CHEMISTRY LETTERS, pp. 1279-1282, 1973. Published by the Chemical Society of Japan

EFFECT OF PRESSURE ON INTERSYSTEM CROSSING OF ANTHRACENE DERIVATIVES IN SOLUTION

Fujio TANAKA and Jiro OSUGI
Department of Chemistry, Faculty of Science,
Kyoto University, Kyoto 606

The pressure dependences of the fluorescence yields for anthracene, 1-, 2-, 9-methylanthracene, 1-, 2-, and 9-chloroanthracene were obtained in n-hexane at room temperature up to 3000 kg/cm^2.

Results were interpreted in terms of a change of Franck-Condon factor in the intersystem crossing rate.

The deactivation processes of the lowest excited singlet state S_1 of anthracene derivatives have received a considerable interest in view of the intersystem crossing to the higher triplet state T_2.1) In the previous paper,2) the authors reported that the fluorescence yield of 9-methylanthracene increased remarkably with increasing pressure while the increase was slight in anthracene. And it was suggested that the intersystem crossing rate ($S_1 \dashrightarrow T_2$) was dependent on pressure through the change of the energy gap between the S_1 state and the T_2 state. To clarify further the effect of pressure on the intersystem crossing rate, similar experiments were carried out in n-hexane at room temperature up to 3000 kg/cm^2 for other derivatives; anthracene(A), 1-, 2-, 9-methylanthracene(9-mA), 1-, 2-, and 9-chloroanthracene(9-cA).

Fluorescence quantum yields at normal pressure were determined using rhodamine B as photocounter and 9,10-diphenylanthracene as a standard substance(Φ_f=0.83)3). Those at high pressure were obtained from the change of intensities at the peaks of fluorescence spectra as described previously2). Sample solutions for measurements of quantum yields at normal pressure were degassed by several freeze-thaw cycles, and in the measurements at high pressure degassed solutions were put into the cell under a stream of nitrogen gas.

Fluorescence spectra of 2-methylanthracene are shown in Fig.1. In contrast with 9-derivatives, the distinct decrease of intensity with increasing pressure was observed in 2-derivatives. The degrees of pressure-induced red shift were nearly equal in all compounds. The pressure dependences of fluorescence yields(Φ_f) are shown in Fig.2. The previous results of anthracene and 9-methylanthracene are displayed with a slight modification based on further examinations.

Evidently, pressure dependences of fluorescence yields are affected by the substituted position in both methyl- and chloro-derivatives.

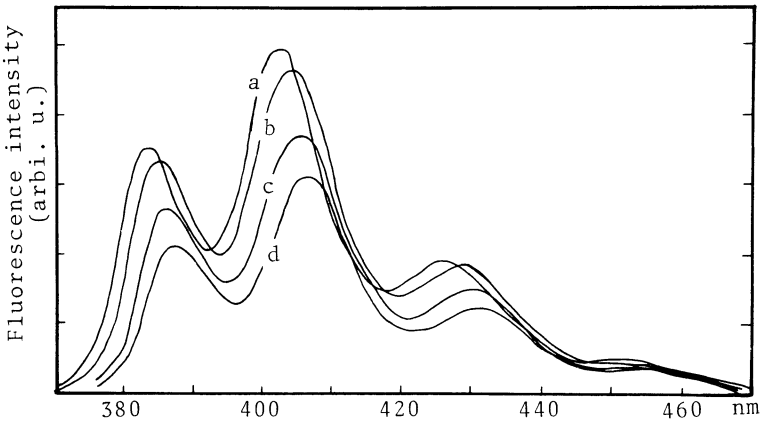

Fig.1 Uncorrected spectra of fluorescence of 2-methylanthracene in n-hexane at room temperature. The concentration is 2.5×10^{-4} mol/l at normal pressure. a: normal pressure, b: 1000 kg/cm^2, c: 2000 kg/cm^2, d: 3000 kg/cm^2.

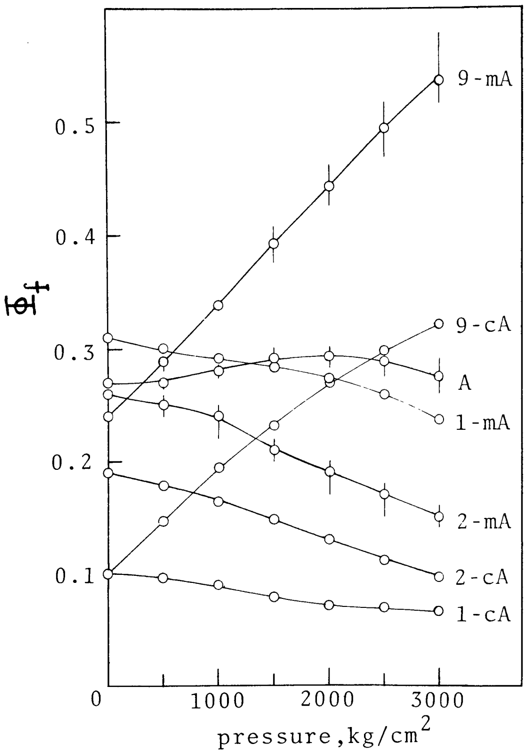

Fig.2 Pressure dependence of fluorescence yield at room temperature.

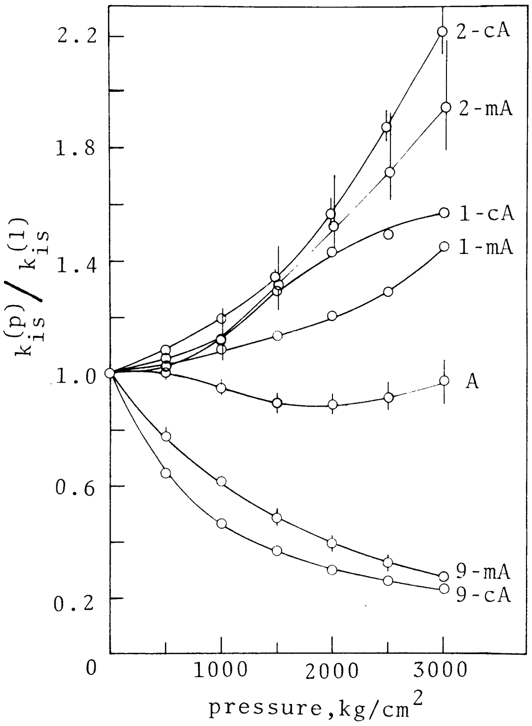

Fig.3 Pressure dependence of intersystem crossing rate at room temperature.

Deactivation parameters of the S_1 state of anthracene derivatives are only the fluorescence radiative rate (k_f) and intersystem crossing rate (k_{is}), and the internal conversion process has been verified to be negligible.[4,5] The pressure dependence of intersystem crossing rate is obtained from the following equation on assumption that the fluorescence radiative rate scarcely depends on pressure.

$$k_{is} = k_f(\Phi_f^{-1} - 1)$$

Fig.3 shows explicitly the effect of the substituted position on the pressure dependence of intersystem crossing rate. Maybe, this distinct difference is based on the variation of the relative position of the S_1 state to the T_2 state.

A nonradiative transition rate is expressed by the following general formula,

$$k_{nr} = \frac{2\pi}{\hbar} V^2 \rho F$$

where V, ρ and F are an electronic matrix element, a density of final state, and a Franck-Condon factor, respectively. Among three variables it is likely that V and ρ are insensitive to pressure. So it would be considered that the pressure dependences of k_{is} shown in Fig.3 express those of the Franck-Condon factor. Of course, in the present results the Franck-Condon factor means the average value because of the thermal distribution in the S_1 state at room temperature.

The table shows the wavelengths of 0-0 band of absorption and fluorescence at normal pressure. The energy of the S_1 state is in the following order in both substituents; anthracene > 2- > 1- > 9-derivative. It has been indicated from the temperature effect on the intersystem crossing rate[5,6,7] that the situation of the relative position between the S_1 state and the T_2 state are $S_1 > T_2$ in anthracene and 2-derivatives, while $S_1 < T_2$ in 9-derivatives. Corresponding to the position of the S_1 state, 1-derivatives are probably in the intermediate situation.

Assuming that pressure lowers the electronic energy of the S_1 state more than the T_2 state as discussed previously,[2] the S_1-T_2 gap decreases with increasing pressure in the derivative where the S_1 state is situated above the T_2 state while it increases where the S_1 state is below the T_2 state.

The S_1 state lies about 600 cm^{-1} above the T_2 state in anthracene,[8] and the pressure-induced lowering of the S_1 state is about 200~300 cm^{-1} at 3000 kg/cm^2 in all derivatives.

Table. The energies of S_0-S_1 of anthracene derivatives in n-hexane at normal pressure.

	λ0-0 (nm) absorp.	λ0-0 (nm) fluore.
anthracene	375	377.5
2-methyl	377	382
1-methyl	379	384
9-methyl	386	389.5
anthracene	375	377.5
2-chloro	380	382.5
1-chloro	382	384
9-chloro	388.5	391

According to Fig.3, the Franck-Condon factor increases in 2-derivatives as the S_1-T_2 gap decreases and it decreases in 9-derivatives as the gap increases. It seems that 1-derivatives are still in the situation of $S_1 > T_2$ on account that the Franck-Condon factor increases with increasing pressure. But, anthracene where the S_1 state lies above the T_2 state exhibits a very different behavior from 2-derivatives. In general, when two states taking part in the transition are very close to each other, it is considered that the Franck-Condon factor between those states does not always increase as the energy gap decreases, but shows a vibronic structure caused by some specific modes of molecular vibration. Indeed, the S_0-S_1 absorption[9], T_1-S_0 phosphorescence[10] and T_1-T_2 absorption[8] for anthracene show the clear vibronic progressions of low wavenumbers; ca.400 cm^{-1}, 400 cm^{-1} and 600 cm^{-1}, respectively. Therefore, it may be also predicted that the Franck-Condon factor between the S_1 state and the T_2 state shows the peaks at the electronic energy gap equal to ca.400 cm^{-1} and 600 cm^{-1} as well as at the position where the gap disappears (i.e. 0-0 position) and so does not have a monotonous relation to the energy gap. According to the above view, in n-hexane at normal pressure anthracene would possess such a S_1-T_2 gap that the Franck-Condon factor has nearly an extreme value (maximum or minimum) and is insensitive to the change of the energy gap by pressure. Also as for 1- and 2-derivatives, it seems clear that the S_1 state lies above the T_2 state and that these derivatives possess the S_1-T_2 gaps at normal pressure where the Franck-Condon factor increases with decreasing energy gap, because the Franck-Condon factor decreases monotonously with increasing energy gap if the S_1 state lies below the T_2 state. However, at the present stage it could not be determined clearly how much S_1-T_2 gap these derivatives possess. Anyway, taking account of the strong dependence of the Franck-Condon factor on the energy gap between the two electronic states very close to each other, the pressure dependence of Franck-Condon factor would vary remarkably according to the amount of the energy gap at normal pressure.

The relation between the Franck-Condon factor and the energy gap in anthracene derivatives will be discussed in more detail in the near future.

References

1) R.S.Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley Interscience, (1969), p.141, and therein cited references.
2) F.Tanaka and J.Osugi, Rev. Phys. Chem. Japan, 42, 85 (1972)
3) W.H.Melhuish, J. Phys. Chem., 65, 229 (1961)
4) T.Medinger and F.Wilkinson, Trans. Faraday Soc., 61, 620 (1965)
5) E.C.Lim, J.D.Laposa and J.M.H.Yu, J. Mol. Spectry, 19, 412 (1966)
6) W.R.Ware and B.A.Baldwin, J. Chem. Phys., 43, 1194 (1965)
7) R.G.Bennet and P.J.McCartin, ibid., 44, 1969 (1966)
8) R.E.Kellog, ibid., 44, 411 (1966)
9) particularly prominent at low temperature, for instance E.Clar, Spectrochim. Acta, 4, 116 (1950)
10) M.R.Padhye, S.P.McGlynn and M.Kasha, J. Chem. Phys., 24, 588 (1956)

(Received August 23, 1973)