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INTERSYSTEM CROSSING AND LOWEST TRIPLET STATES OF 4-CHROMANONE, CHROMONE, AND FLAVONE

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Using pico- and nanosecond spectroscopy methods, $T_n \leftarrow T_1$ absorption spectra and their build-up times have been measured for 4-chromanone, chromone, and flavone. From these results, combined with the results of a conventional flash photolysis, the electronic configuration of the lowest triplet state was discussed.

Matsushima et al.[1)] have reported that photolysis of flavanone in benzene gave a ring cleavage product (2'-hydroxychalcone), while in 2-propanol coupling products (pinacols and solvent adducts) were obtained. Similar irradiation of 4-chromanone in benzene gave no photoproducts, while irradiation in 2-propanol gave 4-chromanone pinacols. These authors assumed that photoformation of chalcone from flavanone in benzene might involve $\pi\pi^*$ triplet state. To the contrary, flavanone in 2-propanol and 4-chromanone seemed to have essentially $n\pi^*$ character in their triplet states. Our preliminary experiments in photolysis of 4-chromanone, chromone, and flavone gave the results that 4-chromanone in hexane or 2-propanol gave coupling product, chromone gave a mixture of ring cleavage product and a coupling product, and flavone gave a cleavage product irrespective of the polarity of solvents.[2)]

We now wish to measure the rate of ISC and to determine the character of the lowest triplet states for 4-chromanone, chromone, and flavone, on which qualitative discussion as to the photochemical reaction has already been given.[1,2)]

Since the details of the methods of pico- and nanosecond laser photolyses have been given in a previous paper,[3)] we will describe it only briefly here. A picosecond mode-locked ruby laser was used and the second harmonic at 347.2 nm with an approximately 26-psec mean pulse width was used to excite a sample. A nanosecond Q-switched ruby laser generated a pulse containing about 1.5 J of red light of wavelength 694.3 nm whose half-peak duration was 22 nsec. The KDP frequency doubler converted a few percent of the energy of 694.3-nm beam to that of 347.2-nm beam. All laser experiments were carried out at room temperature, and the sample solutions were not degassed in a picosecond photolysis and were degassed in a nanosecond photolysis. Conventional flash photolysis experiments were carried out at 77 K in degassed rigid glasses.

The time resolved absorption spectra in a picosecond photolysis of 4-chromanone in ethanol and benzene are shown in Fig. 1. Figure 2 shows the results obtained by a nanosecond photolysis at room temperature and a conventional flash photolysis at 77 K. Compared these results with that of Fig. 1, the transient spectrum in Fig. 1

can be assigned to the $T_n \leftarrow T_1$ absorption which undoubtedly originated from the lowest triplet state T_1. At room temperature, the decay times of this spectrum were 0.4 μsec in ethanol and 0.3 μsec in benzene. At 77 K, the decay times (τ) of $T_n \leftarrow T_1$ absorption and phosphorescence lifetimes (τ_p) were nearly the same irrespective of the polarity of solvents, i.e., 99 msec (τ_p) in 3-methylpentane, 90 (τ) and 97 msec (τ_p) in 2-methyltetrahydrofuran (2-MTHF), 93 (τ) and 81 msec (τ_p) in EPA (ether/isopentane/ethanol=5:5:2 in volume ratio), 119 (τ) and 92 msec (τ_p) in 1:1 ether-ethanol mixture, 104 (τ) and 90 msec (τ_p) in 1:4 methanol-ethanol mixture. Relatively short lifetimes and a solvent independence, combined with the result of photoproducts, are at least suggestive of a lowest triplet state of nπ* character. This conclusion is consistent with that of Gallivan and Brinen.[4)]

The typical time evolution of the $T_n \leftarrow T_1$ absorption is shown in Fig. 3 for 4-chromanone in benzene. The experimental points are the average absorbances at each delay time, and the error bars give the standard deviation from the average. The smooth curves correspond to the theoretical absorbances calculated with a well-known convolution method,[5)] by assuming a single exponential population of the absorbing triplet state. The most probable build-up times (k^{-1}) of the $T_n \leftarrow T_1$ absorption are 50 to 60 psec as shown in Table 1. One can see no external heavy atom effect on the build-up times of T_1 population. This result can not be explained in terms of the direct ISC from $S_1(n\pi^*)$ to $T_1(n\pi^*)$. The basis for this conclusion is that nπ* triplet undergoes inherently weak spin-orbit coupling with the singlet nπ*.[6)] (Absorption spectra in polar and non-polar solvents at room temperature revealed a lower-lying nπ* singlet transition for 4-chromanone, chromone, and flavone.) As a consequence the magnitude of the spin-orbit coupling induced by the external perturbation due to heavy atoms, must be consequential in the weak ${}^1n\pi^* \rightsquigarrow {}^3n\pi^*$ transition. Since no fluorescence has ever been detected

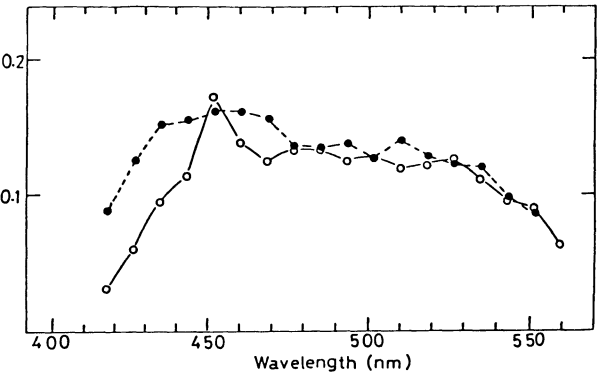

Fig. 1 Time resolved absorption spectra of 4-chromanone in ethanol (○) and benzene (●) at 110 psec delay

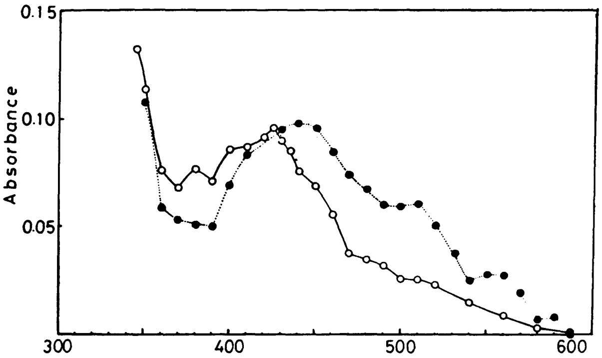

Fig. 2 $T_n \leftarrow T_1$ absorption spectra of 4-chromanone
●; in ethanol at room temperature at 150 nsec delay
○; in EPA at 77 K by a conventional flash photolysis

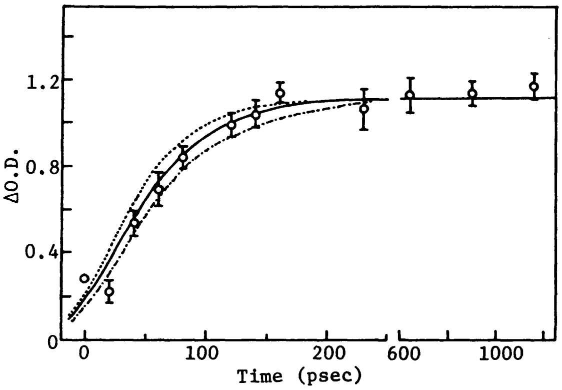

Fig. 3 Time dependence of the $T_n \leftarrow T_1$ absorption of 4-chromanone in benzene at room temperature The smooth curves are the theoretical absorbances. —·—·—, k^{-1}=60 psec; ———, 50 psec; ·········, 40 psec

Table 1 Build-up times of $T_n \leftarrow T_1$ absorption

Solvents	4-Chromanone (at 450 nm)	Chromone (at 560 nm)	Flavone (at 560 nm)
Ethanol	50±10 psec	30±6 psec	42±8 psec
Benzene	50±10	42±6	40±10
Bromobenzene	60±10	30±10	40±20
CCl_4			30±10

even at 77 K (for 4-chromanone, chromone, and flavone), ISC from $S_1(n\pi^*)$ to the triplet manifold must be very fast.

The ultra-fast ISC would be related to the presence of a $\pi\pi^*$ triplet state, the transition to which from $S_1(n\pi^*)$ is very rapid due to a favorable spin-orbit coupling. It is concluded, therefore, that the lowest triplet state is $n\pi^*$ and the measured build-up times should correspond to the rate constant of the internal conversion in the triplet manifolds (e.g., $\pi\pi^* \leftarrow n\pi^*$), and the vibronic mixing among these triplet manifolds is not large due to a somewhat greater energy gap between $n\pi^*$ and $\pi\pi^*$ states.[4)] Strong confirmation of our data has been reported by Damschen et al.[7)] These authors studied the build-up times of the triplet absorptions of benzophenone, xanthone, and anthrone, and found fast ISC rates ($k^{-1} \leq 20$ psec) between the lowest singlet excited state and a higher-lying triplet state (or an unrelaxed triplet state). For anthrone, the build-up time of the relaxed $T_n \leftarrow T_1$ absorption was 50 psec.

For chromone the strong $T_n \leftarrow T_1$ absorption with a peak maximum at 650 nm has been observed by a conventional flash photolysis at 77 K. The decay times (τ) of the $T_n \leftarrow T_1$ absorption and phosphorescence lifetimes (τ_p) showed a strong solvent dependence, i.e., 25-46 (τ) and 22-39 msec (τ_p) in EPA, 86-231 msec (τ_p) in 1:1 ether-ethanol mixture, 307 msec (τ) in 1:1 methanol-ethanol mixture. The relatively short lifetimes in less polar solvent and long lifetime in polar solvent, are at least suggestive of a lowest triplet state of $n\pi^*$ character in non-polar solvent and $\pi\pi^*$ character in polar solvent. This conclusion is consistent with that of Gallivan and Brinen,[4)] who observed τ_p=15 ~ 20 msec in 3-methylpentane and τ_p=310 ~ 330 msec in ethanol, and suggested that lower-lying $n\pi^*$ and $\pi\pi^*$ triplet states of chromone are nearly isoenergitic, very strongly mixed and can be reordered by changing solvents.

The transient absorption spectra in a picosecond photolysis were measured at the range of 420 to 580 nm, which showed monotonous increase to the longer wavelength, and the spectral profile was not affected by the polarity of solvents. However, the build-up times of the absorption were slightly changed by the polarity of solvent as shown in Table 1. Since the mean pulse width of the exciting laser pulse is 26±6 psec, we think that the build-up time of 30 psec in ethanol or bromobenzene corresponds to a fast build-up time (less than 30 psec). Thus, the result of Table 1 can be interpreted in terms of the direct ISC from $S_1(n\pi^*)$ to the lowest energy triplet state of mixed orbital character, that is, $S_1(n\pi^*) \rightsquigarrow T(\pi\pi^*)$ transition is responsible for the build-up time in the polar solvent, while $S_1(n\pi^*) \rightsquigarrow T(n\pi^*)$ transition is reponsible in the non-polar solvent. (It looks like that the build-up time in bromobenzene shows the external heavy atom effect.)

For flavone the $T_n \leftarrow T_1$ absorption bands at 365 ~ 370 nm and 640 ~ 650 nm have been observed by both a nanosecond laser photolysis at room temperature and a conventional flash photolysis at 77 K. The decay times of the $T_n \leftarrow T_1$ absorption at 77 K are relatively long and increase as the solvent polarity increases, i.e., 286 (at 370 nm) and 282 msec (at 660 nm) in 9:1 methylcyclohexane-isopentane mixture, 362 (at 365 nm) and 365 msec (at 640 nm) in 2-MTHF, 410 (at 370 nm) and 384 msec (at 640 nm) in EPA, 424 (at 365 nm) and 414 msec (at 640 nm) in 1:1 ether-ethanol mixture, 465 (at 365 nm) and 462 msec (at 640 nm) in 1:4 methanol-ethanol mixture. This result suggests the lowest triplet state of $\pi\pi^*$ character. The same conclusion is also obtained by Pownall,[8)] who has measured phosphorescence spectrum at 77 K in 1:1 ether-ethanol mixture.

The build-up times of the $T_n \leftarrow T_1$ absorption obtained by a picosecond photolysis are shown in Table 1. In bromobenzene, one can not see the clear external heavy atom effect on the build-up times of T_1 population because of the large experimental error. However, in carbon tetrachloride, it seems that the external heavy atom effect is observed. Thus, the result of Table 1 would be related to the presence of a $T_2(n\pi^*)$ triplet state, the transition to which from $S_1(n\pi^*)$ is not so fast as a consequence of El-Sayed's selection rule, and the external perturbation due to heavy atom increases spin-orbit coupling. The relatively small $T_2 - T_1$ splitting[8)] makes it likely that the internal conversion between T_2 and T_1 is fast.

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