

DEPROTONATION OF p-HYDROXYBENZOPHENONE AS A CAUSE OF THE
SUPPRESSION OF THE PHOTOREDUCTION IN ALCOHOLS

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The spectral change of p-hydroxybenzophenone (HOBP) and the relative quantum yields of its photoreduction in ethanol-cyclohexane of various composition have been studied. The results have demonstrated that the hydrogen-bonded species of HOBP with ethanol does not undergo the deprotonation upon excitation at low $[C_2H_5OH]$ and accordingly is photoreduced effectively, and that the proton transfer which occurs upon excitation requires the participation of several ethanol molecules.

Substitution effect on the photoreductivity of benzophenone has been extensively studied by many workers including Porter's, Hammond's and Pitts' group, and it is now generally accepted that the electronic nature of the lowest triplet state is most important in determining the reactivity.¹⁾ For instance, the lowest triplet state of p-aminobenzophenone is $\pi-\pi^*$ in the ethanol solution in which no reaction occurs. The same substance when dissolved in cyclohexane in which the reaction occurs with the quantum yield of 0.2,²⁾³⁾ has $n-\pi^*$ state as the lowest triplet state.

A remarkable exception that cannot be interpreted on the above reasoning is p-hydroxybenzophenone (HOBP). This compound of which the lowest T-state is $n-\pi^*$ both in cyclohexane and ethanol,³⁾⁴⁾ undergoes the photoreduction with the quantum yield of 0.9 in the former solvent, while with only 0.02 in the latter.³⁾

Porter et al. interpreted this anomalous behavior of HOBP as due to the rapid deprotonation of its OH-proton upon excitation.³⁾ They presumed that the deprotonation occurs according to the scheme shown in Fig. 1; thus it occurs most likely in the singlet excited state by passing from the C-T state of a molecule to C-T of ion. They inferred on the basis of Förster's cycle that pK of the lowest $T(n-\pi^*)$ is ~ 3.0 and so if a molecule upon excitation reaches this state without being deprived of a proton, the photoreduction should occur at $pH \approx 1$. This is the reason why they proposed that the proton transfer in the triplet state occurs in the C-T state for which the pK -value is estimated to be ~ -4 . However (as stated above),

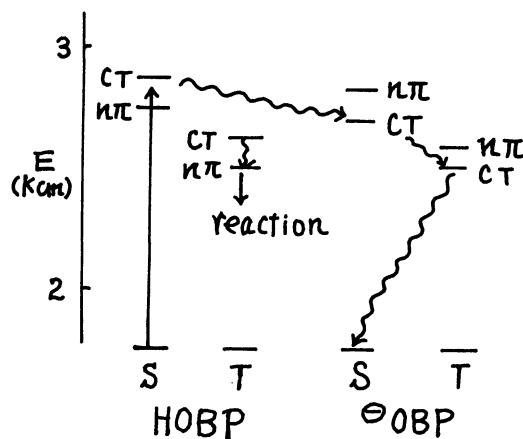


Fig 1 schematic diagram of
deprotonation of HOBP³⁾

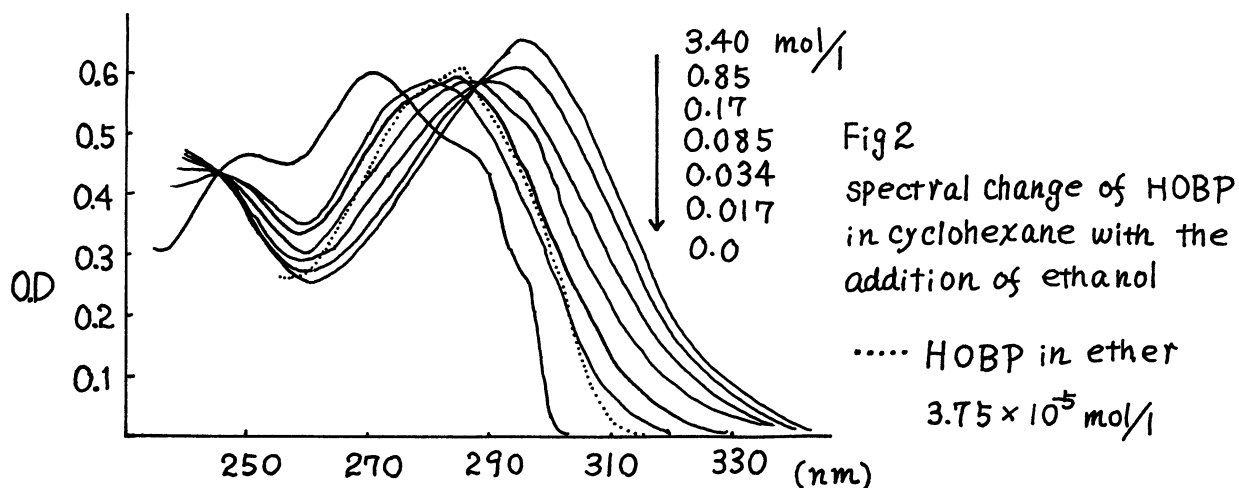
they considered it more likely that the proton transfer occurs in the singlet state for which pK is also -4 . According to this scheme, protonation must occur once again during the lifetime of the excited anion for the $T(n-\pi^*)$ molecule to be produced and accordingly for the photoreduction to occur in ethanol.

Recently a doubt was raised by Matsuyama and Baba⁵⁾ as to the above view of Porter et al. They performed the phosphorescence measurements at 77°K and obtained the results which imply that the proton transfer is so slow that the lowest $T(n-\pi^*)$ is reached without ionic dissociation. Thus when $4.0 \times 10^{-3}M$ of $(CH_3)_3N$ is added to HOBP, $3.05 \times 10^{-5}M$ in the mixed solvent of cyclohexane, isopentane and ether (4:4:1), the absorption spectrum indicates the coexistence of the hydrogen-bonded species and the ion-pair-like species consisting of ^-OBP and $^+HN(CH_3)_3$. The two species have the absorption peak at ~ 300 and 330 nm respectively. An important finding was that different phosphorescence spectra were obtained according to the excitation wavelength i.e., the spectrum attributed to $T(n-\pi^*)$ of molecule in case of 300 nm excitation while the one due to ion-pair, in case of 330 nm.

Therefore, there is no doubt that a hydrogen-bonded species when excited, reaches ultimately $T(n-\pi^*)$ without losing a proton. Matsuyama and Baba concluded their report by stating that it is desirable to reexamine Porter et al.'s results. In addition, they observed that the ion-pair formation between HOBP and $(CH_3)_3N$ occurs in hydrocarbon solvents when ether is added, but not in the absence of ether. This suggests that the ion-pair formation is strongly sensitive to the nature of the environment.

In this communication, we would like to demonstrate on the basis of the experiments using the mixed solvents of ethanol and cyclohexane, that the results of the above two groups do not contradict with each other. In particular we would like to stress that for the eventual proton transfer to occur, the surrounding medium must fulfill some other condition in addition to the formation of hydrogen bond between HOBP and ethanol. In other words, hydrogen-bonded species can undergo the photoreduction in the lower ethanol concentration region where the surrounding medium is not in the state which makes the eventual deprotonation possible.

Figure 2 gives the absorption spectrum of HOBP in the mixed solvents of cyclohexane and ethanol of various composition. It is seen that the change of absorption



spectrum occurs in two steps. Although there is no clear isosbestic point, this may perhaps be due to the superposition of the general solvent effects. The first and the second species will be conventionally called as A- and B-species. The spectrum of A-species is similar to that of HOBP in ether (as shown in Fig. 2) of which oxygen acts most likely as a proton acceptor to HOBP. Therefore A-species must have a structure written below. The nature of B-species is not clear, but it may have a structure with another ethanol molecule attached to A-species, for the following reason. A carbonyl group of benzophenone forms a hydrogen bond of a type $C=O \cdots H-O-R$ ⁶⁾⁷⁾ but the spectral shift ($\pi-\pi^*$ transition) due to such a type of hydrogen bond is very small. For instance, p-CH₃O-benzophenone exhibits only a few nm red shift in pure ethanol as compared in cyclohexane.⁸⁾ We have also found that in case of p-dimethylamino- (stronger electron releasing group than OH) benzophenone, practically no shift is caused by the addition of $1.72 \times 10^{-1} M$ ethanol to cyclohexane. Therefore a rather large red shift in Fig. 2 must be attributed mainly to the interaction of OH group of HOBP with ethanol. It is likely that the strength of H-O bond of HOBP is further weakened by another ethanol molecule attached to A-species. Such an idea was also proposed by Becker.⁹⁾ The equilibrium between A and B may be determined mainly by the association tendency of alcohols.

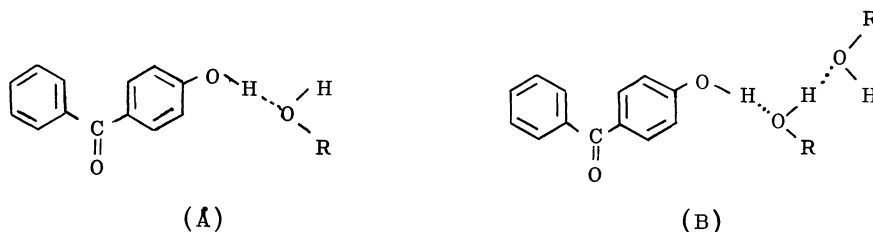
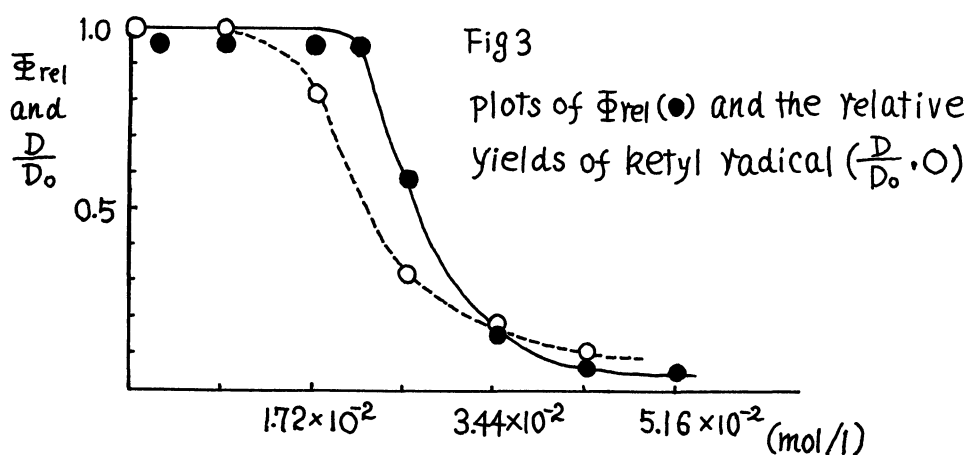


Figure 3 gives the relative quantum yields (Φ_{rel}) for the disappearance of HOBP plotted against the composition of the solvent. It is seen that A-species undergoes



the photoreduction with almost the same quantum yield as that in cyclohexane. A similar result was obtained with ether. As A-species begins to transform to B-species, the quantum yield of the photoreduction decreases much more rapidly than the change in absorption spectrum, as is evident from the comparison between Figs. 2 and 3. Thus the addition of $3.4 \times 10^{-2} M$ of ethanol causes a very slight shift of the spectrum whereas

the quantum yield decreases down to about 20% of that for A-species.

It is certain therefore that A-species with a hydrogen-bonded structure does not undergo the eventual ionic dissociation and accordingly is reduced effectively. This is consistent with Matsuyama and Baba's result. For the proton transfer to occur, A-species has to transform to B-species or more exactly, the concentration of ethanol must be so high as to make this transformation measurable. Indeed we reconfirmed that HOBP in pure ethanol upon flashing yields ^-OBP anion. The anion with a peak at ~ 350 nm which agrees with that of the chemically produced anion, decays bimolecularly with nearly the diffusion rate constant. It is regrettable that we could not determine the yield of the anion in the mixed solvent because of the overlap of the spectrum of anion and ketyl radical with the absorbance about ten times that of the former. However it was established that the yield of ketyl radical as measured by the optical density at 550 nm decreases with the increase in alcohol concentration in almost exactly the same way as the overall quantum yield as shown in Fig. 2. This means that the quenching action of ethanol on the photoreduction occurs prior to the formation of ketyl radical so that it is likely that this is due to the deprotonation of HOBP.

Furthermore the finding that the quantum yield of the photoreduction decreases with the ethanol concentration far more rapidly than the change of the absorption spectrum, strongly supports that the quenching mechanism is a dynamic deprotonation process during the excited state and is not concerned directly with the ground state equilibrium. This is in complete agreement with Porter's interpretation.

However, the non-occurrence of the eventual deprotonation of A-species does not necessarily mean the non-occurrence of the transient proton transfer. If the surrounding medium is in such a condition that the detached proton does not stay a long time apart from the anion, then it will rejoin with anion producing $T(n-\pi^*)$ molecule. Whether such a situation exists or whether even the transient proton transfer does not occur will be discriminated for instance, by the use of laser photolysis of ns order.

The steep decline of the quantum yield with the increase of ethanol concentration suggests that several ethanol molecules participate in the eventual proton transfer. Indeed it has been found that the plot of Fig. 2 is reproduced by the formula

$$\Phi^{-1} = 1 + K [\text{C}_2\text{H}_5\text{OH}]^n$$

where $n = 7$ and $K = 8 \times 10^{10}$. The curve in the figure was calculated by this equation.

The detailed discussion on the basis of this equation will be reported elsewhere.

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