BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 854—856 (1971)

A Spectroscopic Study on Hydrogen Bonding and Proton Transfer in Photo-Excited *p*-Hydroxybenzophenone

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(Received October 6, 1970)

In a previous paper,[1] one of us (H.B.) showed that, in contrast to the case of the usual phenolic compounds,[2–4] proton transfer does not occur from *p*-hydroxybenzaldehyde to triethylamine, a strong proton acceptor, in the excited state in spite of its occurrence in the ground state. This was attributed to the fact that the lowest excited singlet of the *p*-hydroxybenzaldehyde molecule is an (n, π^*) state, where the proton-donating power of the molecule is relatively weak. In their discussion on the photochemical behavior of *p*-hydroxybenzophenone, an analogue of *p*-hydroxybenzaldehyde, Godfrey, Porter, and Suppan[5] assumed that the proton transfer would take place in the excited singlet state. In this study, the emission properties of *p*-hydroxybenzophenone coupled with proton-accepting substances have been examined to get an insight into the validity of these contradictory views.

Figure 1 shows the absorption and phosphorescence spectra of *p*-hydroxybenzophenone at 77°K in the presence of proton acceptors. The absorption spectrum of *p*-hydroxybenzophenone at 77°K in a mixture of hydrocarbons containing ether is obviously

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[1] H. Baba, *J. Chem. Phys.*, **49**, 1763 (1968).

[2] N. Mataga and Y. Kaifu, *ibid.*, **36**, 2804 (1962).

[3] H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965).

[4] S. Suzuki and H. Baba, This Bulletin, **40**, 2199 (1967).

[5] T. S. Godfrey, G. Porter, and P. Suppan, *Discuss. Faraday Soc.*, **39**, 194 (1965).

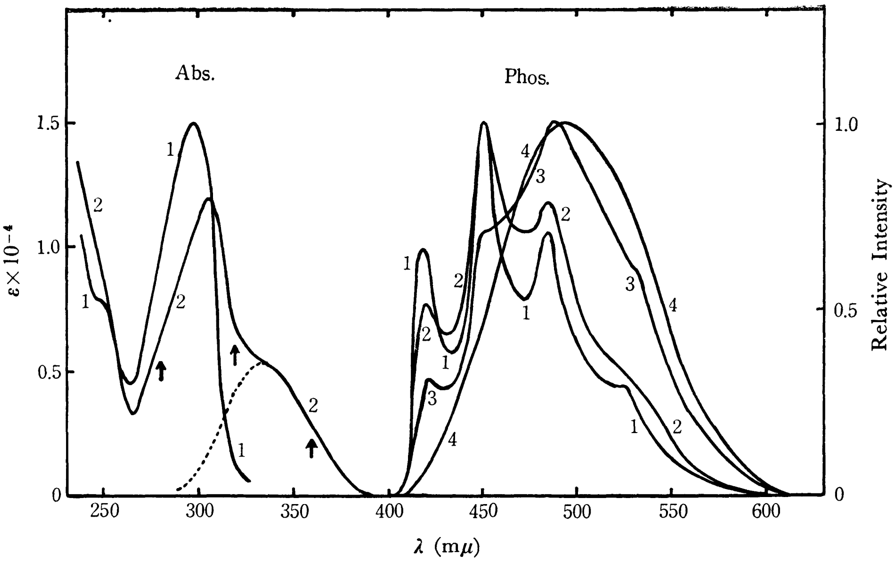

Fig. 1. Absorption (Abs.) and phosphorescence (Phos.) spectra of *p*-hydroxybenzophenone (3.03×10^{-5} mol/*l*) at 77°K.
Absorption: 1, in methylcyclohexane and isopentane (volume ratio, 1:1) containing ethyl ether (0.4 mol/*l*) as a proton acceptor; 2, in methylcyclohexane, isopentane and ethyl ether (4 : 4 : 1) containing triethylamine (4.0×10^{-3} mol/*l*).
Phosphorescence: 1, in methylcyclohexane and isopentane (1 : 1) containing ethyl ether (0.4 mol/*l*), excitation at 290 mμ; 2, 3 and 4, in methylcyclohexane, isopentane and ethyl ether (4 : 4 : 1) containing triethylamine (4.0×10^{-3} mol/*l*), excitation at 280, 320 and 360 mμ, respectively, as indicated by arrows.

ascribable to the simple hydrogen-bonded complex between *p*-hydroxybenzophenone and ether. This complex has at about 350 mμ another absorption band, which is weak and is assigned to an $n\rightarrow\pi^*$ transition. When triethylamine is added as a proton acceptor besides ether, an additional absorption band appears at 77°K in the longer wavelength region. It can be shown that in the latter case the solute molecules are associated with triethylamine owing to the much stronger basicity of the amine compared with ether. Thus, hydrogen bonding occurs between the solute and amine molecules to give a simple hydrogen-bonded complex, followed by proton transfer from the solute to the amine to yield a hydrogen-bonded ion pair. The additional absorption band can be attributed to the proton-transferred complex, *i.e.*, the hydrogen-bonded ion pair, as in the case of previous studies.[1,6,7] In the ground state of the solute molecule, an equilibrium is to be established at 77°K between the simple hydrogen-bonded complex and the ion pair.

It should be noted that in the absence of ether the *p*-hydroxybenzophenone-triethylamine system in the hydrocarbon mixture gives almost exclusively the simple hydrogen-bonded complex. This shows that the degree of proton transfer is sensitive to the polarity of the solvent.

The hydrogen-bonded complex between *p*-hydroxybenzophenone and ether gives an emission spectrum with a vibrational structure (Fig. 1). The emission has a lifetime of the order of millisecond and is assigned to the phosphorescence from the lowest triplet state of an (n, π^*) type.[8,9]

The system containing triethylamine as a proton acceptor exhibits different phosphorescence spectra, depending on the wavelengths of exciting light. Thus, excitation at 280 mμ is largely related to the hydrogen-bonded complex, the observed spectrum being essentially the same as that found in the *p*-hydroxybenzophenone molecule hydrogen-bonded with ether, whereas excitation at 360 mμ leads to a broad, long-lived (≈ 1 sec) and red-shifted phosphorescence spectrum which is entirely different from the spectrum of the simple hydrogen-bonded complex. The broad spectrum resulting from the 360 mμ excitation may be assigned to the $\pi\leftarrow\pi^*$ phosphorescence originating in the proton-transferred complex. In this way, excitation at shorter and longer wavelengths induces phosphorescence from the simple hydrogen-bonded complex and from the proton-transferred complex, respectively. The emission obtained by excitation at intermediate wavelengths (*e.g.*, 320 mμ) is found to be a superposition of phosphorescence emissions from both complexes.

These absorption and emission characteristics of *p*-hydroxybenzophenone in relation to hydrogen bonding and proton transfer are very similar to those of *p*-hydroxybenzaldehyde,[1] except that in the former the lowest triplet is of (n, π^*) type and the proton-transferred complex gives no fluorescence. In the

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[6] H. Baba, A. Matsuyama, and H. Kokubun, *J. Chem. Phys.*, **41**; 895 (1964).

[7] H. Baba, A. Matsuyama, and H. Kokubun, *Spectrochim. Acta*, **25A**, 1709 (1969).

[8] G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

[9] D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

simple hydrogen-bonded complexes (*i.e.*, the protonated forms) of the two compounds, the lowest excited singlet (S_1) is an (n, π^*) state and the next lowest singlet (S_2) is a (π, π^*) state of charge-transfer nature. On exciting the *p*-hydroxybenzophenone-triethylamine system at shorter wavelengths (*e.g.*, 280 mμ), the protonated form is raised to its S_2 level. By the same reasoning as in the case of *p*-hydroxybenzaldehyde,[1] it is concluded that the state S_2 of the protonated form of *p*-hydroxybenzophenone is deactivated by rapid radiationless processes to the lower singlet and triplet states, phosphorescence being emitted from the protonated form itself, and that no proton transfer takes place throughout the deactivation processes.

Godfrey *et al.*[5] found that the photo-excited *p*-hydroxybenzophenone shows an anomalously low reactivity toward abstraction of a hydrogen atom from solvents. In order to interpret this phenomenon, they assumed that the proton transfer would occur in the excited singlet state of the protonated form, in marked contrast to our conclusion. It would be desirable to reexamine the anomalous photochemical behavior of *p*-hydroxybenzophenone in the light of the results of the present spectroscopic investigation.

Experimental

p-Hydroxybenzophenone was recrystallized from a mixture of water and ethanol. Methylcyclohexane of spectroscopic quality was used without further purification. Isopentane was passed through a silica-gel column. Ethyl ether was distilled over metallic sodium. Triethylamine was fractionally distilled over phosphorus pentoxide. Absorption spectra were obtained with a Hitachi EPS-3 spectrophotometer at 77°K. Emission spectra were measured at 77°K with an apparatus which was constructed using a Hitachi G-3 grating monochromator and a Hitachi EPU-2A prism monochromator.