in the solvent cage are involved in the energy transfer mechanism.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (06640651).

References and Notes

(1) For reviews: (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 518. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 296. (c) Saltiel, J.; Atwater, B. W. *Advances in Photochemistry*; Wiley-Interscience: New York, 1987; Vol. 14, p 1.

(2) (a) Birks, J. B. *Organic Molecular Photophysics*; Wiley: New York, 1973; p 403. (b) Rice, S. A. In *Comprehensive Chemical Kinetics. Diffusion-Limited Reactions*; Bamford, C. H., Tripper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985; Vol. 25.

(3) (a) Osborne, A. D.; Porter, G. *Proc. R. Soc. London A* **1965**, *284*, 9. (b) Dainton, F. S.; Henry, M. S.; Pilling, M. J.; Spencer, P. C. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 243. (c) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, K. *J. Am. Chem. Soc.* **1980**, *102*, 6799.

(4) (a) Gierer, A.; Wirtz, K. *Z. Naturforsch.* **1953**, *8A*, 532. (b) Spernol, A.; Wirtz, K. *Z. Naturforsch.* **1953**, *8A*, 522. (c) Reference 2a and references therein.

(5) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.

(6) Turro, N. J.; Schore, N. E.; Steinmetzer, H.-C.; Yekta, A. *J. Am. Chem. Soc.* **1974**, *96*, 1936.

(7) Wamser, C. C.; Medary, R. T.; Kochevar, I. E.; Turro, N. J.; Chang, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 4864.

(8) Murrov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(10) Okamoto, M.; Teranishi, H. *J. Phys. Chem.* **1984**, *88*, 5644.

(11) Okamoto, M.; Teranishi, H. *J. Am. Chem. Soc.* **1986**, *108*, 6378.

(12) For acetonitrile: Dymond, J. H.; Awan, M. A.; Glen, N. F.; Isdale, J. D. *Int. J. Thermophys.* **1991**, *12* (3), 433−447.

(13) For toluene: (a) Dymond, J. H.; Glen, N. F.; Isdale, J. D.; Pyda, M. *Int. J. Thermophys.* **1995**, *16* (4), 877−882. (b) Dymond, J. H.; Awan, M. A.; Glen, N. F.; Isdale, J. D. *Int. J. Thermophys.* **1991**, *12* (2), 275−287.

(14) For methanol: Isdale, J. D.; Easteal, A. J.; Woolf, L. A. *Int. J. Thermophys.* **1985**, *6*, 439−450.

(15) For *n*-hexane: (a) Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1926**, *61*, 57−99. (b) Brazier, D. W.; Freeman, G. R. *Can. J. Chem.* **1969**, *47*, 893−899. (c) Oliveira, C. M. B. P.; Wakeham, W. A. *Int. J. Thermophys.* **1992**, *13*, 773−790.

(16) Porter, G.; Wilkinson, F. *Proc. R. Soc. London A* **1961**, *264*, 1.

(17) Porter, G.; Topp, M. R. *Proc. R. Soc. London A* **1970**, *315*, 163.

(18) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(19) (a) Evance, D. F.; Tominaga, T.; Chan, C. J. *Solution Chem.* **1979**, *8*, 461. (b) Evance, D. F.; Tominaga, T.; Davis, H. T. *J. Chem. Phys.* **1981**, *74*, 1298.

(20) Hirayama, S.; Yasuda, H.; Scully, A. D.; Okamoto, M. *J. Phys. Chem.* **1994**, *98*, 4609, and references therein.

(21) (a) For a review article, see Jonas, J. *Acc. Chem. Res.* **1984**, *17*, 74. (b) Jonas, J.; Hasha, D.; Huang, S. G. *J. Phys. Chem.* **1980**, *84*, 109. (c) Jonas, J.; Hasha, D.; Huang, S. G. *J. Chem. Phys.* **1979**, *71*, 3996.

(22) Jonas, J.; Akai, J. A. *J. Chem. Phys.* **1977**, *66*, 4946.

(23) Dymond, J. H.; Woolf, L. A. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 991.

(24) The values of f_i^{SW}(truncated) were evaluated by neglecting the second parenthetical quantity in eq 12. The value of $r_{i(\mathrm{S})}$ in eq 12 was calculated by using the molar volume, $V_{i(\mathrm{S})}$, of the component, i(S), according to $r_{i(\mathrm{S})} = (3\chi V_{i(\mathrm{S})}/4\pi N_{\mathrm{A}})^{1/3}$, where χ is the space-filling factor (0.74).[4] The values of α^{SW}(truncated) determined from the density data of solvent[12−15] and solute[25] at high pressure were almost independent of pressure, and it was also found that the use of $r_{i(\mathrm{S})}$ estimated by the method of Bondi (Tables 1 and 5) does not lead to significant differences in α^{SW}(truncated). The values of f_i^{SW}(full) were evaluated by eq 12. The pressure dependence of α^{SW}(full), unfortunately, could not evaluated since it is quite difficult to estimate $T_{\mathrm{bp(S)}}$ at high pressure. The values of α^{SW}(truncated) and α^{SW}(full) at 0.1 MPa are listed in Table 6.

(25) Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1945**, *76*, 9.

(26) Anderson, R. W., Jr.,; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500.

(27) The values of k_{diff} calculated by using α (eq 1, Table 6) decrease from 2.7×10^{10} to 0.33×10^{10} $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ on going from 0.1 to 400 MPa for ^{1}TPh*/BZP in *n*-hexane. This means that the quenching occurs in competition with diffusion at lower pressure, but $k_{\mathrm{q}} \sim k_{\mathrm{diff}}$ as pressure increases.

(28) (a) Yoshimura, Y.; Nakahara, M. *J. Chem. Phys.* **1984**, *81*, 4080. (b) Okamoto, M.; Tanaka, F.; Teranishi, H. *J. Phys. Chem.* **1990**, *94*, 669. (c) Okamoto, M.; Tanaka, F. *J. Phys. Chem.* **1993**, *97*, 177.

(29) In the calculation of ΔV, the hard-sphere radii listed in Table 5 and $RT\kappa$ values of 2.0, 1.7, 2.3, and 3.1 cm^3/mol were used for toluene, methanol, acetonitrile, and *n*-hexane, respectively.