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Energy Transfer Concerning the Lowest Triplet State of Tetracyanobenzene with Methyl-Substituted Benzenes

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The quantum-yield ratios of phosphorescence to fluorescence and the phosphorescence lifetimes were measured for the charge-transfer complexes of tetracyanobenzene with methyl-substituted benzenes. By combining the observed results with the fluorescence quantum yields and lifetimes reported previously, the upper and lower limits of the rate constants for the intersystem crossing and for the radiative and non-radiative energy-transfer processes from the lowest triplet state to the ground state were obtained with the complexes. The intersystem-crossing rate constant of tetracyanobenzene was found to be decreased by the complex formation. This tendency was explained by the mixing of the charge-transfer configuration with the appropriate singlet and triplet states of the component molecules. The phosphorescence radiative rate constant was found to be determined by the contribution of the higher excited singlet configurations of each complex to the phosphorescent state. The temperature dependence of the phosphorescence-quenching rate constant was determined, and the activation energy of the process was interpreted as being due to intramolecular out-of-plane bending vibrations.

The phosphorescences of charge-transfer (abbreviated hereafter to CT) complexes have been studied by several authors,[1–7] the trinitrobenzene, tetrahalophthalic anhydride, and tetracyanobenzene (abbreviated hereafter to TCNB) complexes with several donors having been taken as examples. The excited triplet states of some CT complexes may be expected to have the characters of a locally-excited (abbreviated hereafter to LE) triplet of acceptor, an LE triplet of donor, and a CT triplet, which can be represented by $^3(DA^*)$, $^3(D^*A)$, and $^3(D^+A^-)$, respectively. In actuality, phosphorescence spectra from these three types of triplet states have been observed.[1,4–7] In this connection, the TCNB complexes are especially remarkable, because the CT phosphorescence was first observed with the complex with hexamethylbenzene (abbreviated hereafter to HMB) and the above-mentioned three types of phosphorescence were all observed by changing donors.[6,7]

The natures of the lowest triplet states of CT complexes have also been studied by the ESR measurement.[8–10] Hayashi *et al.*[8,9] first succeeded in finding

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1) C. Reid, *J. Chem. Phys.*, **20**, 1212 (1952).

2) S. P. McGlynn and J. D. Boggus, *J. Amer. Chem. Soc.*, **80**, 5096 (1958).

3) S. P. McGlynn, J. D. Boggus, and E. Elder, *J. Chem. Phys.*, **32**, 357 (1960).

4) J. Czekalla and K. J. Mager, *Z. Elektrochem.*, **66**, 65 (1962).

5) N. Christodouleas and S. P. McGlynn, *J. Chem. Phys.*, **40**, 166 (1964).

6) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 2813 (1967).

7) S. Iwata, J. Tanaka, and S. Nagakura, *J. Chem. Phys.*, **47**, 2203 (1967).

8) H. Hayashi, S. Nagakura, and S. Iwata, *Mol. Phys.*, **13**, 489 (1967).

9) H. Hayashi, S. Iwata, and S. Nagakura, *J. Chem. Phys.*, **50**, 993 (1969).

10) P. Krebs, E. Sackmann, and J. Schwarz, *Chem. Phys. Lett.*, **4**, 65 (1969); **8**, 417 (1971).

the ESR signal of the lowest triplet states of CT complexes and in clarifying their nature by analyzing the observed fine structure constants.

From the above-mentioned phosphorescence and ESR studies, the natures of the phosphorescent states of CT complexes have been clarified unambiguously and understood systematically. The dynamical aspects of the phosphorescence of CT complexes, however, are still open to question, although Christdouleas and McGlynn studied the phosphorescence lifetimes and quantum yields for the naphthalene complexes with several acceptors.$^{5)}$

Under these circumstances, we have undertaken to study energy-transfer processes concerning the triplet states of several TCNB complexes with methyl-substituted benzenes, by obtaining the rate constants for the intersystem crossing and also for the phosphorescence emitting and quenching processes.

Experimental

The preparation and purification of materials, and also the measurements of the absorption and fluorescence spectra were described in a previous paper.$^{11)}$ Sample solutions used for the measurements of phosphorescence lifetimes and quantum yields were degassed by the freeze-thaw technique. The phosphorescence lifetimes were determined by analyzing exponential decay curves measured by an oscilloscope. The phosphorescence quantum yields were determined by measuring quantum-yield ratios of phosphorescence to fluorescence, the quantum yields of which were obtained in the previous paper.$^{11)}$

During the measurement of the phosphorescence lifetime, the sample was kept in a Dewar vessel into which cold nitrogen gas was allowed to flow, in order to keep it at a temperature between ~100°K and ~280°K.

Results and Discussion

Phosphorescence Quantum Yield. The quantum-yield ratio of phosphorescence to fluorescence was measured by two different methods.

In method I, a fluorescence spectrum was obtained by subtracting the phosphorescence from a total emission spectrum, as is shown in Fig. 1. Thus, we obtained the quantum-yield ratio of the phosphorescence to the fluorescence. For the systems containing TCNB–durene and TCNB–HMB in methyl methacrylate (hereafter abbreviated to MMA), however, the total emission has only one peak: therefore, the separation into the two parts is rather optional and may cause a large error. For these cases, method II was used.

In method II, we measured the intensities of the total emission and phosphorescence by rotating two sectors in-phase and out-of-phase, respectively, as is shown in Fig. 2, keeping the sample in the same position and fixing the voltage of a photomultiplier and the sensitivity of a recorder. The total emission intensity was reduced by a neutral density filter to an intensity appropriate to be measured. The quantum-yield ratio of phosphorescence to fluorescence was evaluated from the observed intensities of total emission, $I_{\mathrm{Tot}}^{\mathrm{in}}$, and phosphorescence, $I_{\mathrm{P}}^{\mathrm{out}}$, with the aid of Eq. (1) derived from Eqs. (A-9)—(A-13) in the Appendix.

$$\frac{\Phi_{\mathrm{P}}}{\Phi_{\mathrm{F}}} \cong \frac{T_1+T_2}{T_1}\,\frac{I_{\mathrm{P}}^{\mathrm{out}}}{I_{\mathrm{Tot}}^{\mathrm{in}}-I_{\mathrm{P}}^{\mathrm{out}}} \tag{1}$$

where T_1 and T_2 are the duration times of the "on" and "off" states of the sector.

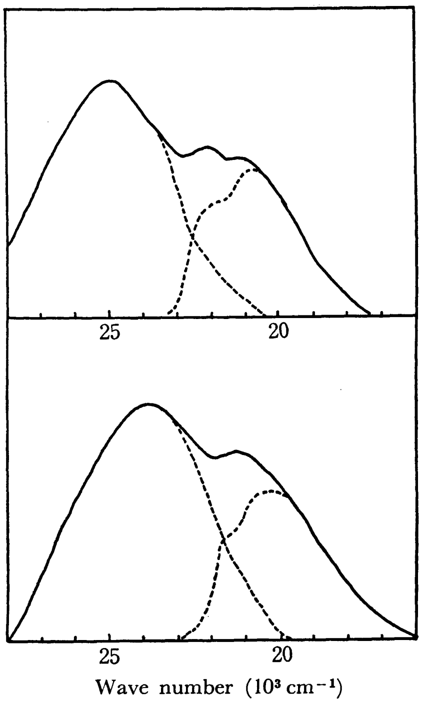

Fig. 1. The total emissions observed for the TCNB complexes with benzene (upper figure) and toluene (lower figure) and separation into fluorescence and phosphorescence.

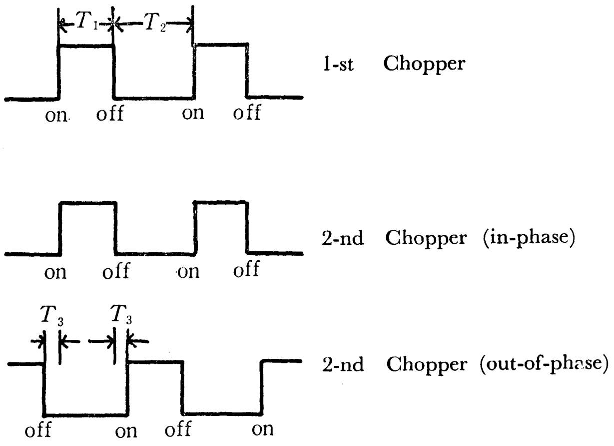

Fig. 2. Phases of the 1-st and 2-nd choppers.

The quantum-yield ratios obtained by methods I and II are given in Table 1. We adopted the values obtained by method II for the TCNB complexes with durene and HMB and the average values of methods I and II for the other TCNB complexes.

Determination of Rate Constants. The observed phosphorescence lifetimes and the evaluated quantum

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11) T. Kobayashi, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 2603 (1971).

TABLE 1. PHOSPHORESCENCE LIFETIMES (τ_P), FLUORESCENCE AND PHOSPHORESCENCE QUANTUM YIELDS (Φ_F AND Φ_P), AND SEVERAL RATE CONSTANTS OF TCNB COMPLEXES

Donor a)	I_P (eV) b)	Φ_P/Φ_F (I) c)	Φ_P/Φ_F (II) c)	$(\Phi_P/\Phi_F)_a$ c)	Φ_F d)	Φ_P	τ_P (sec)	k_2(max)	k_3(max)	k_3(min)	k_4(max)	k_4(min)	k_5(max)
								(	10^6 sec^{-1}	)	(	sec^{-1}	)
Benzene	9.245	0.48	0.44	0.46	0.63	0.29	3.0	2.1	9.7	7.6	0.33	0.26	0.072
Toluene	8.82	0.55	0.53	0.54	0.55	0.30	2.4	2.8	8.8	6.0	0.42	0.29	0.13
m-Xylene	8.56	0.56	0.54	0.55	0.51	0.28	2.3	2.8	6.6	3.8	0.43	0.25	0.19
p-Xylene	8.445	0.69	0.67	0.68	0.46	0.31	2.5	3.2	7.5	4.4	0.40	0.24	0.16
Mesitylene	8.39	0.56	0.52	0.54	0.47	0.25	2.3	3.3	6.2	2.9	0.43	0.20	0.23
Durene	8.03	0.1	0.14		0.25	0.035	1.7	12	13	0.60	0.59	0.027	0.56
HMB	7.85	0.1	0.10		0.16	0.016	0.76	21	22	0.41	1.32	0.025	1.3

a) The measurements were made for the durene and HMB complexes in MMA and for the other complexes in donor.
b) The ionization potential of each donor.
c) Φ_P/Φ_F (I) and Φ_P/Φ_F (II) are the quantum-yield ratio of phosphorescence to fluorescence obtained by methods I and II, respectively, and $(\Phi_P/\Phi_F)_a$ is the average of these two values.
d) Fluorescence quantum yields were obtained in Ref. (11).

yields are given in Table 1. In this table, k_3, k_4, and k_5 are the rate constants for the intersystem crossing, phosphorescence, and phosphorescence-quenching processes, respectively, and k_2 is the rate constant for the fluorescence-quenching process other than the intersystem crossing.

The quantum yields, Φ_F and Φ_P, and also the lifetimes τ_F and τ_P, are obtained with the aid of the rate constants:

$$\Phi_F = \frac{k_1}{k_1+k_2+k_3}, \quad \Phi_P = \frac{k_3}{k_1+k_2+k_3}\,\frac{k_4}{k_4+k_5} \tag{2}$$

$$\tau_F = \frac{1}{k_1+k_2+k_3}, \quad \tau_P = \frac{1}{k_4+k_5} \tag{3}$$

where k_1 is the fluorescence radiation decay constant. From Eqs. (2) and (3) we obtain the following relationships:

$$k_1 = \frac{\Phi_P}{\tau_F} \tag{4}$$

$$0 \leqq k_2 \leqq \frac{1}{\tau_F}(1-\Phi_F-\Phi_P) \tag{5}$$

$$\frac{\Phi_P}{\tau_F} \leqq k_3 \leqq \frac{1}{\tau_F}(1-\Phi_F) \tag{6}$$

$$\frac{1}{\tau_P}\,\frac{\Phi_P}{1-\Phi_F} \leqq k_4 \leqq \frac{1}{\tau_P} \tag{7}$$

$$0 \leqq k_5 \leqq \frac{1}{\tau_P}\,\frac{1-\Phi_F-\Phi_P}{1-\Phi_F}. \tag{8}$$

By the aid of Eqs. (4)—(8), the upper and lower limited values of k_2, k_3, k_4, and k_5 can be represented as follows:

$$k_2(\text{min}) = k_5(\text{min}) = 0 \tag{9}$$

$$k_2(\text{max}) = \frac{1}{\tau_F}(1-\Phi_F-\Phi_P) \tag{10}$$

$$k_3(\text{min}) = \frac{\Phi_P}{\tau_F} \tag{11}$$

$$k_3(\text{max}) = \frac{1}{\tau_F}(1-\Phi_F) \tag{12}$$

$$k_4(\text{min}) = \frac{1}{\tau_P}\,\frac{\Phi_P}{1-\Phi_F} \tag{13}$$

$$k_4(\text{max}) = \frac{1}{\tau_P} \tag{14}$$

$$k_5(\text{max}) = \frac{1}{\tau_P}\,\frac{1-\Phi_F-\Phi_P}{1-\Phi_F} \tag{15}$$

The limited values actually evaluated by Eqs. (10)—(15) are tabulated in Table 1.

Intersystem-Crossing Rate Constant, k_3. In discussing the rate constants for intersystem crossing given in Table 1, we divide the systems under consideration into two groups, groups A and B. Group A contains the TCNB–benzene, TCNB–toluene, TCNB–*m*-xylene, TCNB–*p*-xylene, and TCNB–mesitylene systems, and group B, the TCNB–durene–MMA and TCNB–HMB–MMA systems.

First, let us consider the TCNB–benzene and TCNB–toluene systems belonging to group A. In both systems, the sums of the fluorescence and phosphorescence quantum yields are nearly equal to unity as may easily be seen in Table 1; therefore, the fluorescence quenching is mainly due to the intersystem crossing.

The fact that TCNB is nonfluorescent means that, when the internal conversion may be disregarded,[12] its intersystem-crossing rate constant is much larger than its fluorescence radiation decay constant which is evaluated from the intensity of the absorption spectrum to be 2.0×10^7 sec^{-1}. Therefore, the intersystem-crossing rate constants, k_3's, for the systems of group A are smaller than that of the acceptor molecule itself. On the other hand, Christdouleas and McGlynn showed that k_3 of naphthalene was increased by the complex formation with trinitrobenzene and tetrahalophthalic anhydrides.[5] The intersystem-crossing rate constant of naphthalene can be estimated to be smaller than 5.8×10^6 sec^{-1} from the lifetime (103 nsec) and quantum yield (~0.4) in the literature.[13,14]

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[12] The rate constant of internal conversion from the first singlet state to the ground state was found to be very small for several compounds (T. Medinger and F. Wilkinson. *Trans. Faraday Soc.*, **61**, 620 (1965)).

[13] T. V. Ivanova, P. I. Kudrysahov, and B. Ya. Sevshinikov, *Dokl. Akad. Nauk. SSSR*, **138**, 572 (1961).

[14] E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, **23**, 399 (1965).

The great difference in the intersystem-crossing rate constant between TCNB and naphthalene may be the reason why the TCNB complexes of group A and the naphthalene complexes with trinitrobenzene and tetrahalophthalic anhydrides show reverse tendencies with regard to the effect of complex formation on the intersystem-crossing rate constant. The CT complex formation may bring about the mixing of the CT configuration with the appropriate excited singlet and triplet states of component molecules. This mixing may decrease the great rate constant of TCNB and increase the small rate constant of naphthalene.

For complexes of group B, the $\Phi_F+\Phi_P$ values are considerably smaller than those for the complexes of group A, as is seen in Table 1. This increases the difference between k_3(min) and k_3(max), and makes it difficult to estimate the real values of k_3 for the complexes of group B. In order to remove this difficulty, we discuss the two limiting cases: namely, case 1 where the true k_2, k_3, k_4, and k_5 values are, respectively, close to k_2(min), k_3(max), k_4(min), and k_5(max); case 2, where they are, respectively, close to k_2(max), k_3(min), k_4(max), and k_5(min). As is clearly seen in Table 1, in case 1 k_3 has no correlation with the ionization potentials of the donors, while in case 2 there is a correlation between them. In view of the fact that the ionization potential of the donor may be expected to be related with the contribution of CT configurations to the lowest triplet state[9] and therefore related also with k_3, case 2 is more probable than case 1.

Consideration of k_4. On the assumption that there is only one singlet state $|S_p>$, which makes a major contribution to the perturbation of the lowest triplet state, $|T_1>$, the rate constant, k_4, and the transition moment, $\vec{M}$, for the phosphorescence are written as follows:

$$k_4 \simeq \frac{64\pi^4\nu_P{}^3}{3\boldsymbol{h}\boldsymbol{c}^3}|\vec{M}|^2 \tag{16}$$

$$\vec{M} = \frac{<S_p|H_{SO}|T_1>}{E(S_p)-E(T_1)}<S_p|\vec{er}|S_0> \tag{17}$$

where ν_P is the frequency of the phosphorescence maximum, $E(S_p)$ and $E(T_1)$ are the energies of $|S_p>$ and $|T_1>$ states, H_{SO} is the spin orbit interaction hamiltonian, and $\boldsymbol{h}$, $\boldsymbol{c}$, and $\boldsymbol{e}$ are universal constants. Here, $|S_0>$, $|S_p>$, and $|T_1>$ are expanded into the ground, CT, and LE configurations;

$$|S_0> \cong |G> \tag{18a}$$

$$|S_p> \cong c_1{}^p|{}^1LE^p> + c_2{}^p|{}^1CT^p> \tag{18b}$$

$$|T_1> \cong c_3|{}^3LE> + c_4|{}^3CT> \tag{18c}$$

where $|G>$ is the ground configuration, $|{}^1LE^p>$ and $|{}^1CT^p>$ are the singlet LE and CT configurations, respectively which make major contributions to the expansion of $|S_p>$, $|{}^3LE>$, and $|{}^3CT>$ are the lowest triplet LE (within the acceptor) and lowest triplet CT configurations, respectively, and c_1^p, c_2^p, c_3, and c_4 are their coefficients in the expansion. By inserting Eqs. (18a—c) into Eq. (17), we can obtain:

$$\vec{M} \cong K\vec{M}(\text{G–LE}) + L\vec{M}(\text{G–CT}). \tag{19}$$

Here, K, L, $\vec{M}$(G–LE), and $\vec{M}$(G–CT) are defined as follows:

$$K = c_1^pN \tag{20a}$$

$$L = c_2^pN \tag{20b}$$

$$\begin{aligned} N = \{&c_1^pc_4<{}^1LE^p|H_{SO}|{}^3CT> + c_2^pc_3<{}^1CT^p|H_{SO}|{}^3LE> \\ &+ c_1^pc_3<{}^1LE^p|H_{SO}|{}^3LE> + c_2^pc_4<{}^1CT^p|H_{SO}|{}^3CT>\} \\ &\times \{E(S_p)-E(T_1)\}^{-1} \end{aligned} \tag{20c}$$

$$\vec{M}(\text{G–CT}) = <{}^1CT^p|\vec{er}|G> \tag{20d}$$

$$\vec{M}(\text{G–LE}) = <{}^1LE^p|\vec{er}|G>. \tag{20e}$$

In the case where $|S_p>$ is the lowest excited singlet state, $|S_1>$, which mainly consists of the lowest singlet LE (within the acceptor) configuration, $|{}^1LE>$, and the lowest singlet CT configuration, $|{}^1CT>$,[15] k_4 is given by the following equation from Eqs. (16)—(20):

$$\begin{aligned} k_4 &\propto \frac{\nu_p{}^3|(c_1{}^1c_4+c_2{}^1c_3)|^2\{|c_1{}^1\vec{M}(\text{G–LE})/\boldsymbol{e}|^2+|c_2{}^1\vec{M}(\text{G–CT})/\boldsymbol{e}|^2\}}{\{E(S_1)-E(T_1)\}^2} \\ &\equiv \frac{A}{\{E(S_1)-E(T_1)\}^2} \end{aligned} \tag{21}$$

where $c_1{}^1$ and $c_2{}^1$ are the coefficients of $|{}^1LE>$ and $|{}^1CT>$ in the expansion of $|S_1>$.

By the use of the values of $|\vec{M}(\text{G–CT})/\boldsymbol{e}|=0.1$ Å and $|\vec{M}(\text{G–LE})/\boldsymbol{e}|=0.3$ Å, and of $|c_1{}^1|^2$, $|c_2{}^1|^2$, $|c_3|^2$, and $|c_4|^2$ given in Refs. (9) and (11), we can evaluate the right-hand side of Eq. (21). The relative values of A and $A/\{E(S_1)-E(T_1)\}^2$ are listed in Table 2, the corresponding values of the TCNB–benzene system being taken as the standards. The relative values of $A/\{E(S_1)-E(T_1)\}^2$ are much larger than those of k_4(max) except for the toluene complex.[16] On the other hand, the relative values of A coincide considerably well with those of k_4(max). This means that the discrepancy in the relative values between $A/\{E(S_1)-E(T_1)\}^2$ and k_4(max) is due to the too large change in the $\{E(S_1)-E(T_1)\}^2$ term in Eq. (21) from one complex to another. This difficulty can

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15) Amano *et al.* measured the polarization of phosphorescence spectra for several TCNB complexes, and obtained the preliminary results of a ratio $\left|\frac{K\vec{M}(\text{G–LE})}{L\vec{M}(\text{G–CT})}\right| = \left|\frac{c_1^p\vec{M}(\text{G–LE})}{c_2^p\vec{M}(\text{G–CT})}\right|$ to be 2.4, 2.1, 1.4, 1.3, and 1.2 for the complexes with HMB, durene, mesitylene, *p*-xylene, and benzene, respectively. The results shows that the ratio increases with the decrease in the ionization potential of the donor. This means that the $|S_p>$ state has the decreasing $\left|\frac{c_1^p}{c_2^p}\right|$ value with the increasing ionization potential of donor. The lowest excited singlet state satisfied this condition.[11]

16) The relative value of $A/\{E(S_1)-E(T_1)\}^2$ for the TCNB–durene complex is larger than that for the TCNB–HMB complex. This is due to the fact that the energy separation $E(S_1)-E(T_1)$ is smaller for the former complex than for the latter. This tendency is found in solvents other than MMA; namely, the $(E(S_1)-E(T_1))$ are 1000 and 1300 cm^{-1} for the TCNB–durene complex in ethanol and a 1 : 1 mixed solvent of ethyl ether and isopentane, while the corresponding values for the TCNB–HMB complex are 1600 and 1700 cm^{-1}, respectively.

TABLE 2. THE RELATIVE VALUES OF A, $\frac{A}{\{E(\mathrm{S}_1)-E(\mathrm{T}_1)\}^2}$, AND k_4(max), AND THE $\{E(\mathrm{S}_1)-E(\mathrm{T}_1)\}^2$ VALUES

Donor	A	$\frac{A}{\{E(\mathrm{S}_1)-E(\mathrm{T}_1)\}^2}$	k_4(max)	$\{E(\mathrm{S}_1)-E(\mathrm{T}_1)\}^2$ (10^6 cm^{-2})
Benzene	$\equiv$1.00	$\equiv$1.00	$\equiv$1.00	16.81
Toluene	1.29	1.99	1.27	10.89
m-Xylene	1.77	6.73	1.30	4.41
p-Xylene	1.85	7.04	1.21	4.41
Mesitylene	1.77	6.13	1.30	4.84
Durene	2.23	46.3	1.79	0.81
HMB	2.30	11.9	4.00	3.24

easily be removed by considering that the $|\mathrm{S_P}\rangle$ state is not $|\mathrm{S}_1\rangle$ but a higher excited singlet state, the energies of which, $E(\mathrm{S_p})$, is high, and that $\{E(\mathrm{S_p})-E(\mathrm{T}_1)\}^2$ changes to a considerably smaller extent than $\{E(\mathrm{S}_1)-E(\mathrm{T}_1)\}^2$ from the benzene complex to the HMB complex.

Temperature Dependence of k_5. In a preceding paper,[11] we found that k_1 is temperature-independent in a rigid medium (polymethyl methacrylate) in the range from 300°K to 77°K. From the same reason, the phosphorescence radiative rate constant, k_4, can safely be assumed to be temperature-independent in polymethyl methacrylate in a similar temperature range.

Let us express the temperature dependence of k_5 in the following way:[17]

$$k_5 = k_5{}^0\left[1+B\exp\left(\frac{-\Delta E}{kT}\right)\right]. \tag{22}$$

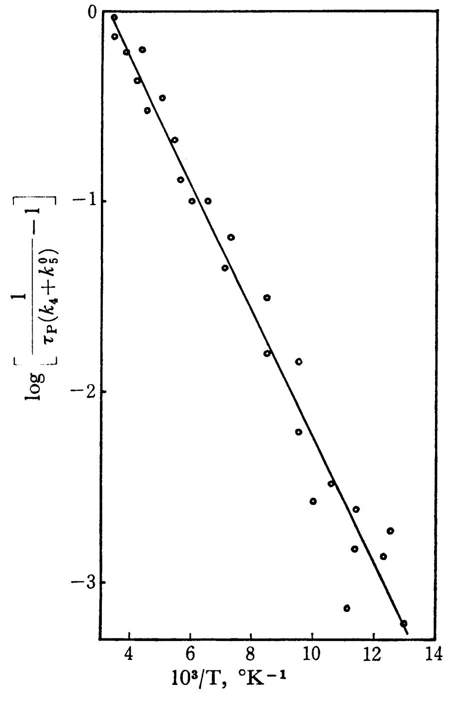

Fig. 3. Plot of $\log\left[\frac{1}{\tau_\mathrm{P}(k_4+k_5^0)}-1\right]$ *versus* $1/T$ for the system including TCNB-durene in polymethyl methacrylate.

The temperature dependence of the phosphorescence lifetime is given by the following equations:

$$\tau_\mathrm{P}{}^{-1} = (k_4+k_5{}^0) + Bk_5{}^0\exp\left(-\frac{\Delta E}{kT}\right) \tag{23}$$

$$\frac{1}{\tau_\mathrm{P}(k_4+k_5{}^0)} - 1 = \frac{Bk_5{}^0}{k_4+k_5{}^0}\exp\left(-\frac{\Delta E}{kT}\right) \tag{24}$$

From the extraporation of the $\tau_\mathrm{P}{}^{-1}-1/T$ plot for the TCNB–durene complex in polymethyl methacrylate to a low-temperature region, we evaluated $1/(k_4+k_5{}^0)$ to be 1.70 sec. By the use of this value, we plotted $\log\left[\frac{1}{\tau_\mathrm{P}(k_4+k_5{}^0)}-1\right]$ against $1/T$ for the same system. The results shown in Fig. 3 give a straight line as expected from Eq. (24), and ΔE is evaluated to be 535±30 cm^{-1}. From this value, it is revealed that the low-frequency intramolecular vibrations (probably out-of-plane bending modes) are responsible for the temperature dependence of k_5 for the temperature range studied. This is consistent with the conclusion presented by Jones and Siegel[17] after their measurement of the phosphorescence lifetimes of naphthalene-h_8, naphthalene-d_8, phenanthrene-h_{10}, and phenanthrene-d_{10}.

We should like to express our deep gratitude to Dr. Takako Amano, Department of Chemistry, Kyushyu University, for her kindness in offering her experimental results to us before publication.

Appendix

The integrated emission intensity over the observation time region from 0 to T is given by the following equation:

$$I = a\int_0^T D(t)\int_{-\infty}^{t} L(t')E(t-t')\mathrm{d}t'\mathrm{d}t, \tag{A-1}$$

where $L(t')$ is the exciting light intensity at time t', $D(t)$ is the ratio of detected photon number to the one emitted from the sample at time t, $E(t-t')$ is a decay function for the emission, and a is a proportionality coefficient. The integrated emission intensities are given by Eq. (A-2) for the two cases having the excitation and detection sectors "in-phase" and "out-of-phase":

$$I^\alpha = a\int_0^T D^\alpha(t)\int_{-\infty}^{t} L(t')E(t-t')\mathrm{d}t'\mathrm{d}t \tag{A-2}$$

where α indicates "in" or "out" and D, L, and E are as follows:

$$D^{\mathrm{in}}(t) = \begin{cases} D_0 & n(T_1+T_2) \leqq t \leqq n(T_1+T_2) + T_1 \\ 0 & n(T_1+T_2) + T_1 \leqq t \leqq (n+1)(T_1+T_2) \end{cases} \tag{A-3}$$

$$D^{\mathrm{out}}(t) = \begin{cases} D_0 & \mathrm{T}_1 + T_3 + n(T_1+T_2) \leqq t \leqq 2T_1 \\ & \quad + T_3 + n(T_1+T_2) \\ 0 & 2T_1 + T_3 + n(T_1+T_2) \leqq t \leqq T_1 \\ & \quad + T_3 + (n+1)(T_1+T_2) \end{cases} \tag{A-4}$$

$$L(t) = \begin{cases} L_0 & n(T_1+T_2) \leqq t \leqq n(T_1+T_2) + T_1 \\ 0 & n(T_1+T_2) + T_1 \leqq t \leqq (n+1)(T_1+T_2) \end{cases} \tag{A-5}$$

$$E(t) = \frac{\Phi}{\tau}\mathrm{e}^{-t/\tau} \tag{A-6}$$

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[17] P. F. Jones and S. Siegel, *Chem. Phys. Lett.*, **2**, 486 (1968); *J. Chem. Phys.*, **50**, 1134 (1969).

where n is an integer, L_0 is the number of photons absorbed by a sample when the excitation sector is "on" D_0 is the ratio of the number of photons detected to that emitted by the sample when the observation sector is "on", and τ and Φ are the lifetime and quantum yield, respectively. T_3 is a half of the difference between T_2 and T_1. By putting (A-3), (A-4), (A-5), and (A-6) into (A-2), and by integrating over one period, T_1+T_2, I^{in}, and I^{out} are obtained:

$$I^{\mathrm{in}} = aL_0D_0\Phi\left[\tau(1-\mathrm{e}^{-T_1/\tau})(\mathrm{e}^{T_1/\tau}-1)\frac{\mathrm{e}^{-((T_1+T_2)/\tau)}}{1-\mathrm{e}^{-((T_1+T_2)/\tau)}} + T_1 + \tau(\mathrm{e}^{-T_1/\tau}-1)\right] \quad \text{(A-7)}$$

$$I^{\mathrm{out}} = aL_0D_0\Phi\left[\tau(\mathrm{e}^{-T_3/\tau}-\mathrm{e}^{-((T_1+T_3)/\tau)})(\mathrm{e}^{T_1/\tau}-1) \times \frac{\mathrm{e}^{-((T_1+T_2)/\tau)}}{1-\mathrm{e}^{-((T_1+T_2)/\tau)}}\right]. \quad \text{(A-8)}$$

By taking τ and Φ to be τ_{F} and Φ_{F}, or τ_{P} and Φ_{P}, the integrated intensities of the fluorescence or phosphorescence in-phase and out-of-phase over one period T_1+T_2 can be given as follows:

$$I_{\mathrm{F}}^{\mathrm{in}} \cong aL_0D_0\Phi_{\mathrm{F}}T_1 \quad \text{(A-9)}$$

$$I_{\mathrm{F}}^{\mathrm{out}} \cong 0 \quad \text{(A-10)}$$

$$I_{\mathrm{P}}^{\mathrm{in}} \cong I_{\mathrm{P}}^{\mathrm{out}} \cong aL_0D_0\Phi_{\mathrm{P}}\frac{T_1^2}{T_1+T_2} \quad \text{(A-11)}$$

The intensities of the total emissions, $I_{\mathrm{Tot}}^{\mathrm{in}}$ and $I_{\mathrm{Tot}}^{\mathrm{out}}$, are also given as follows:

$$I_{\mathrm{Tot}}^{\mathrm{in}} \equiv I_{\mathrm{F}}^{\mathrm{in}} + I_{\mathrm{P}}^{\mathrm{in}} \cong I_{\mathrm{F}}^{\mathrm{in}} + I_{\mathrm{P}}^{\mathrm{out}} \quad \text{(A-12)}$$

$$I_{\mathrm{Tot}}^{\mathrm{out}} \equiv I_{\mathrm{F}}^{\mathrm{out}} + I_{\mathrm{P}}^{\mathrm{out}} \cong I_{\mathrm{P}}^{\mathrm{out}}. \quad \text{(A-13)}$$