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NATURE OF THE EXCITED STATES OF 2-NAPHTHOL AND 1-ANTHROL HYDROGEN BONDED WITH PYRIDINE

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The transient absorption spectra were observed for 2-naphthol and 1-anthrol in pyridine upon sensitization by suitable triplet energy donors. No transient was produced by direct excitation. The intersystem crossing process is not the deactivation pathway of the singlet excited species hydrogen bonded with pyridine.

The hydrogen bonding (H-B) interaction between two π-electronic systems$^{1)}$ such as 2-naphthol-pyridine and carbazole-pyridine has been studied mainly in the ground and the singlet excited states, but scarcely in the triplet state.$^{2)}$ In a previous paper$^{3)}$ we studied the H-B interaction between 2-naphthol and pyridine in the ground, triplet, and singlet excited states, and obtained the following informations; i) the singlet excited state of hydrogen bonded species is non-fluorescent and produces no transient absorption, ii) the singlet excited state of free species undergoes collisional quenching with pyridine, yielding 2-naphthoxyl radical and perhaps the hydrogen bonded singlet excited state, iii) the triplet state of free species reacts with pyridine at about a diffusion controlled rate to produce the 2-naphthoxyl radical. Thus it was first substantiated that the actual hydrogen atom transfer is an important process of the deactivation due to the H-B interaction in both excited states. However, the reaction scheme of H-B interactions in both excited states was not fully established, because we did not examine both the existence and the reactivity of the hydrogen bonded triplet state.

In order to complete the reaction scheme, we investigated the energy transfer from triplet triphenylene to 2-naphthol in pyridine by a conventional flash technique. Figure 1 shows a transient absorption spectrum obtained for the deaerated solution.

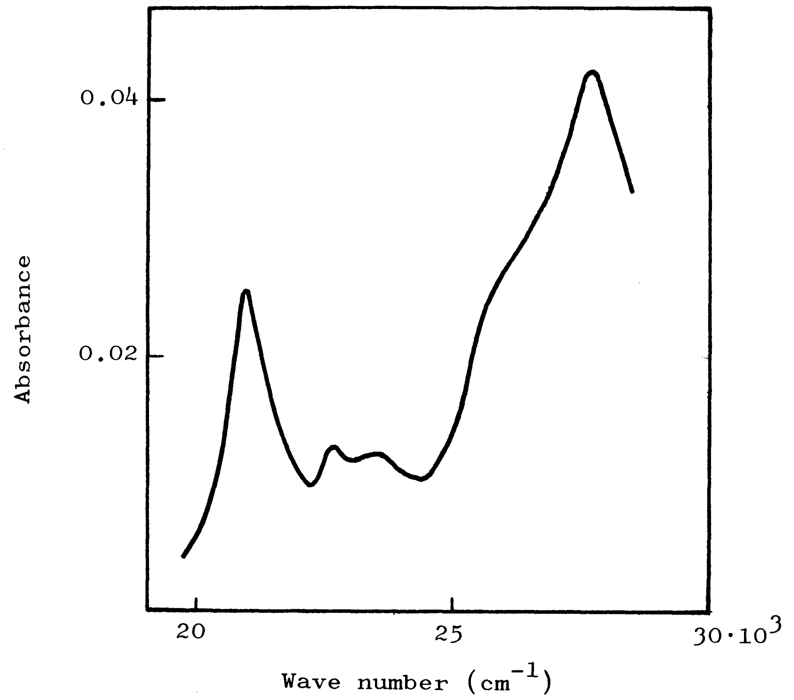


Fig. 1. Absorption spectrum of 2-naphthoxyl radical in pyridine. [2-naphthol] = 1×10^{-4} M, [triphenylene] = 1×10^{-3} M.

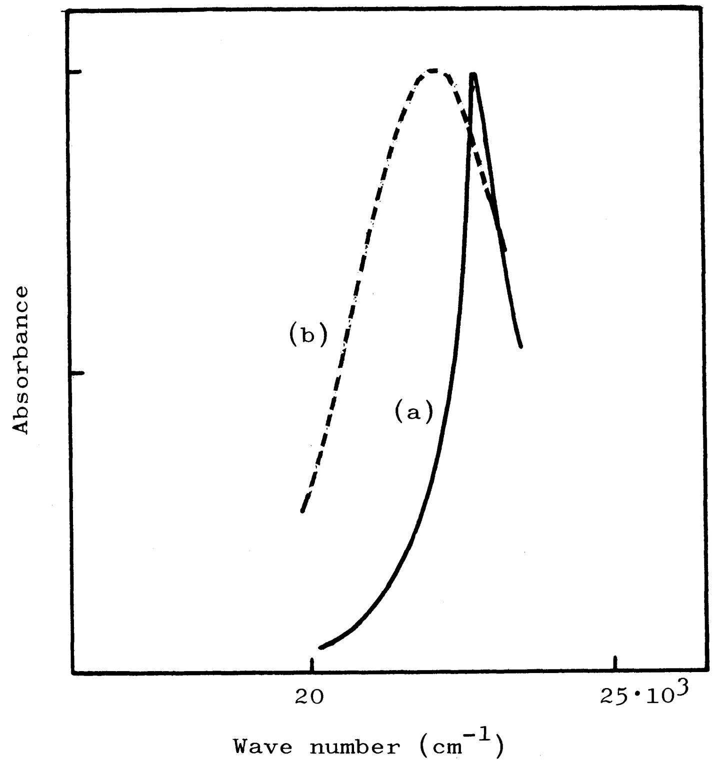


Fig. 2. T-T absorption spectrum of 1-anthrol. (a) : free 1-anthrol in cyclohexane, (b) : hydrogen bonded 1-anthrol in pyridine (sensitizer = 2-acetonaphthone).

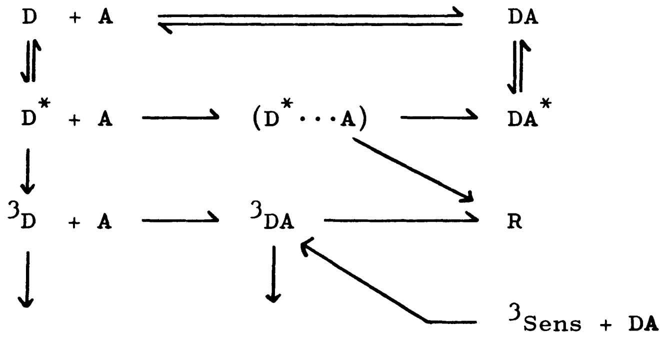
This spectrum is the same as that of the 2-naphthoxyl radical in cyclohexane.3) Since all of 2-naphthol exists as hydrogen bonded species and the triplet absorption of triphenylene was not observed, it may be clear that the energy transfer from triplet triphenylene to 2-naphthol hydrogen bonded with pyridine occurred. Therefore, the hydrogen bonded triplet state may be a reactive state from which the 2-naphthoxyl radical is formed. This result implies that the singlet excited state of 2-naphthol hydrogen bonded with pyridine does not undergo intersystem crossing, since no transient absorption was produced by direct excitation.

Further, we studied the H-B interaction between pyridine and 1-anthrol whose triplet level (14,600 cm^{-1}) is much lower than that of 2-naphthol (21,100 cm^{-1}). Figure 2(a) gives a transient absorption spectrum obtained for the deaerated solution of 1-anthrol in cyclohexane. This spectrum is attributed to the triplet absorption, since delayed fluorescence of 1-anthrol was observed with the intensity proportional to the square of the absorbance. The observed decay rate of triplet 1-anthrol ($k_1 = 3.4 \times 10^3\ s^{-1}$, $k_2/\varepsilon(440\ nm) = 2.9 \times 10^5\ cm\ s^{-1}$) was not virtually affected by pyridine concentrations where the hydrogen bond formation in the ground state is negligible. No transient absorption was observed by direct excitation in pyridine where all of 1-anthrol is hydrogen bonded with pyridine. However, the transient absorption as shown in Fig. 2(b) was observed in pyridine when a triplet sensitizer such as 1,2,5,6-dibenzanthracene, pyrene, or 2-acetonaphthone was used. The decay was of first order process with the rate constant $k = 5.8 \times 10^3\ s^{-1}$, and the decay rate increased with the addition of perylene. Therefore, this spectrum was assigned to the triplet absorption of triplet 1-anthrol hydrogen bonded with pyridine.

The results obtained above strongly suggest that the interaction between triplet 2-naphthol and pyridine leads to the hydrogen bonded triplet state which instantaneously reacts to produce the 2-naphthoxyl radical.

On the basis of the results obtained in both previous and present studies, we can summarize the H-B interaction in excited states as follows; i) the dynamic interaction in the triplet state forms the hydrogen bonded triplet state which may or may not react, ii) the static interaction in the singlet excited state does not results in fluorescence, reaction, and intersystem crossing, iii) the dynamic interaction in the singlet excited state produces the hydrogen bonded singlet excited state and the naphthoxyl radical through the non-relaxed encounter complex, $(D^{*}\cdots A)$. The scheme is consistent with the above conclusions.

Reaction scheme



D : 2-naphthol or 1-anthrol, A : pyridine,

R : 2-naphthoxyl radical, Sens : triplet sensitizer,

DA : 2-naphthol or 1-anthrol hydrogen bonded with pyridine

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