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Journal of Photochemistry and Photobiology A: Chemistry 186 (2007) 229–233
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Dual phosphorescence and excited state dynamics of *p*-bromotoluene

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Received 20 February 2006; received in revised form 24 July 2006; accepted 21 August 2006

Abstract

Excited state dynamics of dual phosphorescent *p*-bromotoluene (PBT) was investigated in low temperature matrix between 77 K and 91 K. Dual phosphorescence was ascribed to two low-lying triplet states, $^3\pi\pi^*$ and $^3\pi\sigma^*$. The phosphorescence decay rate constants were divided into temperature dependent and independent terms. The temperature independent decay rate constants of $^3\pi\pi^*$ state was 180 times larger than that of *p*-chlorotoluene (PCT). The decay rate constant of chlorobenzene (CB) and bromobenzene (BB) were determined in our previous study, and the ratio of the decay rate constants were 13, which has been successfully explained by increase of spin–orbit interaction due to internal heavy atom effect. In the case of *p*-bromotoluene, the large decay rate constant is partly explained by taking into account of non-radiative decay process due to spin–vibronic interaction through promoting vibrational modes possible even at 77 K. Moreover, homolysis reaction to produce bromine atom was also suggested to induce non-radiative process within triplet manifold.

Keywords: Dual phosphorescence; *p*-Bromotoluence; *p*-Chlorotoluene; Non-radiative decay

1. Introduction

The properties of the lowest triplet states of halogenated benzenes have been received attention [1–5]. Chlorobenzene and chlorotoluenes exhibit dual phosphorescence originating from two low-lying triplet states, $^3\pi\pi^*$ and $^3\pi\sigma^*$states [6]. Potential energy surfaces of the low-lying triplet states of chlorobenzene were calculated by the *ab initio* Hartree–Fock (UHF) method [7]. The C–Cl equilibrium bond length of the $^3\pi\pi^*$ state was reported to be close to that of the ground state, while the C–Cl equilibrium bond length of the $^3\pi\sigma^*$state was about 0.6 Å longer than that of $^3\pi\pi^*$ state. Dual phosphorescence is composed of slow decaying component due to the transition $^3\pi\pi^* \rightarrow S_0$, and fast decaying component due to $^3\pi\sigma^* \rightarrow S_0$ [8].

It has been noted that bromine substitution in the halogenated benzenes cause large changes in their decay characteristics [9–11]. As the phosphorescence of bromobenzene (BB) was very weak or undetectable, studies on the triplet state of bromine substitute benzenes were carried out using phosphorescent compounds. For bromine containing benzonitriles, anisoles and anilines, the second order effect of spin–orbit mixing is the most important in zero-field splitting [12]. For *p*-bromochlorobenzene, *p*-dibromobenzene and *p*-dichlorobenzene, phosphorescence decays from each triplet sublevels were investigated by zero-field ODMR and MIDP techniques [13].

In our previous study, we have investigated dual phosphorescence of *p*-chlorotoluene (PCT) and revealed that non-radiative decay rates were influenced by the viscosity of matrix in the triplet states [14]. In highly viscous matrices, like methylcyclohexane, lifetime of triplet states became longer and phosphorescence yield became larger. Utilizing such solvent effect, we have first observed phosphorescence spectrum of BB in highly viscous rigid glass solutions in glycerol, 4-methylhepthane and 3-methyloctane [15]. Quantum yield of the phosphorescence was determined as 0.03 in glycerol at 77 K. Radiative rate constant (k_r) and non-radiative rate constant of $^3\pi\pi^*$ state (k_{nr}) were determined as $1.8 \times 10^3\ s^{-1}$ and $1.0 \times 10^3\ s^{-1}$, respectively. The k_r value of bromobenzene was 13 times larger than that of chlorobenzene, and the difference were successfully explained by internal heavy atom effect due to increase in spin–orbit interaction. Rasmusson et al. investigated photodissociation of BB

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doi:10.1016/j.jphotochem.2006.08.019

in solution by femtosecond transient absorption experiment. They observed phenyl radical within 10 ps after the excitation and reported that predissociation took place within the singlet manifold [18]. Thus, the intersystem-crossing yield of BB is considered small. Due to decomposition reaction, phosphorescence quantum yields of halogenated benzenes and bromobenzene are small. On the other hand, halogenated toluene emits phosphorescence stronger than halogenated benzenes. Thus, halogenated toluene becomes good candidate to discuss excited state dynamics.

p-Bromotoluene (PBT) is expected to be a prototype to clear the non-radiative decay process. In this study, the dual phosphorescence of PBT was investigated. The phosphorescence decay rate constants were divided into temperature dependent and independent terms. In the case of PCT, temperature independent terms involve mainly radiative decay rate constant, whereas, the value of PBT is fairly larger than the value of PCT expected from heavy atom effect. This indicates that the non-radiative deactivation process happens in the case of PBT even in the temperature range around 77 K. We, here, discuss the non-radiative decay process induced by vibrational motions within the triplet state.

2. Experimental

p-Bromotoluene (Tokyo Kasei G.R.) and *p*-chlorotoluene (Tokyo Kasei G.R.) were purified by vacuum distillation. G.R. grade methylcyclohexane was purchased from Wako Pure Chemical and used as solvent without further purification.

Absorption spectra were recorded on a Hitachi U3300 spectrophotometer. Emission spectra were measured by a Hitachi M-850 spectrofluorometer. Time-resolved phosphorescence spectra and phosphorescence lifetimes were simultaneously measured using a Unisoku TSP 601 H nanosecond laser photolysis system with an Nd^{3+}:YAG laser (266 nm output of fourth harmonic, pulse width 3 ns, GCR-130, Spectra Physics) and an oscilloscope (GOULD 4090). Liquid nitrogen cryostat (Oxford DN-1704) and temperature controller (Oxford ITC-1) were used to control temperature of the sample. Vibrational modes and frequencies are calculated by PM3/AM-1 method.

3. Results and discussion

Fig. 1 shows emission, excitation and absorption spectra of PBT and phosphorescence spectrum of PCT in 3-methylcyclohexane at 77 K. The excitation spectrum is very similar to the absorption spectrum, and therefore the observed emission is considered to originate from PBT. Both emissions are broad and show no prominent vibrational structure. Observed emission has a peak at 520 nm, which shifts by 100 nm to longer wavelength than that of PCT. Emission quantum yields were determined to be 0.06 by comparing with the reported value of PCT [5,14].

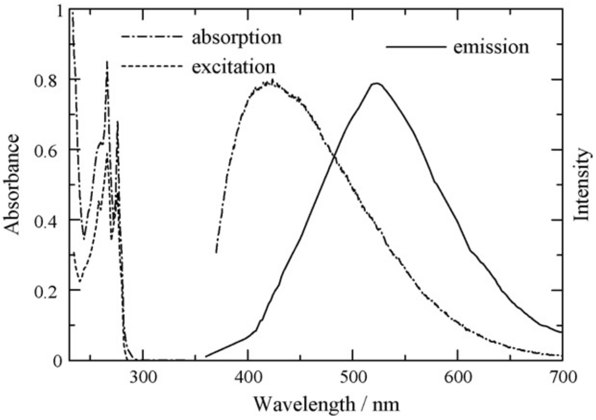

Fig. 1. Steady state phosphorescence excited at 266 nm of *p*-bromotoluene and *p*-chlorotoluene, phosphorescence excited spectrum of *p*-bromotoluene monitored at 500 nm and absorption spectrum of *p*-bromotoluene in methylcyclohexane at 77 K.

To obtain more detailed information on the triplet state of PBT, time-resolved measurements were carried out, and the phosphorescence spectra observed at 7, 20 and 80 μs after the laser flash are shown in Fig. 2(a). Decay time profile could not be fitted by single-exponential decay but successfully fitted by bi-exponential decay. At the temperatures concerned in this study (77–91 K), the phosphorescence decays monitored in the range of 350–700 nm were analyzed by bi-exponential function. The decay time-profile of the phosphoresce intensity $I_{p\lambda}$ monitored at a wavelength can be expressed in the form:

$$I_{p_\lambda}(t) = C_s(\lambda)\, e^{-k_s t} + C_f(\lambda)\, e^{-k_f t} \qquad (1)$$

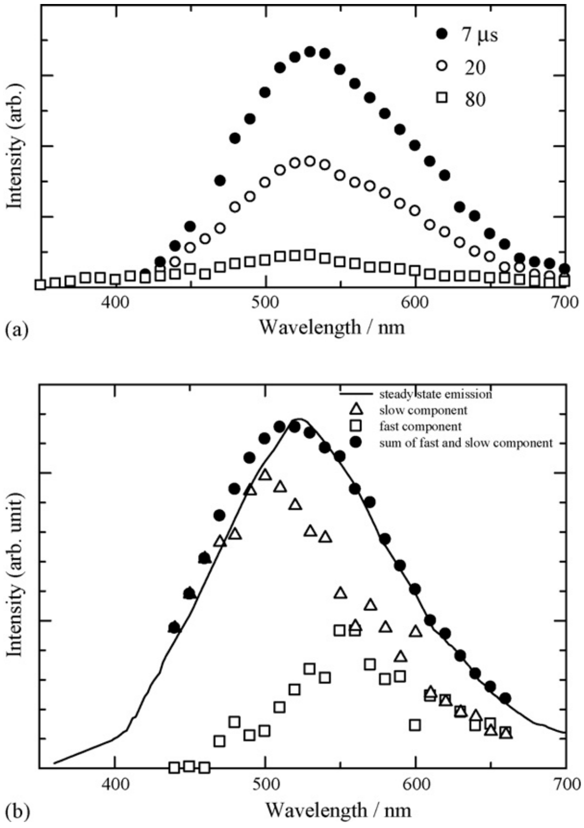

Fig. 2. (a) Time resolved phosphorescence spectra of PBT observed at 7 μs (●), 20 μs (○) and 80 μs (□) after the laser flash. (b) Steady state phosphorescence spectrum and resolved phosphorescence spectra of slow component $C_{s\lambda}/k_s^0$ (△) and fast component $C_{f\lambda}/k_f^0$ (□) and sum of $C_{s\lambda}/k_s^0$ and $C_{f\lambda}/k_f^0$ (●) of *p*-bromotoluene in methylcyclohexane at 77 K.

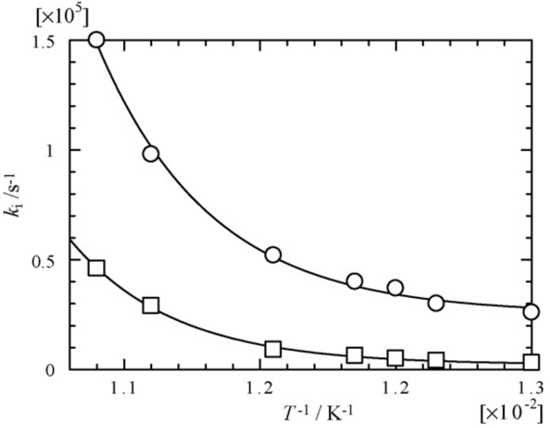

Fig. 3. Plots of k_i (i = s, f) against T^{-1} in methylcyclohexane and fitting curves by Eq. (2).

where k_s and k_f are decay rate constants with $k_s < k_f$, *i.e.*, s and f refer to the slow and fast decay of the phosphorescence, respectively. C_s and C_f are pre-exponential factors of the slow and fast components. The lifetimes of the fast and slow components were determined to be 20 μs and 91 μs at 77 K, respectively. It was confirmed experimentally that the decay constants k_s and k_f are independent of the monitoring wavelength λ Fig. 2(b) shows the plots of C_s/k_s and C_s/k_f against λ, which represent the resolved phosphorescence spectra of the fast and slow components. The sum of C_s/k_s and C_f/k_f is identical with the steady-state phosphorescence spectrum. Longer wavelength phosphorescence is assigned to originate from $^3\pi\sigma^*$ and shorter wavelength one from $^3\pi\pi^*$ to the ground state, followed after the assignments of the dual phosphorescence of CB [6].

In our previous study of CB and BB, the decay rate constants k_i (i = s or f) were expressed in the form:

$$k_i = k_i^0 + A_i\,\mathrm{e}^{-\Delta E_i/RT} \tag{2}$$

where k_i^0 is the temperature independent decay constant and is regarded as phosphorescence radiative rate constant. A_i is a frequency factor, and ΔE_i is activation energy. The temperature-dependent term in Eq. (2) is considered to the non-radiative decay rate constant [5]. In this study, life times were measured at various temperatures and the result are plotted in Fig. 3. The values of k_i^0, A_i and ΔE_i were determined by curve fitting shown in Fig. 3, where k_i (i = s, f) are plotted against the inverse of the temperature T.

Table 1 summarizes kinetic parameters of CB, BB, PCT and PBT. Here, we will focus our attention to the slow decay rate constant k_s^0 from $^3\pi\pi^*$ state. In our previous study, we reported that k_i^0 of CB and BB showed following relation:

$$\frac{k_s^0(\mathrm{CB})}{k_s^0(\mathrm{BB})} = \left(\frac{\zeta_{\mathrm{Cl}}}{\zeta_{\mathrm{Br}}}\right)^2 \tag{3}$$

where k_s^0(BB) and k_s^0(CB) are the radiative phosphorescence lifetimes of BB and CB and ζ_{Cl} and ζ_{Br} are spin–orbit coupling factors of chlorine and bromine atom. The k_s^0 of chloro- and bromo-benzenes in glycerol at 77 K were 1.4×10^2 s^{-1} and, 1.8×10^3 s^{-1}, respectively, and the ratio of radiative lifetime $k_s^0(\mathrm{BB})/k_s^0(\mathrm{CB})$ is 13, being close to the calculated ratio $(\zeta_{\mathrm{Br}}/\zeta_{\mathrm{Cl}})^2$, 18 [16]. Therefore, shorting in the radiative decay rate, k_s^0, was explained by the internal heavy atom effect.

In the case of PCT and PBT, the rate constants k_s^0(PCT) and k_s^0(PBT) are 40 s^{-1} and 7200 s^{-1}, respectively. The ratio $k_s^0(\mathrm{PBT})/k_s^0(\mathrm{PCT})$ is 180, which is 10 times larger than the expected values from heavy atom effect. This result strongly suggests that non-radiative decay process is involved in the case of PBT. We examined possibility of non-radiative decay process through spin–vibronic pathways. Normal vibrational modes and energies are calculated by PM3/AM-1 method. The modes of the vibration are selected of which energies are below 300 cm^{-1}, because at 77 K distribution of a $v = 1$ level is lower than 0.01 at 300 cm^{-1}. We choose three vibrational modes, internal rotation of methyl group, out-of-plane, and in-plane modes. Fig. 4 shows the scheme of vibrational modes, energies and Boltzmann distributions when $v = 0$ level is defined as unity.

The energy of the internal rotation of methyl group are reported for PCT for ground and lowest singlet excited state of PCT [17]. The barrier heights are 35 cm^{-1} and 75 cm^{-1} for the S$_0$ and S$_1$ states, respectively. However, the barrier height of the $^3\pi\pi^*$ is not known, internal rotation is thought not to enhance non-radiative deactivation. The reason can be explained as follows. PCT has longer phosphorescence lifetime and larger phosphorescence quantum yield compared to CB, in spite of PCT has internal rotational modes of methyl group. The same

Table 1
Kinetic data of dual phosphorescences of halogenated benzenes and toluenes

Slow compounds	k_s (s^{-1})	k_s^0 (s^{-1})	$k_s - k_s^0$ (s^{-1})	A_s	ΔE_s (kJ mol^{-1})	Solvent
CB	1.5×10^2	1.4×10^2	1.0×10^1	5.1×10^3	6.0	Glycerol [15]
BB	2.8×10^3	1.8×10^3	1×10^3	2.3×10^3	5.3	Glycerol [15]
PCT	1.5×10^2	4.0×10^1	1.1×10^2	1.9×10^{15}	22	MCH, this work
PBT	1.1×10^4	7.2×10^3	3.8×10^3	1.2×10^{15}	18	MCH, this work
Fast compounds	k_f (s^{-1})	k_f^0 (s^{-1})	$k_f - k_f^0$ (s^{-1})	A_f	ΔE_f (kJ mol^{-1})	Solvent
CB	4.6×10^2	1.8×10^2	2.8×10^2	1.8×10^5	4.8	Glycerol [15]
BB	1.3×10^4	1.2×10^4	1.0×10^3	1.8×10^{10}	11	Glycerol [15]
PCT	7.0×10^2	3.3×10^2	3.7×10^2	7.9×10^{15}	20	MCH, this work
PBT	5.1×10^4	2.5×10^4	2.6×10^4	5.2×10^{13}	15	MCH, this work

out-of-plane vibration (b_1)

in-plane vibration (b_2)

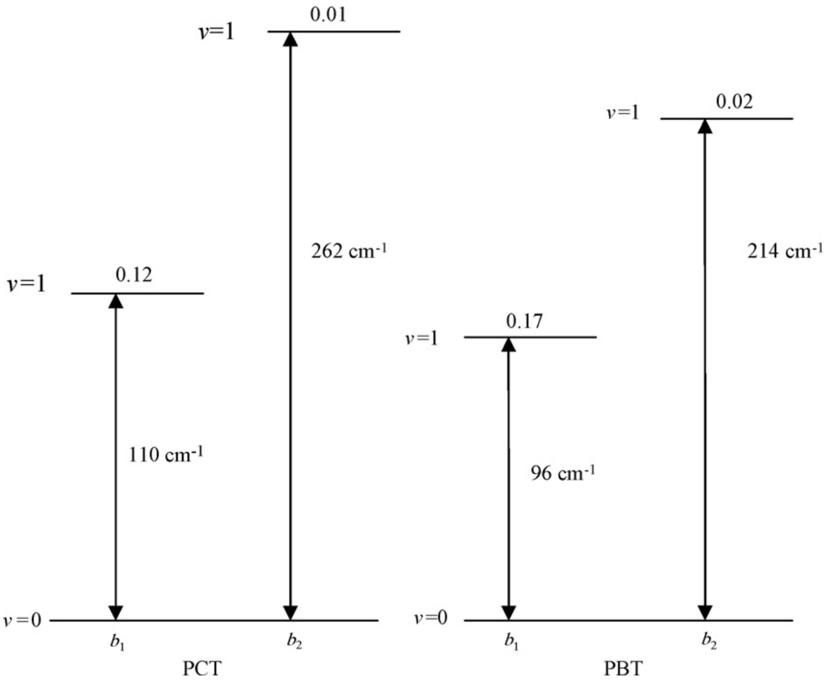

Fig. 4. Low frequency normal vibration modes of *p*-bromotoluene. Out-of-plane mode and in plane mode. Vibrational energies and those Boltzman distributions of normal modes of PCT and PBT.

relation also consists between BB and PBT. Thus, the internal rotational motion of the methyl group does not to induce non-radiative decay process.

We will treat molecular symmetry of PBT as C_{2v} as an approximation, though molecular symmetry of PBT belongs to C_s. The symmetry of out-of plane belongs to b_1, and in-plane mode belongs to b_2, respectively. These vibrational modes and energies are illustrated in Fig. 4. The distributions of the $v = 1$ level of out-of-plane mode are 0.12 and 0.17 for CPT and PBT, respectively. The distributions of in-plane mode are 0.01 and 0.02 for PCT and PBT, respectively. In each case, the distributions of PBT are larger than that of PCT.

We will discuss whether those vibrations can induce non-radiative decay process. The non-radiative decay process through spin–vibronic interaction becomes allowed when product out of the symmetries of electronic part, spin part and vibration is totally symmetry A_1. The symmetry of the electronic part of $\pi\pi^*$ is A_1, the symmetries of the spin sublevels T_X, T_Y and T_Z are product out of the electronic symmetry and symmetry of rotation (R_X, R_Y and R_Z). The symmetries of T_X, T_Y and T_Z become B_2, B_1 and A_2, respectively. Thus, the T_X (B_2) state can deactivate through b_2 vibration and T_Y (B_1) sublevel deactivate through b_1 vibration. Since the symmetry of T_Z sublevel is A_2, and no a_2 vibration with low energy region, this state cannot undergo non-radiative deactivation. Thus, b_1 out-of-plane and b_2 in-plane vibration can act as promoting modes.

Finally, we discuss the factor of the rate enhancement. Factors of enhancement of the rate constants through non-radiative decay process are calculated by Arrhenius equation are 1.3 and 2.5 for b_1 and b_2 promoting modes, respectively. Internal heavy atom effect is estimated to be the factor of 18 for spin–orbit interaction. The products are 23 (b_1) and 45 (b_2), respectively. These results are not satisfactory to explain the experimental result of 180 times larger value between PCT and PBT.

We should take into account another pathway. Dissociation reaction that produces bromine atom is most provable.

Acknowledgements

This work was supported by a grant-in-aid for Scientific Research on Priority Areas (432) (nos. 15033213, 14540527 and 15350004) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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