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PHOTOENOLIZATION OF 2-METHYLBENZOPHENONE

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Two kinds of transient absorption spectra were obtained for the ethanol solution of 2-methylbenzophenone by conventional and laser flash photolysis. The short-lived transient was assigned to the cis-enol and the long-lived to the trans-enol. These transients arise separately from the different excited states.

Benzophenones substituted at the ortho position by an alkyl group containing an α-hydrogen undergo intramolecular hydrogen abstraction to give the corresponding enol under ultraviolet irradiation.$^{1)}$ Porter and Tchir found five transients by conventional and laser flash photolysis of 2,4-dimethylbenzophenone$^{2)}$ and the other ortho-derivatives, and assigned some of these transients.$^{3)}$ However, there remained some questions in their assignments since the short-lived transient B according to their notation is an open question. In the present work, the transients observed in the ethanol solution of 2-methylbenzophenone were assigned and their formation processes were studied by conventional and laser flash experiments.

By conventional and laser flash photolysis of 2-methylbenzophenone these transients were found in ethanol. Figure 1 shows two transient absorption spectra. The spectrum (a) of the short-lived transient B (τ = 4.5 μs) was observed by laser flash photolysis. The spectrum (b) of the long-lived transient D was observed after the disappearance of the spectrum (a). The lifetime of D varied considerably from sample to sample. The decays of B and D are of first order.

Other transient absorption spectra were observed after the disappearance of above spectra, but we do not consider them since their intensities are very weak. After the disappearance of these transients the parent molecule was almost completely regenerated.

Figure 2 shows the pH dependence of the decay constants of B and D in ethanolwater. In the pH range 0 to 2, the decay constant of D decreases with increasing pH value (plot (b)), but that of B does not change practically (plot (a)). The decay constants of B and D increase gradually in the pH range above 7 and 5, respectively. The slopes of the plot (b) are -1.0 in the pH range 0 to 2 and +1.0 in the pH range 5 to 8. These results suggest that the decay process of D is associated with the protonation in the pH range 0 to 2 and the deprotonation in the pH range above 5, and that the decay process of B is associated with the deprotonation in the pH range above 7, but not with the protonation in the pH range 0 to 7.

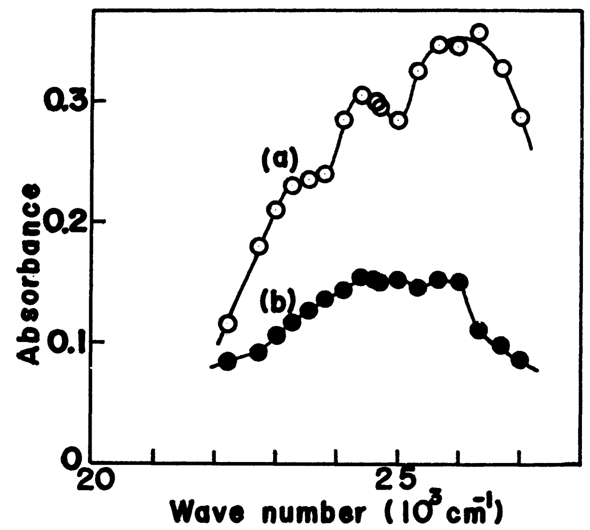


Fig.1. Transient absorption spectra of 2-methylbenzophenone in ethanol.

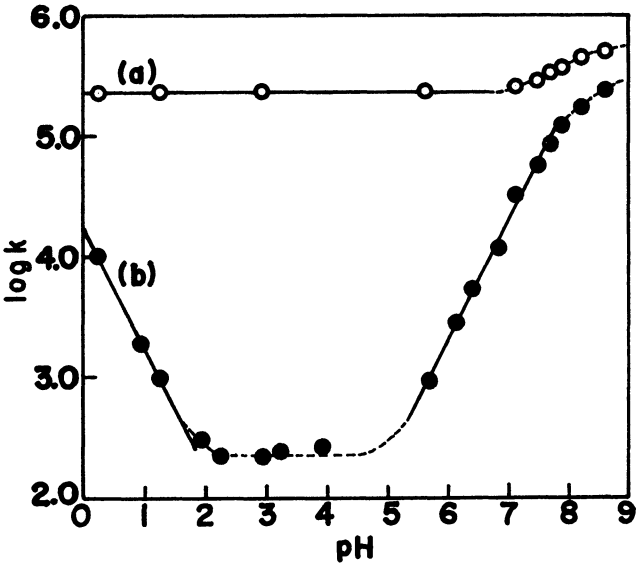


Fig.2. The pH dependence of the decay constants of B(curve(a)) and D(curve(b)).

The lifetime of B is 50 ns in cyclohexane and 20 μs in pyridine, and the absorption maxima lie at 25500 cm^{-1} in cyclohexane and 24400 cm^{-1} in pyridine. When pyridine was added to the cyclohexane solution, the lifetime becomes longer in proportion to the pyridine concentration as shown in Fig. 3. Since these facts suggest the hydrogen bond formation of B with pyridine, the decay processes of B may be expressed by:

$$\begin{tikzcd} B + \text{Pyridine} \arrow[r, shift left, "k_1"] \arrow[d, "k_o"] & (B\cdots\text{Pyridine}) \arrow[l, shift left, "k\text{-}1"] \arrow[d, "k_{HB}"] \\ {} & {} \end{tikzcd}$$

The equilibrium is maintained throughout the decay process in the pyridine concentration above 0.1 M, because the decay curve is the single exponential at any pyridine concentration studied.

The lifetime of the equilibrium mixture is expressed by:[4,5)]

$$\tau = (1 + K[\text{Pyridine}]) / (k_0 + k_{HB}K[\text{Pyridine}]) \qquad (1)$$

where $K = k_1/k_{-1}$. The result shown in Fig. 3 requires the following relation,

$$k_0 \gg k_{HB}K[\text{Pyridine}] \qquad (2)$$

Accordingly, we obtain

$$\tau = (K/k_0)[\text{Pyridine}] + (1/k_0) \qquad (3)$$

The slope of the plot in Fig. 3 is $K/k_0 = 2.84 \times 10^{-6} M^{-1}s$ at 23°C. Using $k_0 = 2 \times 10^7\ s^{-1}$, we obtain $K = 57\ M^{-1}$ at 23°C which is as same as the equilibrium constant of the hydrogen bond between phenol and pyridine.$^{6)}$ Since the relation (2) holds at pyridine concentration of 1 M, k_{HB} in cyclohexane is estimated as $k_{HB} \ll 3.5 \times 10^5\ s^{-1}$, which is consistent with the lifetime in pyridine. It is noteworthy that the lifetime of the hydrogen bonded species is much longer than that of the free species.

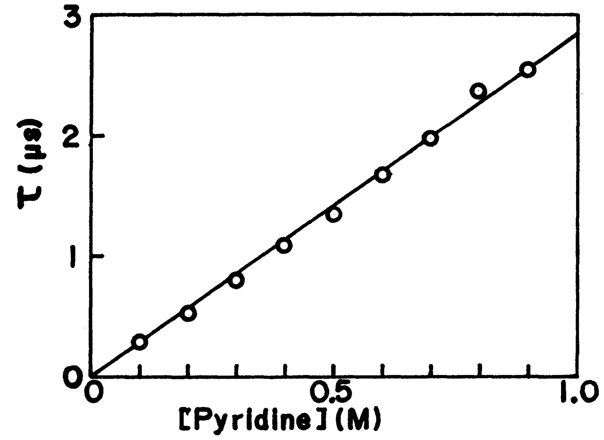


Fig.3. The relationship between the lifetime of B and pyridine concentration.

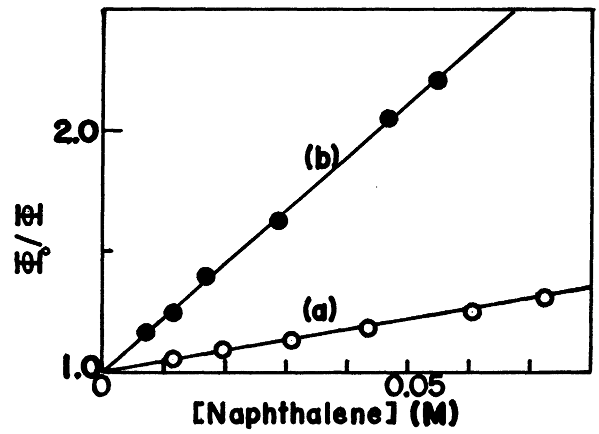
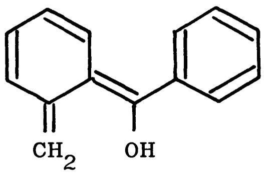


Fig.4. The Stern-Volmer plots for the yields of B(plot(a)) and D(plot(b)).

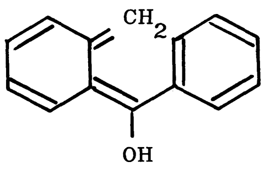
When naphthalene was added in the ethanol solution, the decay rates of B and D did not change, but the yields of B and D decreased. Moreover, the T-T absorption of naphthalene appeared under the condition that naphthalene was not excited directly. The Stern-Volmer plots for the yields of B and D are shown in Fig. 4(a) and (b), respectively. From these plots the quenching constants were obtained as $7 \pm 3\ M^{-1}$ for B and $35 \pm 2\ M^{-1}$ for D. On the assumption that the quenching reactions are the diffusion controlled ($k_{diff} = 5 \times 10^9\ M^{-1}\ s^{-1}$), the lifetimes of the precursors of B and D are estimated to be 1.4 ns and 7.0 ns, respectively. These results suggest that B is produced from the short-lived triplet state and D from the long-lived.

Porter and Tchir$^{2)}$ have suggested that B is the 1,4-biradical and D is the cis-enol or the equilibrium mixture of the cis- and the trans-enol. Recently, Findlay and Tchir$^{7)}$ has reported that B is presumably an enol triplet rather than the 1,4-

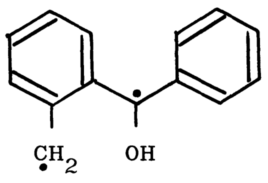
biradical. If B is the 1,4-biradical or an enol triplet, D must be the cis-enol or the equilibrium mixture of the cis- and the trans-enol, and D must be produced from B. In this case, the effects of naphthalene concentration on the yields of B and D should be same in contradiction to the results shown Fig. 4. Therefore, B is neither the 1,4-biradical nor the enol triplet.



cis-enol



trans-enol



1,4-biradical

Consequently, it is concluded that B is the cis-enol and D is the trans-enol. With these assignments the experimental results are explained as follows. B and D are produced separately from the short-lived and the long-lived triplet states. B undergoes a rapid intramolecular proton transfer to yield the parent molecule, accordingly the decay is little affected by the hydrogen ion concentration. In the alkaline solution, the intermolecular deprotonation from the -OH group may compete with the intramolecular proton transfer, and hence the decay of B is accelerated. When B is hydrogen bonded with pyridine, the intramolecular proton transfer is suppressed, so that the decay of the hydrogen bonded species is much slower than that of the free species. On the other hand, the intramolecular proton transfer of D is slow on account of the trans-structure. Therefore, the reketonization of D is enhanced by the protonation to the $=CH_2$ group and the deprotonation from the -OH group.

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