Evidence for the Shortening of the $\pi \leftarrow\!\!\!- \pi^*$ Phosphorescence Lifetime Due to the Presence of a Low-lying (n, π^*) Singlet State

Hiroaki BABA and Takeshi TAKEMURA

Research Institute of Applied Electricity, Hokkaido University, Sapporo

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If a phosphorescent triplet state is of a (π, π^*) type, the natural lifetime, τ_0, of the $\pi \leftarrow \pi^*$, $S_0 \leftarrow T$ (π, π^*) transition is known to be, in general, very long ($\tau_0 > 10$ sec).[1] Recently, Hochstrasser and Marzzacco[2] and Vanquickenborne and McGlynn[3] have pointed out that spin-orbit coupling between $T(\pi, \pi^*)$ and $S(n, \pi^*)$ states may lead to a decrease in the lifetime for the $S_0 \leftarrow T(\pi, \pi^*)$ transition. The present report will be concerned with our recent observations, which clearly show the participation of a low-lying (n, π^*) singlet state in the shortening of the $\pi \leftarrow \pi^*$ phosphorescence lifetime ($\tau_0 \approx 10^{-1}$ sec).

From the results of our polarization measurements and vibrational analysis, we have reached the conclusion that, in some substituted benzaldehydes and acetophenones, the phosphorescence originates from their (π, π^*) triplet states;[4] this is in contrast with the cases of the unsubstituted compounds, in which the phosphorescence stems from the (n, π^*) triplet. It was found that the phosphorescence lifetimes of the substituted compounds are definitely longer than those of the unsubstituted compounds (Table 1), but they are still markedly shorter than the lifetimes for the usual $S_0 \leftarrow T(\pi, \pi^*)$ transitions. Also, it was found that the quantum yield undergoes no appreciable change upon substitution. The phosphorescence quantum yields for benzaldehyde and acetophenone have been reported to be 0.49 and 0.62 respectively.[5] Therefore, the natural lifetimes should not be significantly different from the observed lifetimes, given in Table 1 (the former may be at most about twice as long as the latter).

TABLE 1

Compound	Observed lifetime* sec
Benzaldehyde	0.0026
p-Hydroxybenzaldehyde	0.14
p-Methoxybenzaldehyde	0.11
Acetophenone	0.0043
p-Hydroxyacetophenone	0.50
p-Aminoacetophenone	0.86

* In rigid glass at 77°K.

In general, the natural lifetime, τ_0 in sec, is expressed as:

$$\tau_0 = 1.50 \frac{(E_S - E_T)^2}{\langle S | H_{SO} | T \rangle^2} \frac{\nu_S}{\nu_T{}^3} \frac{1}{f_{S_0 \to S}} = \tau \frac{1 - \Phi_F}{\Phi_P}, \quad (1)$$

where ν is the frequency in cm^{-1} of the $S_0 \leftrightarrow S$ or $S_0 \leftrightarrow T$ transition, and where τ is the observed lifetime; the other symbols have the usual meanings.[1] For the substituted compounds, $T \equiv T(\pi, \pi^*)$, and we assume the mixing singlet state, S, to be the lowest $S(n, \pi^*)$. Although $f_{S_0 \to S}$ should be small, $\langle S(n, \pi^*) | H_{SO} | T(\pi, \pi^*) \rangle$ is expected to have a relatively large absolute value;[1] moreover, the energy gap, $E_S - E_T$, is small, since $S(n, \pi^*)$ is the lowest singlet-excited state. The lifetimes, τ_0, for the substituted compounds should, therefore, become significantly shorter than in the usual aromatic compounds.

This is supported by a quantitative estimation of the lifetime. Consider *p*-hydroxybenzaldehyde (HBA) as an example. If the spatial configurations of $S(\pi, \pi^*)$ and $T(n, \pi^*)$ are identical with those of $T(\pi, \pi^*)$ and $S(n, \pi^*)$ respectively, then:

$$\langle S(n, \pi^*) | H_{SO} | T(\pi, \pi^*) \rangle^2_{HBA} = \langle S(\pi, \pi^*) | H_{SO} | T(n, \pi^*) \rangle^2_{HBA}$$

The insertion of the experimental data for benzaldehyde (BA) in Eq. (1) leads to $\langle S(\pi, \pi^*) | H_{SO} | T(n, \pi^*) \rangle^2_{BA} = 4.5 \times 10^{-6} (eV)^2$. It is assumed that the above matrix element for BA is not appreciably changed by the hydroxyl substituent; thus, $\langle S(n, \pi^*) | H_{SO} | T(\pi, \pi^*) \rangle^2_{HBA}$ is put equal to 4.5×10^{-6} $(eV)^2$. By the use of this matrix element value, together with the spectral data, the natural lifetime, τ_0, of HBA is calculated from Eq. (1) to be 0.3 sec.

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