June, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 56, 1851—1852 (1983)* 1851

Solvent Effects on the Nonradiative Relaxation Processes of the Lowest Excited Singlet States of Meso-substituted Bromoanthracenes

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(Received November 15, 1982)

Synopsis. From the measurements of the fluorescence lifetimes and the 0-1 emission maxima in solutions, it is concluded that the solvent dependence of the nonradiative transition rates of the lowest excited singlet states of 9-bromoanthracene and 9,10-dibromoanthracene is due to the different extent to which the lowest excited singlet and adjacent higher excited triplet states are stabilized by solvents.

The nonradiative process of the fluorescing state in anthracene derivatives has been studied extensively,[1,2] and it is well known that the fluorescence quantum yields of 9- and 9,10-substituted anthracenes in fluid media decrease as the temperature is increased. This temperature dependence has been attributed to thermally activated intersystem crossing (isc) from the lowest excited singlet state S_1 to an adjacent higher excited triplet state T_n.

Our direct measurements of the temperature dependence of the fluorescence lifetimes of 9-bromoanthracene (BA) and 9,10-dibromoanthracene (DBA)[2] have allowed the determination of the rate constant for isc in the form $k_{\mathrm{isc}}=A_{\mathrm{isc}}\exp(-\Delta E/kT)$, with activation energies of 600 and 1100 cm^{-1} for BA and DBA in 3-methylpentane, respectively.

From the measurements of the 0-1 emission maxima and of the fluorescence lifetimes by single photon counting method in solutions, Wu and Ware[3] have concluded that the solvent dependence of the nonradiative transition rate of the lowest excited singlet state in DBA is due to the different extent to which S_1 and T_n are stabilized by the solvent.

Since the S_1 lifetimes of BA are very short and the single photon counting method in subnanosecond region sometimes gives some errors, this article reports the results of the solvent effects on the S_1 lifetimes of BA and DBA using a streak camera by picosecond laser photolysis in order to see whether Wu and Ware's relation can generally be applied or not.

Experimental

9-Bromoanthracene (EP grade) was purchased from Tokyo Kasei Kogyo Co., Ltd., and 9,10-dibromoanthracene was synthesized by bromination of anthracene.[4] After repeated crystallization from methanol, both samples were purified by vacuum sublimation. G.R.-grade 3-methylpentane (Wako) and spectral-grade ethanol (Nakarai), diethyl ether (Merck) and all the other solvents (Dojin) were used without further purification. The sample solution were degassed by several freeze-pump-thaw cycles. By the excitation of the sample using the third harmonic (355 nm) with a pulse width of 15 ps from a mode-locked Nd^{3+}: YAG laser, the decay of $S_1 \rightarrow S_0$ fluorescence was measured by a Hamamatsu C-979 streak camera with an S-20 cathode. The streak image was detected by a TV camera and treated by a Hamamatsu C-1098 microprocessor. Steady-state fluorescence spectra were taken with a Shimadzu RF-502 fluorescence spectrophotometer. All the experiments were carried out at room temperature (296 K) and the concentration of the sample was about 1×10^{-4} mol dm^{-3}.

Results and Discussion

A typical fluorescence decay of BA is shown in Fig. 1. The smooth curve (dotted line) in Fig. 1 is calculated by a least-squares method assuming a single exponential decay of fluorescence. All the experimental fluorescence decays could be fitted with high precision to a single exponential decay function, that is, the average deviation for fitting to the experimental data was within ±0.3% and the standard deviations of the best fit rate constants (k) were between 3 and 8%.

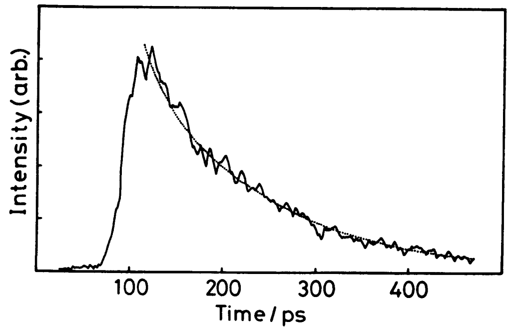

Fig. 1. Fluorescence decay curves of 9-bromoanthracene in acetonitrile at 296 K. ——: Observed curve by a streak camera, ……: simulated curve based on a single exponential decay with $k=6.25\times10^{9}\ \mathrm{s}^{-1}$.

As the relative energy of the S_1 state, the wave number of the 0-1 emission band, $\tilde{\nu}(0,1)$, of the fluorescence spectrum was taken instead of that of the 0-0 emission band, $\tilde{\nu}(0,0)$, because $\tilde{\nu}(0,1)$ could be determined more accurately. Table 1 gives the values of S_1 lifetimes ($\tau=k^{-1}$) and $\tilde{\nu}(0,1)$ of BA and DBA.

Although the fluorescence lifetimes of DBA are consistent with those observed by Wu and Ware[3] and Cherkasov *et al.*,[5] the values of BA are an order of magnitude shorter than those observed by Cherkasov *et al.*[5] and Dreeskamp and Pabst.[6] This discrepancy is probably due to uncertainty of their single photon counting method in the subnanosecond region, because the fluorescence lifetimes of BA in acetonitrile are 0.16 ns by the present Nd^{3+} : YAG laser photolysis and 0.5 ns by our single photon counting method, the latter value being the lowest measurable value which the apparatus can give.

As have described in our previous paper,[2] the total rate of the S_1 decay process is expressed as

Table 1. Values of S_1 lifetimes and $\bar{\nu}(0,1)$ of BA and DBA in various solvents

	Solvent	BA		DBA	
		Lifetime τ/ps	$\bar{\nu}(0,1)$ / cm^{-1}	Lifetime τ/ns	$\bar{\nu}(0,1)$ / cm^{-1}
(1)	Hexane	113±6	24100	1.12±0.01	23220
(2)	Diethyl ether	124±8	24040	1.21±0.02	23180
(3)	3-Methylpentane	126	24050	1.11	23250
(4)	Cyclohexane	137	24010	1.46	23150
(5)	Methanol	145±2	24030	0.94±0.02	23220
(6)	Ethanol	148±3	24000	1.39	23170
(7)	Acetonitrile	160	23920	1.27±0.02	23150
(8)	Methylcyclohexane	203±5	24000	3.36	23120
(9)	Acetone	269±2	23920	1.41	23120
(10)	Tetrahydrofuran	291±3	23870	—	—
(11)	Benzene	313	23720	2.54	22890
(12)	Carbon tetrachloride	318	23750	2.62±0.04	22940
(13)	Toluene	322	23720	2.50±0.19	22900
(14)	Chloroform	335	23780	2.73±0.02	22940
(15)	Bromobenzene	483±7	23570	3.67±0.14	22720
(16)	1,2-Dichloroethane	370	—	3.15	22960

$$k = k_r + A_{isc}\exp(-\Delta E/kT), \tag{1}$$

where k_r is the rate constant for the $S_1 \rightarrow S_0$ fluorescence, and the temperature-dependent component for the $S_1 \rightarrow T_n$ intersystem crossing is described by an Arrhenius term of frequency factor A_{isc} and activation energy ΔE.

Assuming the Arrhenius parameter A_{isc} is constant through the series of solvents, Wu and Ware[3) gave the following relation between activation energy and $\bar{\nu}(0,1)$ for DBA,

$$(\alpha-1)[\bar{\nu}(0,1)-\bar{\nu}_0(0,1)] = \Delta E - \Delta E_0, \tag{2}$$

where $\bar{\nu}_0(0,1)$ and ΔE_0 refer to a reference solution and α is the ratio of the solvent stabilization energies of the T_n state to that of the S_1 state, *i.e.*, α=0.31±0.02.

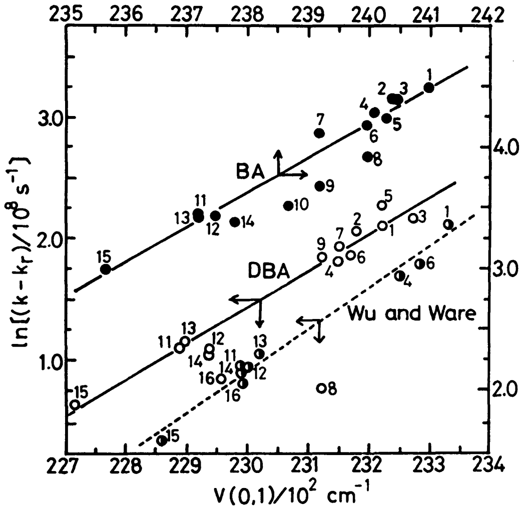

Fig. 2. Plots of $\ln[(k-k_r)/10^8\ s^{-1}]$ *vs.* $\bar{\nu}$ (0, 1).
Numbers of the points refer to Table 1. Dotted line show the results of Wu and Ware for DBA.[3)

Plots of $\ln(k-k_r)$ *vs.* $\bar{\nu}(0,1)$ for BA and DBA are shown in Fig. 2 together with the result of Wu and Ware for DBA,[3) where k_r is the average of the radiative rate constants at 77 K in 3-methylpentane and EPA (ether/isopentane/ethanol=5 : 5 : 2 in volume ratio), that is, $k_r = 7.81\times10^7$ and $8.20\times10^7\ s^{-1}$ for BA and DBA, respectively.[2) It is obvious from Fig. 2 that all the experimental points lie reasonably close to a straight line. The values of α obtained by the least-squares method are 0.43±0.01 for BA and 0.39±0.06 for DBA, that is, the stabilization energy of T_n by solvents is about 40% to that of S_1 stabilization. Our values of α and $(k-k_r)$ for DBA is nearly equal to those obtained by Wu and Ware. As can be seen from Fig. 2, the solid line for DBA comes to the dotted line (Wu and Ware) by the horizontal shift of 1—2 nm. Thus, one can say that our result is identical with that obtained by Wu and Ware for DBA.

In conclusion, the relation obtained by Wu and Ware may be applicable to 9- and 9,10-substituted anthracenes who have activation energies in isc processes.

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