CHEMISTRY LETTERS, pp. 247-250, 1978. Published by the Chemical Society of Japan

TEMPERATURE EFFECT ON THE INTERSYSTEM CROSSING OF ACRIDINE IN VARIOUS SOLVENTS

Koji UJI-IE, Kunihiko KASAMA, Koichi KIKUCHI, and Hiroshi KOKUBUN
Department of Chemistry, Faculty of Science,
Tohoku University, Aoba, Aramaki, Sendai 980

The relative yield of the lowest triplet state of acridine increases with increasing temperature in water, ethanol, and iso-propanol, but decreases in methylmethacrylate (MMA) and polymethylmethacrylate (PMMA). In benzene it remains constant in the range of 278 to 336 K. The lowest excited singlet state is of π,π^* character in all the solvents studied. The energy gap between the singlet π,π^* and n,π^* states is larger in the order of water $>$ alcohols $>$ MMA, PMMA and benzene. The intersystem crossing through the singlet n,π^* state becomes less singnificant for larger energy gap.

Acridine is fluorescent only in proton donating solvents at room temperature.[1-3] This is explained by the change of the character in the first excited singlet state, S_1; S_1 is of π,π^* character in proton donating solvents and of n,π^* in others.[1,4,5] In a pervious paper,[6] we found that the third excited triplet state, $T_3(\pi,\pi^*)$, lies at 420 cm^{-1} above S_1 and plays an important role in the intersystem crossing of acridine and that $S_2(n,\pi^*)$ does not contribute to the intersystem crossing in polyvinylalcohol (PVA).

In order to discriminate the solvent effects on the intersystem crossing processes, we studied the temperature dependence of the relative yields of the lowest triplet state, $T_1(\pi,\pi^*)$, in water, ethanol, iso-propanol, benzene, MMA and PMMA by a conventional flash photolysis. Temperature dependences of the absorbance of the $T_n \leftarrow T_1$ absorption immediately after flashing in these solvents are shown in Fig. 1. In water, ethanol and iso-propanol the relative yield of $T_1(\pi,\pi^*)$ increases with increasing temperature. In benzene it remains constant in the range of 278 to 336 K. In MMA and PMMA it decreases with increasing temperature.

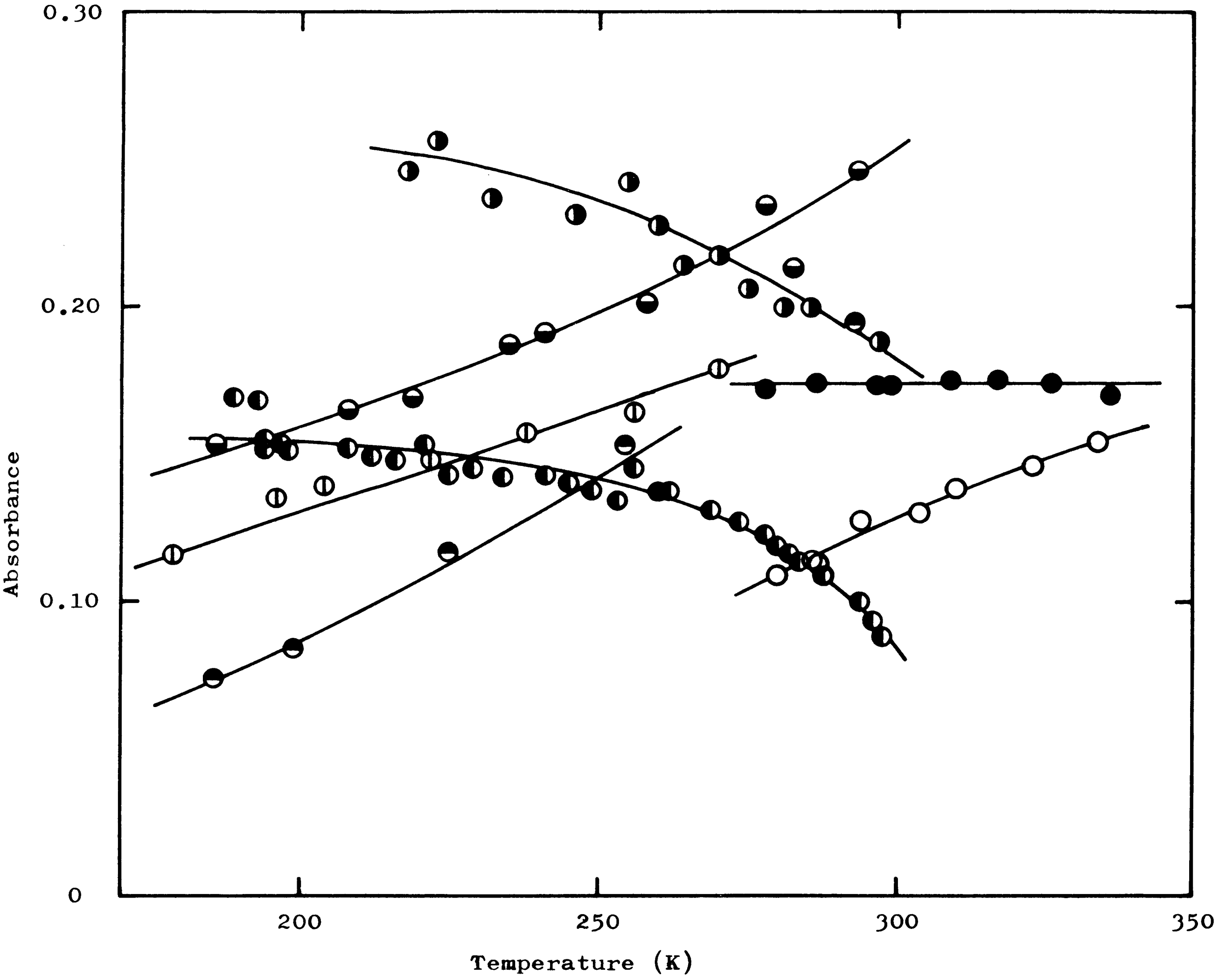

Fig. 1. Temperature dependences of the absorbance of the T-T absorption immediately after flashing in various solvents.

—○— water containing 2 x 10^{-2}M NaOH, —⦶— PVA(x 10), —◓— ethanol, —◒— iso-propanol, —◑— MMA, —◐— PMMA, and —●— benzene.

It is known that the excited acridine does not react in water and benzene but in ethanol and iso-propanol.7) It was found that acridine is photoreduced to yield acridane and its derivatives with the quantum yields of 0.059 and 0.008 in the deaerated and aerated MMA solutions, respectively, and 0.006 in PMMA at 298 K.

The fluorescence lifetime of acridine is reported to be 10.3 ns in water and 0.72 ns in ethanol at 298 K8), and 12.1 ns in PVA at 286 K.6) The lifetime of S_1 has recent been evaluated by the measurement of the rise of the $T_n \leftarrow T_1$ absorption; 12.5 ps in iso-octane4) and 33.3 ps in n-hexane5) at room temperature. The fluorescence at 77 K was reported for ether-iso-pentane9) and n-octane10) matrices. We could observe the intrinsic fluorescence in PMMA and methylcyclohexane at 77 K.

On the basis of the results described above and the informations obtained in a previous study on the deactivation of $S_1(\pi,\pi^*)$ in PVA, we are able to consider the solvent effect on the intersystem crossing from S_1 to $T_1(\pi,\pi^*)$ and the fluorescence characteristics.

Since the fluorescence was observed in hydrocarbons, it is undoubted that S_1 is of π,π^* character in all the solvents studied in contrast to earlier suggestions.1,4,5) The rate of the temperaure independent intersystem crossing is $1.4 \times 10^7\ s^{-1}$ in PVA,6) which may be attributed to $S_1(\pi,\pi^*) \longrightarrow T_2(n,\pi^*)$ intersystem crossing, because $S_1(\pi,\pi^*) \longrightarrow T_1(\pi,\pi^*)$ transition is negligible in anthracenes.11) The possibility that $S_1(\pi,\pi^*) \longrightarrow T_2(n,\pi^*)$ transition is enhanced in less polar solvents than PVA does not exist, because the energy level of π,π^* state is raised and that of n,π^* state is lowered with decreasing the solvent polarily.12) On the other hand, the pre-exponential factor of the temperature dependent intersystem crossing which was assigned to be $S_1(\pi,\pi^*) \longrightarrow T_3(\pi,\pi^*)$ transition is $3.7 \times 10^8\ s^{-1}$ in PVA.6) It is the same order of magnitude for the rate of the intersystem crossing of aromatic hydrocarbons.13) Therefore, the considerably shorter lifetimes of $S_1(\pi,\pi^*)$ in ethanol and nonpolar solvents than in PVA should be ascribed to the participation of $S_2(n,\pi^*)$. Consequently, it is concluded that the relative energy levels of $S_1(\pi,\pi^*)$, $S_2(n,\pi^*)$ and $T_3(\pi,\pi^*)$ are changed by solvent polarity as follows.

In benzene, MMA and PMMA, the level of $S_2(n,\pi^*)$ is slightly higher than those of $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$ which nearly equal to each other, so that the thermal activation is not important for $S_1(\pi,\pi^*) \longrightarrow T_3(\pi,\pi^*)$ and $S_1(\pi,\pi^*) \longrightarrow S_2(n,\pi^*) \longrightarrow T_3(\pi,\pi^*)$ transitions and the latter transition is very rapid. Therefore, the yield of $T_1(\pi,\pi^*)$ does not increase with increasing temperature and the lifetime of S_1 may be very short at room temperaure in these solvents as in saturated hydrocarbons.4,5) It is noteworthy that in PMMA both yields of the fluorescence and intersystem crossing increase with decreasing temperature; non-radiative deactivation other than intersystem crossing increases with increasing temperature. Since acridine is photoreduced in MMA and PMMA, it is suggested that the photoreduction occurs in $S_2(n,\pi^*)$ by thermal acrivation and reduces the yield of $T_1(\pi,\pi^*)$. In benzene acridine is not photoreduced, so that the yield of $T_1(\pi,\pi^*)$ is high14) and temperature independent.

In ethanol and iso-propanol, $S_2(n,\pi^*)$ is higher than $S_1(\pi,\pi^*)$, and $T_3(\pi,\pi^*)$ lies between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$. The temperature dependent intersystem crossing can occur through two pathways; $S_1(\pi,\pi^*) \xrightarrow{kT} T_3(\pi,\pi^*)$ and $S_1(\pi,\pi^*) \xrightarrow{kT} S_2(n,\pi^*) \longrightarrow T_3(\pi,\pi^*)$.

Since the larger energy is necessary for the thermal activation of $S_1(\pi,\pi^*)$ into $S_2(n,\pi^*)$ in ethanol and iso-propanol than in nonpolar solvent, the fluorescence of low yield is observed even at room temperature[3,15] and the intersystem crossing is enhanced with increasing temperature. The photoreduction in $S_2(n,\pi^*)$ reduces the yield of $T_1(\pi,\pi^*)$ in reactive solvents.[7,15]

In water and PVA, $S_2(n,\pi^*)$ is much higher than $S_1(\pi,\pi^*)$, and $T_3(\pi,\pi^*)$ lies between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$. The contribution of $S_2(n,\pi^*)$ to the decay of $S_1(\pi,\pi^*)$ is much smaller in water and PVA than in other solvents. Therefore, the decay of $S_1(\pi,\pi^*)$ is slow in water[8] and PVA[6] and the fluorescence yield is high in water at room temperature.[3]

REFERENCES

1) N. Mataga, Y. Kaifu and M. Koizumi, Bull. Chem. Soc. Jpn., 29, 373 (1956)
2) N. Mataga and S. Tsuno, Bull. Chem. Soc. Jpn., 30, 368 (1957)
3) E. J. Bowen, N. J. Holder and G. B. Woodger, J. Phys. Chem., 66, 2491 (1962)
4) Y. Hirata and I. Tanaka, Chem. Phys. Letters, 41, 336 (1976)
5) V. Sundstrom, P. M. Rentzepis and E. C. Lim, J. Chem. Phys., 66, 4287 (1977)
6) K. Kikuchi, K. Uji-ie, Y. Miyashita and H. Kokubun, Bull. Chem. Soc. Jpn., 50, 879 (1977)
7) M. Koizumi, Y. Ikeda and H. Yamashita, Bull. Chem. Soc. Jpn., 41, 1056 (1968)
8) H. Kokubun, Bull. Chem. Soc. Jpn., 42, 919 (1969)
9) S. J. Ladner and R. S. Becker, J. Phys. Chem., 67, 2481 (1963)
10) L. A. Klimova, G. N. Nersesova, B. A. Progovskaya and G. S. Ter-Sarkisyan, Teor. Eksp. Khim., 12, 233 (1976)
11) A. Kearvell and F. Wilkinson, Transition Non-Radiatives dans les Molecules, Paris, 1969; J. Chim. Phys., 1970, 125
12) A. A. Lamola, J. Chem. Phys., 47, 4810 (1967)
13) J. B. Birks, "Organic Molecular Photophysics," Vol. 1, ed. by J. B. Birks, John Wiley & Sons, London (1973), p. 41
14) A. Kellmann, J. Phys. Chem., 81, 1195 (1977)
15) K. Tokumura, K. Kikuchi and M. Koizumi, Bull. Chem. Soc. Jpn., 46, 2279 (1973)

(Received September 22, 1977)