

INTERSYSTEM CROSSING OF NITROANTHRACENE DERIVATIVES STUDIED BY
PICOSECOND SPECTROSCOPY

Kumao HAMANOUE*, Satoshi HIRAYAMA**, Toshihiro NAKAYAMA*,
and Hiroshi TERANISHI*

* Department of Chemistry, Faculty of Technology, Kyoto Institute of
Technology, Matsugasaki, Sakyo-ku, Kyoto 606

** Faculty of Textile Fibers, Kyoto Institute of Technology

By a picosecond spectroscopy method, build-up times of $T^1 \leftrightarrow T_1$ absorption have been measured for 9-nitroanthracene derivatives. Rather long build-up times (72 to 86 psec) lead us to the conclusion that the observed build-up times represent the rates of internal conversion ($T_n \rightsquigarrow T_1$) and that the indirect ISC is the most important.

Recently, the study of the nonradiative process of the fluorescing state in anthracene derivatives has received considerable attention both from experimental and theoretical points of view.¹⁾ For example, Bennett and McCartin²⁾ have concluded that in those anthracene derivatives which show a significant variation of fluorescence yield with temperature, radiationless deactivation proceeds entirely by intersystem crossing (ISC), and the existence of a triplet state (T_2) which is approximately isoenergetic with the fluorescing state has been demonstrated. For anthracenes, therefore, it is clear that ISC is the most important nonradiative decay process from the fluorescing state. The importance of ISC is amplified for the anthracene derivatives with nonbonding orbitals, since El-Sayed's selection rule³⁾ predicts that ISC between states arising from different types of electronic promotion (e.g., $n\pi^* \leftrightarrow \pi\pi^*$) should be at least an order of magnitude greater than ISC between states of the same type of electronic configuration (e.g., $n\pi^* \leftrightarrow n\pi^*$ or $\pi\pi^* \leftrightarrow \pi\pi^*$).

We now wish to apply his rule to an important class of molecules, the nitroanthracene derivatives. Amongst several nitroanthracene derivatives, we selected 9-nitroanthracene (9-NO₂-A), 9-benzoyl-10-nitroanthracene (9-Bz-10-NO₂-A), and 9-cyano-10-nitroanthracene (9-CN-10-NO₂-A) on which qualitative discussion as to the photochemical reactions have already been given elsewhere.^{4,5)} Detailed information on the energy dissipation processes of these compounds is not only important in itself but would be valuable in understanding their photochemical processes.⁵⁾

Since the details of the method of picosecond laser photolysis and transient spectral measurements have been given in a previous paper,⁶⁾ we will describe it only briefly here. An improved JEOL mode-locked ruby laser was used. The second harmonic at 347.2 nm generated by a phase-matched KDP crystal was used to excite a sample. The monitoring-light pulse was continuous self-phased-modulated (SPM) light obtained by passing the focussed fundamental through a 15 cm cell containing

carbon tetrachloride. The mean pulse width and point $t=0$ were determined from the overlap of exciting and probe pulses by a technique of Hochstrasser et al.,⁷⁾ by measuring the build-up of $S_n \leftarrow S_1$ absorption at 560 nm in benzene solution of 9-cyanoanthracene, and the overlap was well represented by a 26 psec mean pulse width with an estimated error of 4 psec. After passing through the sample cell, this probe pulse was fed in a Mizojiri SD-12V-P spectrograph with a recording film of Tri-X-Pan. A 10° angle between the probe and exciting pulses kept the latter out of the spectrograph. A densitometer trace vertically across the photographic spectrum at a given wavelength was recorded with a modified Sakura PDM-5 micro-densitometer. The concentrations of the samples were 1.59 to 4.80×10^{-3} M, making the absorbances of the solutions at 347.2 nm to be 1.58 to 2.18 in a cell of 2 mm path length. The sample solutions were not deaerated and were excited at room temperature.

The time resolved absorption spectrum of 9-NO₂-A in ethanol is shown in Fig. 1. We also show the result obtained by a conventional flash photolysis at 77 K in the deaerated system. The lifetime of the transient species at 77 K is 17.7 msec. From these results, one can say that the transient spectra show the characteristic absorption bands around 450 nm and the observed spectra can be assigned to the $T_n \leftarrow T_1$ absorption which undoubtedly originated from the lowest triplet state $T_1(\pi\pi^*)$. The same result is also obtained for 9-Bz-10-NO₂-A (the T_1 lifetime is 16.0 msec at 77 K). The time resolved absorption spectra of 9-CN-10-NO₂-A in pico- and nano-second photolyses are nearly the same, but they are a little different from those of 9-NO₂-A and 9-Bz-10-NO₂-A, and no triplet absorption could be detected even at 77 K by a conventional flash photolysis. In a nanosecond pulse radiolysis using a Febetron 707,⁸⁾ we can get absorption spectrum due to the anion radical of 9-CN-10-NO₂-A when small amount of triethylamine is added to the solution. In the absence of triethylamine, transient spectrum which is very similar to that obtained by

nanosecond laser photolysis both with regard to the position of the absorption band and its intensity distribution is obtained. Since triethylamine works as a good cation radical scavenger, the transient spectrum

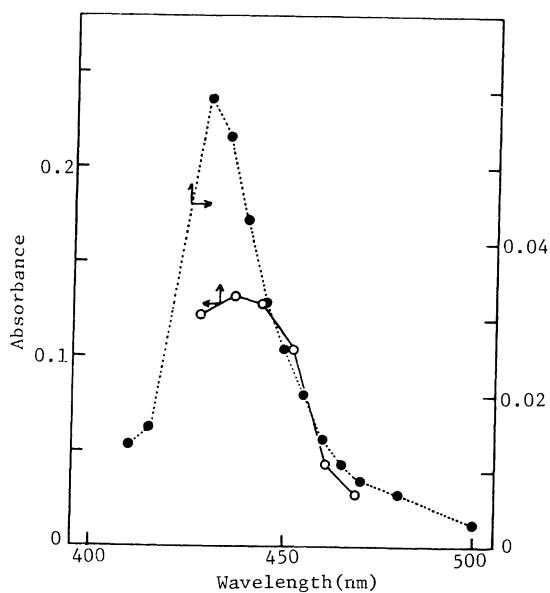


Fig. 1 Time resolved absorption spectrum of 9-NO₂-A in ethanol at 170 psec delay. (Dotted line is the result obtained by a conventional flash photolysis at 77 K.)

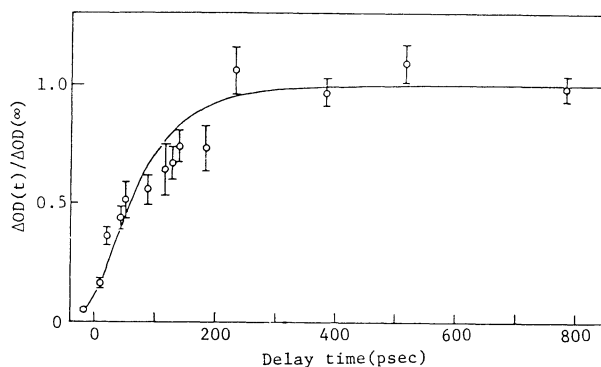


Fig. 2 Absorbances $\Delta OD(t)/\Delta OD(\infty)$ at 452 nm due to the excited state absorption of 9-NO₂-A in benzene resulting from singlet state excitation at 347.2 nm. The ϕ are normalized absorbances and the smooth curve is the calculated value.

obtained in pulse radiolysis may be due to the triplet state of 9-CN-10-NO₂-A originated from the recombination between an anion radical of 9-CN-10-NO₂-A and a solvent cation radical. Thus, the observed spectrum by picosecond photolysis may be also ascribed to the T_n←T₁ absorption.

The time evolution of the T_n←T₁ absorption are shown in Figs. 2 to 4. The smooth curve corresponds to a theoretical absorbance calculated with a well-known convolution method.^{7,9)} The build-up times of the T_n←T₁ absorption for the nitroanthracene derivatives are about 72–86 psec as shown in Table 1. One can see no external heavy atom effect on the build-up time of T₁ population. This result can not be explained in terms of the direct ISC from S₁(ππ*) to T₁(ππ*). Since nitroanthracene derivatives are usually nonfluorescent, it is expected that there exists a very fast nonradiative process from S₁, and direct ISC to T₁ will be of minute importance because of the extremely unfavorable Franck-Condon factors for such a process.

If we assume the fluorescence rate constant to be of the order of 10⁸ sec⁻¹ and experimental build-up time corresponds to the rate constant of ISC, the calculated fluorescence quantum yields become greater than 0.007 which means the S₁→S₀ fluorescence should be detectable with a present sensor device. Since no such emission has ever been detected even at 77 K, ISC from S₁(ππ*) to the triplet manifold must be fast with a rate constant ≥ 10¹¹ sec⁻¹. The ultra-fast ISC would be related to the presence of an nπ* triplet state, near or very slightly below the lowest excited singlet state, the transition to which from S₁(ππ*) is very rapid due to a favorable spin-orbit coupling and large Franck-Condon factor. It is concluded, therefore, that the measured build-up times should correspond to the rate

Table 1 Build-up times of T_n←T₁ absorptions

9-NO ₂ -A (at 452 nm)	86±6 psec in ethanol 76±6 psec in benzene or bromobenzene
9-Bz-10-NO ₂ -A (at 452 nm)	72±6 psec in ethanol 82±6 psec in benzene or bromobenzene
9-CN-10-NO ₂ -A (at 470 nm)	76±6 psec in benzene or bromobenzene

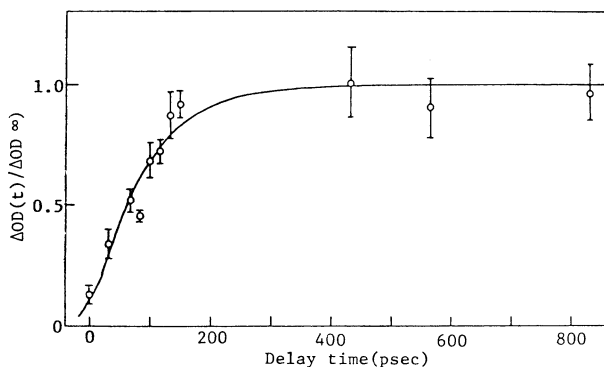


Fig. 3 Absorbances $\Delta OD(t)/\Delta OD(\infty)$ at 452 nm due to the excited state absorption of 9-Bz-10-NO₂-A in benzene resulting from singlet state excitation at 347.2 nm. The ϕ are normalized absorbances and the smooth curve is the calculated value.

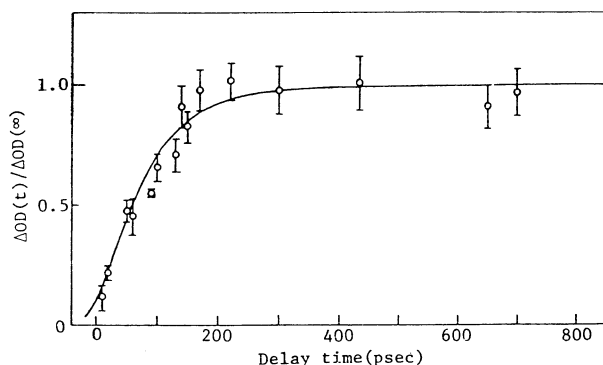


Fig. 4 Absorbances $\Delta OD(t)/\Delta OD(\infty)$ at 470 nm due to the excited state absorption of 9-CN-10-NO₂-A in benzene resulting from singlet state excitation at 347.2 nm. The ϕ are normalized absorbances and the smooth curve is the calculated value.

constants of the internal conversion in the triplet manifolds (e.g., $n\pi^* \rightarrow T_1$) and that the vibronic mixing among these triplet manifolds is not large. Since the large S_1-T_1 splitting makes it likely that there is a second or third triplet state between S_1 and T_1 , the internal conversion from $T_n(n\pi^*)$ to T_1 may well pass through these states.

Kokubun et al.¹⁰⁾ determined $T_2 \rightarrow T_1$ internal conversion rate to be $\approx 10^{11} \text{ sec}^{-1}$ for meso-anthracenes. However, from the studies on the photochemical sensitization, Liu and co-workers¹¹⁾ obtained $\tau(T_2) \approx 200 \text{ psec}$ for several meso-anthracenes. Gillispie and Lim¹²⁾ also suggested $\tau(T_2) \approx 200 \text{ psec}$ from an empirical energy gap correlation of internal conversion rates. Much stronger confirmation of our data has been reported by Hirayama and Kobayashi.¹³⁾ These authors studied the build-up time of $T_n \leftarrow T_1$ absorption in four carbonyl derivatives of anthracene and found $\tau(T_n)$ between 20 and 300 psec.

Our conclusion is consistent with other observations that have confirmed the importance of the $^1\pi\pi^* \rightarrow ^3n\pi^*$ or $^1n\pi^* \rightarrow ^3\pi\pi^*$ decay channel in planar heteroaromatics,¹⁴⁾ in nitronaphthalene⁹⁾ and aromatic ketones.^{13,15)}

This work was partly financed by Grant in Aid for Scientific Research from the Ministry of Education (No. 221620).

References

- 1) J.B.Birks, "Photophysics of Aromatic Molecules", p.142, Wiley-Interscience, New York (1970).
- 2) R.G.Bennett and P.J.McCartin, J.Chem.Phys., 44, 1969 (1966).
- 3) S.K.Lower and M.A.El-Sayed, Chem.Rev., 66, 199 (1966).
- 4) O.L.Chapman, D.C.Heckert, J.W.Reasoner and S.P.Thackaberry, J.Am.Chem.Soc., 88, 5550 (1960).
- 5) S.Hirayama, K.Hamanoue, H.Ohya and H.Teranishi, to be published; ASC/CSJ Chemical Congress (Physical Chemistry, No.38), Honolulu, Hawaii (1979).
- 6) K.Hamanoue, S.Hirayama, M.Okamoto, T.Nakayama and H.Teranishi, Mem.Fac.Ind. Arts, Kyoto Tech.Univ., 27, 61 (1978).
- 7) R.W.Anderson Jr., R.M.Hochstrasser, H.Lutz and G.W.Scott, J.Chem.Phys., 61, 2500 (1974).
- 8) K.Hamanoue, H.Ohya, H.Teranishi, M.Washio, S.Tagawa and Y.Tabata, to be published; The 22th Symposium on Radiation Chemistry, Nagoya (1979).
- 9) R.W.Anderson Jr., R.M.Hochstrasser, H.Lutz and G.W.Scott, Chem.Phys.Lett., 28, 153 (1974).
- 10) S.Kobayashi, K.Kikuchi and H.Kokubun, Chem.Phys., 27, 399 (1978).
- 11) R.S.H.Liu and P.E.Kellog, J.Am.Chem.Soc., 91, 250 (1969); R.S.H.Liu and J.R.Edman, *ibid.*, 91, 1492 (1969); R.O.Campbell and R.S.H.Liu, *ibid.*, 95, 6560 (1973); C.C.Ladwig and R.S.H.Liu, *ibid.*, 96, 6210 (1974).
- 12) G.D.Gillispie and E.C.Lim., Chem.Phys.Lett., 63, 193 (1979).
- 13) S.Hirayama and T.Kobayashi, *ibid.*, 52, 55 (1977).
- 14) P.E.Zinsli and M.A.El-Sayed, *ibid.*, 34, 304 (1975); *ibid.*, 36, 290 (1975).
- 15) D.E.Damschen, C.D.Merritt, D.L.Perry, G.W.Scott and L.D.Tally, J.Phys.Chem., 82, 2268 (1978).

(Received January 5, 1980)