Fast Internal Conversion in Nonfluorescent Carbonyl Anthracenes

Fujio Tanaka,* Tomoaki Furuta, Masami Okamoto,[†] and Satoshi Hirayama[††]
College of Integrated Arts and Sciences, Osaka Prefecture University,Gakuen-cho, Sakai 599-8531
[†]*Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585*
[††]*Laboratory of Physical Chemisty, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585*

The quantum yield of triplet formation (ϕ_T) for two nonfluorescent molecules of 9-acetylanthracene and 9-benzoylanthracene was determined with a time-resolved thermal lensing method (TRTL). The value of ϕ_T for 9-benzoylanthracene was 0.19 in cyclohexane, indicating that a fast internal conversion process with a rate constant of $4.0 \times 10^{10}\,\mathrm{s^{-1}}$ exists in the deactivation from the first excited singlet state (S_1).

The nonradiative transition is a fundamental process in the deactivation of electronically excited molecules.[1] Aromatic carbonyl molecules are often nonfluorescent or weakly fluorescent, and the mechanism for fast nonradiative transition from the S_1 state has been long studied. Efficient intersystem crossing (ISC) based on the enhanced spin–orbit coupling between $\pi\pi^*$ and $n\pi^*$ states[2] is considered to be a predominant nonradiative process. It was pointed out that internal conversion (IC) is also responsible for the fast nonradiative decay in some cases,[3–5] but experimental and theoretical understanding about IC in aromatic carbonyl molecules is scarce in comparison to ISC.

The contribution of the two nonradiative channels of ISC and IC in nonfluorescent molecules can be determined from the triplet yield. However, it is somewhat difficult to obtain accurate values of the triplet yield by transient triplet–triplet absorption, because of experimental restrictions associated with the determination of transient molar absorption coefficients. Instead, TRTL is a very convenient method to determine the value of triplet yield.[6–8] In the present work, this method was applied to nonfluorescent carbonyl derivatives of anthracene, in order to estimate the contribution of IC.

9-Acetylanthracene is nonfluorescent at room temperature but fluoresces at 77 K, whereas 9-benzoylanthracene does not fluoresce at any temperature.[9–12] The fluorescence behavior of these molecules and their analogues was at first explained on the basis of ISC and its temperature dependence.[9–12] Thereafter, it was pointed out[4] that IC as well as ISC was responsible for nonradiative transition in these molecules, based on the temperature dependence in the intensity of triplet–triplet absorption. However, the absolute values of ϕ_T have not been measured for these molecules. In this paper, we report the values of ϕ_T in various solvents and clarify the fraction of contribution of the two ISC and IC channels.

The TRTL system in this work, which utilizes a nitrogen pulse laser as excitation light and a He–Ne laser as probe light, is similar to those reported by other researchers.[7,13] Sample solutions were deaerated by freeze-pump-thaw cycles. TRTL signals measured for 9-acetylanthracene and 9-benzoylanthracene in deaerated cyclohexane are shown in Figures 1 and 2, respectively. The fast rising component (Uf) corresponds to heat released by vibrational relaxation in the S_1 state, IC and
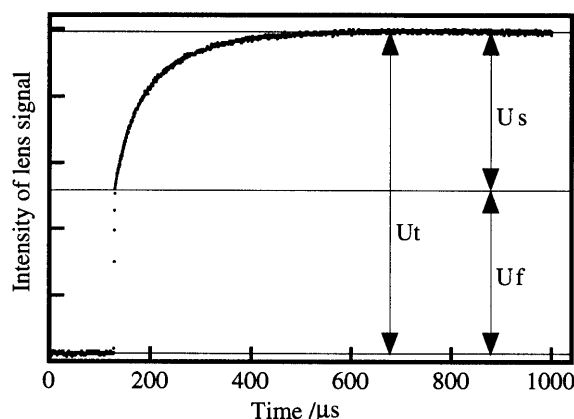
Figure 1. Time-resolved thermal lens signal of the deaerated cyclohexane solution of 9-acetylanthracene at room temperature.
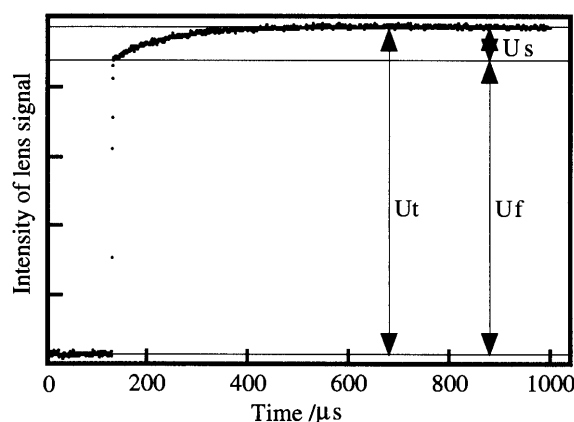
Figure 2. Time-resolved thermal lens signal of the deaerated cyclohexane solution of 9-benzoylanthracene at room temperature.

ISC. The slow rising component (Us) corresponds to heat released by nonradiative deactivation from the triplet state to the ground state. The magnitude of Us for 9-benzoylanthracene is markedly small in comparison with 9-acetylanthracene, indicating a large difference in the triplet yield between the two molecules. Similarly, the Us component of TRTL signals measured in air-saturated cyclohexane was much smaller for 9-benzoylanthracene than for 9-acetylanthracene, and this result also reflects the difference in the triplet yield since the Us component observed for air-saturated solutions is related to the yield of singlet oxygen formed by the oxygen quenching of the triplet state.[13]

The value of ϕ_T for nonfluorescent molecules is obtained from the ratio of Us to the total signal (Ut) by the following equation with the excitation energy of a nitrogen laser (E_e=355 kJ/mol) and the triplet energy (E_T = 176 kJ/mol for both molecules[12]).

$$Us / Ut = \phi_T \, E_T / E_e$$

In order to eliminate the influence of multiphoton processes which may be caused by excitation of high intensity, all measurements were carried out in a low range of excitation intensity where the fraction of a decrease in the intensity (Ut) to an incident intensity of probe light was from 1.5% to 3.5%. In this range the value of Us/Ut was constant within experimental errors. The influence of population lens and transient absorption in TRTL measurements should be also considered for obtaining accurate values of ϕ_T, because TRTL signals may include contributions from these effects besides thermal lens.[14] However, these influences are thought to be insignificant in the present measurements regarding anthracene derivatives whose absorption spectra from the ground and triplet states are analogous to those of anthracene, since the influence of population lens and transient absorption is negligible in the TRTL signal of anthracene measured with a He–Ne laser (633 nm) as probe light.[14]

The obtained values of ϕ_T in various solvents at room temperature (20–25 °C) are listed in Table 1. The values for 9-acetylanthracene are approximately unity and the nonradiative process is only ISC in all the solvents except alcohols. This result is discordant to the previous argument[4] that IC is significantly responsible for the nonradiative transition of 9-anthryl alkyl ketones such as 9-acetylanthracene in hydrocarbon solvents. The ϕ_T values less than unity for 9-acetylanthracene in methanol and ethanol demonstrate that IC as well as ISC works as a nonradiative channel in these solvents. On the other hand, the ϕ_T values of 9-benzoylanthracene are definitely less than unity in all the solvents studied and hence, both ISC and IC processes contribute to the nonradiative transition. In particular, the small values of 0.19–0.24 for ϕ_T in hexane, cyclohexane and methylcyclohexane indicate that IC is a predominant nonradiative process.

Table 1. The quantum yield of triplet formation (ϕ_T) and the ratio of rate constants of IC and ISC (k_{ic}/k_{isc}) at room temperature

Solvent	9-Acetylanthracene		9-Benzoylanthracene	
	ϕ_T	k_{ic}/k_{isc}	ϕ_T	k_{ic}/k_{isc}
HEX[a]	0.97±0.03	~0	0.19±0.02	4.3
CH[b]	0.97±0.04	~0	0.19±0.02	4.3
MCH[c]	1.00±0.03	~0	0.24±0.02	3.2
BEN[d]	0.99±0.02	~0	0.46±0.02	1.2
TOL[e]	0.96±0.05	~0	0.35±0.01	1.9
MOH[f]	0.69±0.04	0.45	0.38±0.02	1.6
EOH[g]	0.77±0.02	0.30	0.60±0.01	0.67
AC[h]	1.00±0.04	~0	0.80±0.05	0.25

[a]Hexane. [b]Cyclohexane. [c]Methylcyclohexane. [d]Benzene. [e]Toluene. [f]Methanol. [g]Ethanol. [h]Acetonitorile.

The ratio of IC to ISC in the rate constant (k_{ic}/k_{isc}) is evaluated by the following equation and the values obtained are listed in Table 1.

$$k_{ic} / k_{isc} = 1/\phi_T - 1$$

This ratio concerning 9-benzoylanthracene is strongly dependent on the solvent. The value of k_{ic}/k_{isc} in hexane and cyclohexane is about 17 times larger than that in acetonitrile, with a tendency that the value decreases in polar solvents.

Each value of k_{ic} and k_{isc} can be obtained if a lifetime of the S_1 state (τ_S) is known. All of three τ_S-values reported for 9-acetylanthracene and 9-benzoylanthracene in toluene[11] and 9-benzoylanthracene in cyclohexane[15] are 20 ps. The rate constants obtained from ϕ_T and τ_S are $k_{isc} = 5 \times 10^{10}$ s^{-1} for 9-acetylanthracene in toluene, $k_{ic} = 4.0 \times 10^{10}$ s^{-1} and $k_{isc} = 9.5 \times 10^9$ s^{-1} for 9-benzoylanthracene in cyclohexane, and $k_{ic} = 3.3 \times 10^{10}$ s^{-1} and $k_{isc} = 1.7 \times 10^{10}$ s^{-1} for 9-benzoylanthracene in toluene. The occurrence of a very fast IC process in the nonradiative transition from the S_1 state of 9-benzoylanthracene was thus confirmed.

The rate constant of IC concerning nonfluorescent or weakly fluorescent aromatic carbonyl compounds has been scarcely estimated so far because accurate data concerning both τ_S and ϕ_T are very limited. Further studies on the contribution of IC process, the estimation of IC rate constant and the mechanism for the very fast IC are needed for carbonyl anthracenes and other aromatic carbonyl compounds.

References
1 N. J. Turro, "Modern Molecular Photochemistry," The Benjamin/Cummings Publishing Company, Memlo Park, California (1978), Chap. 6.
2 S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).
3 E. C. Lim, *J. Phys. Chem.*, **90**, 6770 (1986).
4 T.-I. Lai and E. C. Lim, *J. Am. Chem. Soc.*, **107**, 1134 (1985).
5 E. C. Lim, in "Advances in Photochemistry," ed. by D. C. Neckers, D. H. Volman, and G. von Bünau, John Wiley & Sons, New York (1997), Vol. 23, p. 165.
6 S. E. Braslavsky and G. E. Heibel, *Chem. Rev.* **92**, 1381 (1992).
7 M. Terazima and T. Azumi, *Chem. Phys. Lett.*, **141**, 237 (1987).
8 K. Suzuki, H. Tanabe, S. Tobita, and H. Shizuka, *J. Phys. Chem. A*, **101**, 4496 (1997).
9 T. Matsumoto, M. Sato, and S. Hirayama, *Chem. Phys. Lett.*, **13**, 13 (1972).
10 T. Matsumoto, M. Sato, and S. Hirayama, *Chem. Phys. Lett.*, **18**, 563 (1973).
11 S. Hirayama and T. Kobayashi, *Chem Phys. Lett.*, **52**, 55 (1977).
12 S. Hirayama, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2411 (1982).
13 G. Rossbroich, N. A. Garcia, and S. E. Braslavsky, *J. Photochem.*, **31**, 37 (1985).
14 M. Terazima, T. Hara, and N. Hirota, *J. Phys. Chem.*, **97**, 10554 (1993).
15 K. Hamanoue, T. Nakayama, Y. Amijima, and K. Ibuki, *Chem. Phys. Lett.*, **267**, 165 (1997).