September, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2731—2736 (1972) 2731

Order of Quencher Participation in Photochemistry. I. Proton Transfer from the Excited *p*-Hydroxybenzophenone in Mixed Solvents of Cyclohexane and Alcohols

Mikio Hoshino and Masao Koizumi

Department of Chemistry, Faculty of Science, Tohoku University, Katahira, Sendai

(Received January 20, 1972)

The change in the absorption spectrum of *p*-hydroxybenzophenone (HOBP) and relative quantum yields Φ_{rel} for the photoreduction of HOBP have been studied in mixed solvents consisting of cyclohexane and four kinds of alcohol. The change in absorption spectrum occurs in two steps with methanol, ethanol, and 2-propanol, suggesting the following equilibria, $HOBP+S \rightleftarrows A$, and $A+S \rightleftarrows B$ (S, alcohol molecule). Φ_{rel} changes in two steps with methanol and ethanol and in one step with 2-propanol and amyl alcohol roughly in line with the spectral change. The changes in Φ_{rel} have been interpreted to be due to the deprotonation of HOBP. $\Phi_{rel}=1/(1+K[S]^n)$ holds for them with $n=5.5$ for 2-propanol and $n=7$ for other alcohols. A linear relation holds between $1/(n-1)\log K$ and Hammett's constant of alkyl group of alcohols, suggesting that the deprotonation tendency depends upon the specific interaction between alcohol molecules. The reactivity of A-species is considered to depend largely on the dielectric nature of the solvent.

We examined Porter and Suppan's mechanism[1,2] for the suppression of the photoreduction of *p*-hydroxybenzophenone (HOBP) in ethanol and obtained additional information.[3] The proton transfer from the excited HOBP, was reconfirmed as a cause for the non-occurrence of the photoreduction. It was found that a hydrogen-bonded species consisting of HOBP and ethanol does not necessarily undergo the ionic dissociation upon excitation. Such a species (A) is formed in cyclohexane when a small amount of ethanol is added, but under such conditions it does not undergo the proton transfer and accordingly it is photoreduced efficiently. This result is consistent with the finding of Matsuyama and Baba that a hydrogen-bonded species of HOBP and $(CH_3)_3N$ in cyclohexane–isopentane–ether (4: 4: 1) exhibits the phosphorescence from molecular $T(n\text{-}\pi^*)$ state at 77°K.[4] For the proton transfer to occur, a certain condition is necessary which is realized at higher ethanol concentrations. With an increase in ethanol concentration, it was suggested from the change of the absorption spectrum that in addition to A another species, perhaps HOBP with two C_2H_5OH attached to OH of HOBP (B) is formed in equilibrium with A. However, the proton transfer was found to occur much more rapidly with the increase of ethanol concentration than the formation of B. Therefore the proton transfer which occurs upon excitation is not directly concerned with the ground state equilibrium suggested by the absorption spectra. In fact, the decrease of the quantum yield of photoreduction with the increase of ethanol concentration caused by the proton transfer, was found to obey the equation

$$\Phi_{rel} = \frac{1}{1+K[\text{ethanol}]^n} \qquad (1)$$

wher $n=7$.

The present paper reports on the previous communication in detail together with results obtained for methanol, 2-propanol and amyl alcohol. The relative quantum yields have been found to be reproduced by Eq. (1) in all cases.

Experimental

A 6W germicidal lamp was employed as a light source of the steady light experiments. Spectral change was measured with a Hitachi ESP-3T spectrophotometer. Apparatus and procedures for the flash experiment are the usual ones employed in our laboratory.

Alcohols and cyclohexane were purified by the usual methods. *p*-Hydroxybenzophenone of G.R. grade of Wako Junyaku was recrystallized three times from aqueous ethanol.

Results

Absorption Spectra of HOBP in the Mixed Solvents of Cyclohexane and Alcohols. The change in absorption spectrum of HOBP in cyclohexane is given in Fig. 1 as a function of the ethanol concentration. With the addition of ethanol the peak located at 272 nm in cyclohexane gradually shifts to longer wavelength. It is seen that the change occurs in two steps, the first

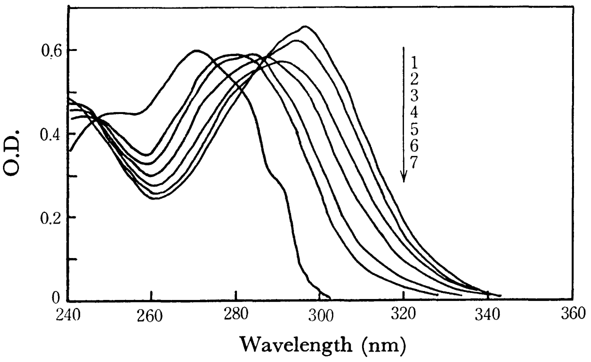


Fig. 1. Spectral change of HOBP in cyclohexane (3.65×10^{-5} M) with the addition of ethanol. Concentration of ethanol; 1) 3.4, 2) 8.5×10^{-1}, 3) 1.7×10^{-1} 4) 8.5×10^{-2}, 5) 3.4×10^{-2}, 6) 1.7×10^{-2}, 7) 0 M (Downward at 300 nm).

---

[1] G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1164 (1965).

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

[3] M. Hoshino and M. Koizumi, *Chem. Lett.*, **1972**, 189.

[4] A. Matsuyama and H. Baba, This Bulletin, **44**, 855 (1971).

step ending at $\sim 3\times 10^{-2}$M and the second occurring from 3×10^{-2}M to pure ethanol.

An isosbestic point is not observed in the first step. It appears in the second step, but not so clearly. Taking into account the superposition of the general solvent effect, which obscures the existence of the isosbestic point, one may safely assume the following equilibrium.

$$\text{HOBP} + \text{S} \rightleftharpoons \text{A} \qquad \text{A} + \text{S} \rightleftharpoons \text{B} \tag{2}$$

where S denotes an ethanol molecule.

The equilibrium constant of the second step was estimated by the equation

$$(D_\infty - D)K[\text{S}] = D - \varepsilon_\text{A} C_0 \tag{3}$$

which can be derived directly from

$$D = C_\text{A}\varepsilon_\text{A} + C_\text{B}\varepsilon_\text{B} \qquad C_\text{A} + C_\text{B} = C_0$$

$$K = C_\text{B}/C_\text{A}[\text{S}]$$

D; optical density of HOBP at a given ethanol concentration

D_∞; the optical density in pure ethanol

The plots of $(D_\infty - D)$ [S] against D at two wavelengths are shown in Fig. 2. Their slopes have the same magnitude giving $K = 1.2_3\times 10\text{M}^{-1}$.

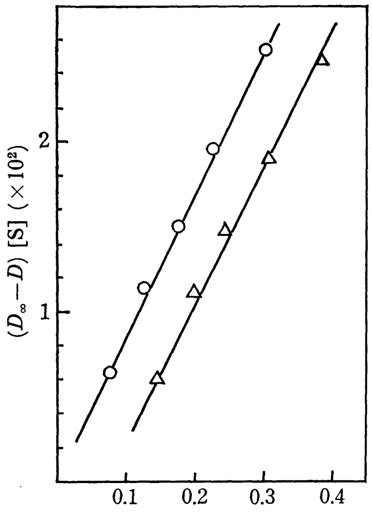


Fig. 2. Examples of the plots of $(D_\infty - D)$ [S] *vs.* D.
○: 310 nm △: 305 nm

The results for methanol, 2-propanol, and amyl alcohol are given in Figs. 3, 4, and 5. In the case of methanol and 2-propanol the change occurs in two steps as in ethanol and so the same type of equilibrium is thought to exist. The above analysis gives for 2-propanol the equilibrium constant for $\text{A}+\text{S}\rightleftarrows\text{B}, K = 2\times 10\text{M}^{-1}$. For methanol, the analysis was not successful. For amyl alcohol the two step change is not so distinguished. The degree of the shift is in the order, methanol>ethanol>2-propanol≈amyl alcohol.

Relative Quantum Yields as a Function of Alcohol Concentration. The spectral change of HOBP in cyclohexane upon irradication is given in Fig. 6, which shows a gradual and monotonous decrease in optical density. This is due to the following reaction as in the

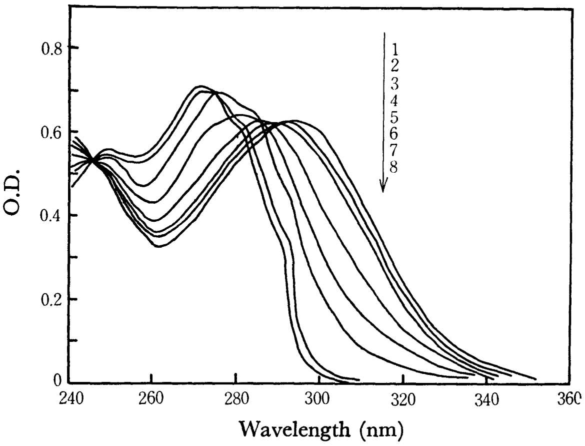


Fig. 3. Spectral change of HOBP in cyclohexane (4.27×10^{-5} M) with the addition of methanol. Concentration of methanol; 1) 1.22×10^{-1}, 2) 9.76×10^{-2}, 3) 6.10×10^{-2}, 4) 4.88×10^{-2}, 5) 4.66×10^{-2}, 6) 3.44×10^{-2}, 7) 1.12×10^{-2}, 8) 0 M (downward at 300 nm).

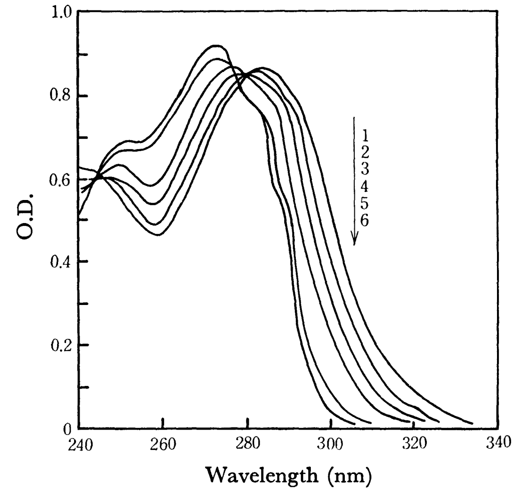


Fig. 4. Spectral change of HOBP in cyclohexane (5.60×10^{-5} M) with the addition of 2-propanol. Concentration of 2-propanol; 1) 5.24×10^{-2}, 2) 3.93×10^{-2}, 3) 2.62×10^{-2}, 4) 1.31×10^{-2}, 5) 6.54×10^{-3} 6) 0 M (downward at 300 nm).

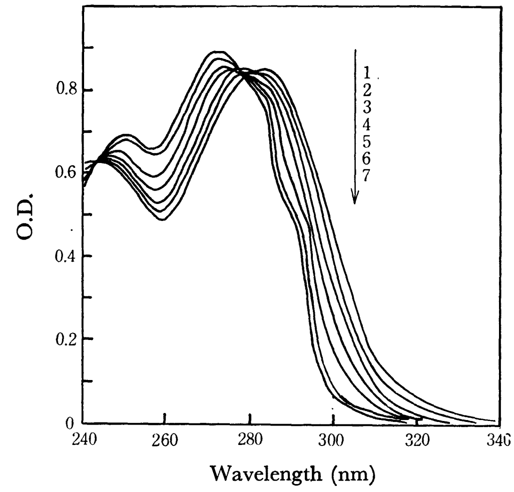


Fig. 5. Spectral change of HOBP in cyclohexane (5.42×10^{-5} M) with the addition of *n*-amyl acohol. Concentration of *n*-amyl alcohol; 1) 2.76×10^{-2}, 2): 2.3×10^{-2}, 3): 1.8×10^{-2}, 4): 1.4×10^{-2}, 5): 9.2×10^{-3}, 6): 4.6×10^{-3}, 7): 0 M (downward at 300 nm).

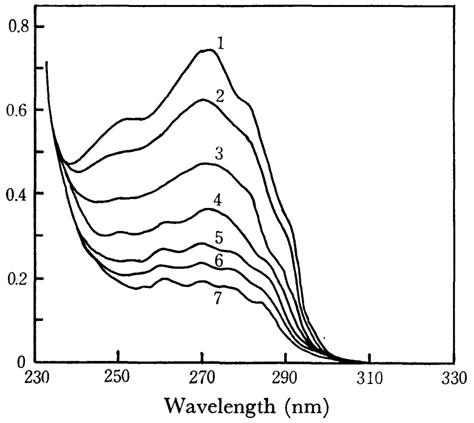
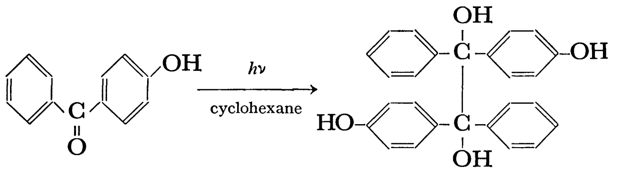


Fig. 6. Spectral change of HOBP in cyclohexane (4.57×10^{-5} M) upon irradiation at 2537 Å. Time of irradiation; 1): 0, 2): 0.5, 3): 1.0, 4): 1.5, 5): 2.0, 6): 2.5, 7): 3.0 min.

case of benzophenone.[5,6]



The rate was evaluated from the following equation, which takes the inner filter effect of the product pinacol into account.

$$-\frac{dC_A}{dt} = \Phi I_0(1-10^{-D})\frac{D_A}{D}$$

where C_A and D_A are the concentration of HOBP and the optical density due to HOBP, respectively. D is the total optical density experimentally obtained.

Integrating, we get

$$C_A{}^0 - C_A(t) = \Phi I_0\int_0^t (1-10^{-D})\frac{D_A}{D}dt.$$

By means of the relations

$$C_A{}^0 - C_A(t) = \frac{\Delta D}{(\varepsilon_A-\varepsilon_B)} \qquad D = D_A + \frac{\varepsilon_B}{(\varepsilon_A-\varepsilon_B)}\Delta D$$

(ε_B, the molar extinction coefficient of pinacol)

we obtain

$$\Delta D/(\varepsilon_A-\varepsilon_B) = \Phi I_0\int_0^t (1-10^{-D})D_A/Ddt = \Phi I_0\int_0^t Ydt. \qquad (4)$$

$\int_0^t Y\,dt$ can be obtained graphically.

An example of the analysis by Eq. (4) is shown in Fig. 7. The appearance of an induction period might be due to the incompleteness of the degassing. The relative quantum yields Φ_{rel} at various ethanol concentrations obtained by the above method are plotted against ethanol concentration in Fig. 8. The decrease of Φ_{rel} seems to occur in two steps, the first step being very small. A remarkable decrease from about 3×10^{-2}M of ethanol can not be reproduced either by Stern-Volmer or Perrin equations. It has been found that the following equation fits the results very well.

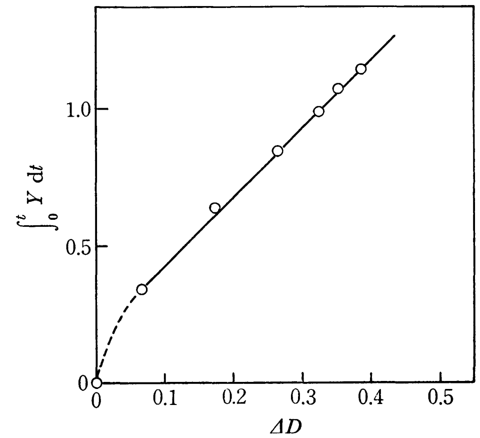


Fig. 7. An example of the plot of $\int_0^t Y\,dt$ *vs.* ΔD. HOBP in cyclohexane (4.57×10^{-5} M).

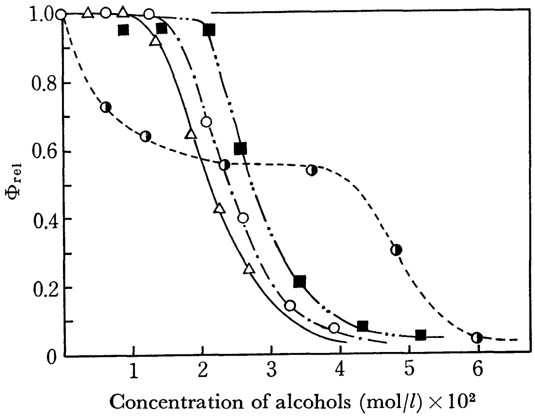


Fig. 8. Dependence of the relative quantum yield for the photoreduction of HOBP upon the concentration of alcohols. ◑: methanol, ○: 2-propanol, ■: ethanol, △: *n*-amyl alcohol.

$$\Phi_{rel} = \frac{1}{1+K[S]^n} \qquad (1)$$

Thus by plotting log $(1/\Phi_{rel}-1)$ against log [S], we obtain a good straight line, which gives $n=7$ and $K=8\times10^{10}$. Hereafter the value of the order of quencher participation will be called n. The curve in Fig. 8 is a calculated one. We see from Figs. 1 and 8 that Φ_{rel} decreases very rapidly in the ethanol concentration region where the absorption spectrum begins to turn from species A to B.

The relative quantum yields obtained for 2-propanol, mechanol, and amyl alcohol by the same method of analysis are also given in Fig. 8.

In the case of methanol the results are conspicuous, the change occurring very clearly in two steps. This implies that species A in this case has much lower photoreactivity than that of HOBP itself. The first step seems to come to an end at about 3×10^{-2}M where the concentration of species B greatly predominates judging from the spectral change given in Fig. 3. The result for methanol ensures the reality of the small decrease of Φ in the low concentration region of ethanol.

The dependence of Φ_{rel} on isopropyl and amyl alcohol concentration is reproduced very satisfactorily

---

5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, (1966), p. 534.

6) A. Schonberg, "Preparative Organic Photochemistry," Springer-Verlag, New York Inc. (1968), p. 206.

by Eq. (1). In the case of methanol, we assumed $\Phi_{rel}=0.58$ as a value at the end of the first step. The quantum yields in the second step were normalized in reference to this value.

The values of K and n and the related quantities are listed in Table 1. Some physical constants which will be referred to later are also included.

Table 1. The values of K and n and the related quantities

	n	K	$C_{1/2}(\mathrm{M})^{a)}$	DK at 25°C	Viscosity at 20C°
Methanol	7	2.5×10^{9}	4.7×10^{-2}	32.63	0.611
Ethanol	7	8.0×10^{10}	2.5×10^{-2}	24.30	1.19
2-Propanol	5.5	9.86×10^{8}	2.2×10^{-2}	18.3	2.39
Amyl alcohol	7	4.7×10^{11}	$2.0_7\times10^{-2}$	13.9	4.36

a) $C_{1/2}$, the concentration at which Φ decreases by one-half.

Studies on Primary Processes by means of Flash Technique. To obtain better insight into the proton transfer, flash photolysis studies have been performed on the HOBP solution in ethanol, cyclohexane and also in their mixture.

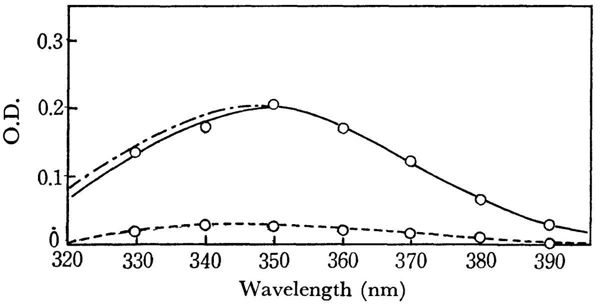


Fig. 9. Transient absorption spectrum of HOBP in ethanol.
—○—: immediately after flashing, --○--: after 500 μsec,
———: O^-BP prepared chemically

The solution of HOBP $5.6\times10^{-5}\mathrm{M}$ in ethanol was subjected to a flash with a power of 80 J/flash. A transient spectrum immediately after the flash is given in Fig. 9. It has a peak at about 350 nm and the spectral shape agrees exactly with that of O^-BP (alkaline alcoholic solution of HOBP). This is in complete agreement with Porter and Becket's result.[7] The decay obeys the second order with a rate constant of $1.6_2\times10^{9}\mathrm{M}^{-1}\mathrm{sec}^{-1}$ which was evaluated by the use of $\varepsilon=2.25\times10^{4}$ at 340 nm. This value is a little smaller than the diffusion controlled rate constant.

The transient spectrum when $5.1\times10^{-5}\mathrm{M}$ HOBP in cyclohexane was subjected to a flash with a power of 150 J/flash is given in Fig. 10. The spectrum resembles very much that of ketyl radical of benzophenone reported by Porter and Wilkinson.[8] The spectrum is observed in the degassed solution but not in the aerated solution. The decay of the ketyl radical is of second order with a rate constant of $1.1\times10^{9}\mathrm{M}^{-1}\mathrm{sec}^{-1}$. This value was evaluated with the use of $\varepsilon=1.08\pm0.22\times10^{4}$ at 550 nm obtained from the optical density divided by the yield of ketyl radical (evaluated from the decrease of HOBP).

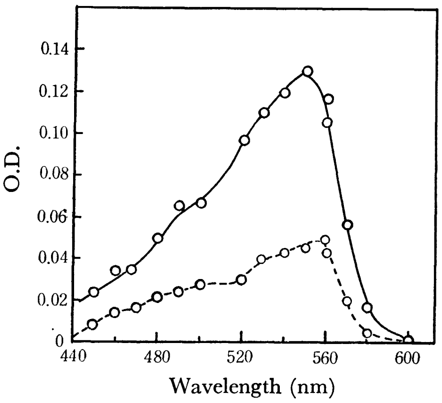


Fig. 10. Transient absorption spectrum of HOBP in cyclohexane.
—○—: immediately after flashing,
--○--: after 100 μsec

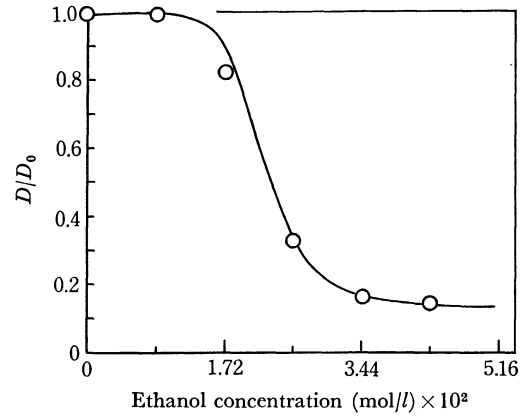


Fig. 11. Dependence of the relative quantum yield of ketyl radical (D/D_0) upon the ethanol concentration.

The yield of ketyl radical immediately after flashing as a function of the ethanol concentration in cyclohexane is given in Fig. 11. The yield was determined by measuring the optical density of ketyl radical in the long wavelength region where there is no absorption of anion. The decline of the curve becomes prominent at about $2.1\times10^{-2}\mathrm{M}$ which is a little smaller than the concentration given in Fig. 8. This may be due to different experimental conditions. The agreement can be said satisfactory. It is concluded that the cause for the quenching of photoreduction occurs prior to the formation of ketyl radical. It is most likely that this is related to deprotonation. It should be added that the rate constant of the disappearance of ketyl radical is scarcely affected by the ethanol concentration.

Discussion and Supplementary Experiments

From the results, it is suggested that two types of molecular associates are formed between HOBP and alcohol in cyclohexane. Thus the change in absorption spectrum occurs in two distinct steps in methanol, ethanol, and 2-propanol. The quantum yield of photoreduction also changes in two steps in methanol

---

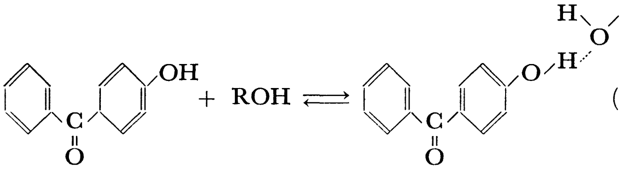
[7] A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 1686 (1963).

[8] G. Porter and F. Wilkinson, *ibid.*, **57**, 1686 (1961).

and ethanol.

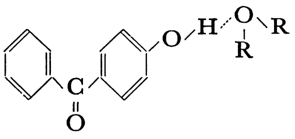
As regards the change in absorption spectrum the isosbestic point is not always observed, this being due to the superposition of the general solvent effect. Thus for methanol, whose dielectric constant is as large as 32.63, no clear isosbestic point is observed in both the first and second steps.

As regards the first step of the spectral change, it is most likely connected with the formation of a hydrogen-bonded species as follows.



(5)

The hypothesis is supported by the absorption spectrum of HOBP in ether shown in Fig. 12 which also gives the spectral change due to the addition of ethanol. It is certain that ether forms a hydrogen bond with HOBP in the following way and a close resemblance



of the absorption spectrum of HOBP in ether to that of species A supports the existence of equilibrium (5). We see from Fig. 12 that the absorption spectrum changes gradually with the increase in ethanol concentration giving no isosbestic point.

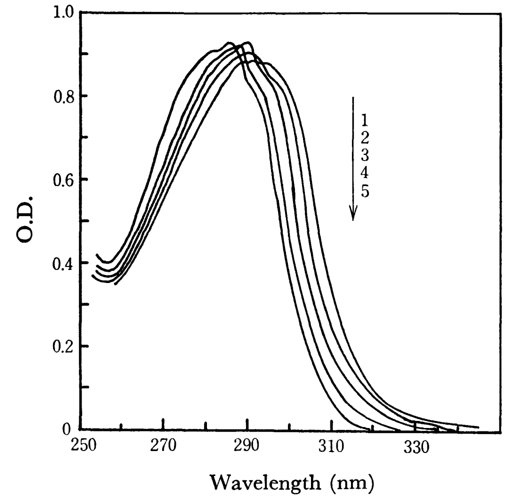


Fig. 12. Spectral change of HOBP in ether (5.50×10^{-5} M) with the addition of ethanol. Concentration of ethanol; 1) 5.1, 2) 3.4, 3) 1.7, 4) 0.85, 5) 0 M (downward at 310 nm).

As regards the second step, a detailed discussion was given on the nature of species B in ethanol-cyclohexane.[3] Some pieces of evidence were presented for the assumption that as long as the spectral behavior is concerned, the second ethanol molecule in species B is attached to the first one bonded to HO and not to the C=O group of HOBP. The present results obtained for other alcohols are also consistent with this view. Furthermore, the equilibrium constants for $A+S\rightleftharpoons B$ are for ethanol and 2-propanol 1.2×10 and 2×10 respectively, which are not incompatible with the association constants of alcohols reported in literature.[9]

As to the spectral shift, two factors are considered to be important, (a) the general solvent effect represented by DK and (b) the specific interaction between solute and solvent molecules such as hydrogen-bonding. The former is the largest in methanol and decreases in the order ethanol, 2-propanol, amyl alcohol. The latter is considered to become larger from methanol to ethanol, amyl alcohol and to 2-propanol. No clear-cut isosbestic point and a large shift in case of methanol can be ascribed to a large DK. In the case of amyl alcohol for which DK is the smallest, the specific interaction only is an important factor, and this is why the two steps are not so distinctly separated.

The relative quantum yields in the mixed solvents clearly demonstrate that species A does not undergo the eventual deprotonation upon excitation and accordingly it is photoreduced efficiently. This is supported by the fact that HOBP is very efficiently photoreduced in ether.[10] Ether has no hydrogen to be detached as a proton and accordingly a hydrogen-bonded species can be reduced even in pure ether.

Analysis of the experimental results using Eq. (4) leads to the quantum yield of 1.35. This suggests the existence of a similar situation to that for the photoreduction of benzophenone in 2-propanol.[11]

A remarkable exception is methanol; in this case Φ_{rel} of species A is 0.58 with reference to free HOBP. Thus the reactivity of H-bonded species in methanol is about one half that of free HOBP. In the case of ethanol the difference in reactivity between free HOBP and hydrogen-bonded species is very small and in other alcohols there is no measureable difference.

The following analyiss supports the view that the above difference in the case of methanol (and perhaps in ethanol) is attributed to the nature of species A and not related with the transient proton transfer or other kinetic phenomena. On the basis of the following scheme involving equilibrium, $\mathrm{HOBP}+\mathrm{S}\rightleftharpoons\mathrm{A}$

$$\begin{tikzcd}
\mathrm{HOBP} \arrow[rr, "(\mathrm{S})"] \arrow[dr, "\Phi_1"'] & & \mathrm{A} \arrow[dl, "\Phi_2"] \\
& \mathrm{Prod.} &
\end{tikzcd}$$

we obtain

$$\Phi=\frac{\Phi_1+\Phi_2\alpha[\mathrm{S}]}{1+\alpha[\mathrm{S}]} \tag{6}$$

where

$$\alpha=\frac{\varepsilon_{\mathrm{A}}}{\varepsilon_{\mathrm{f}}}K,\qquad K=\frac{[\mathrm{A}]}{[\mathrm{HOBP}][\mathrm{S}]}$$

(ε_{f} and ε_{A} are molar extinction coefficients of free HOBP and A-Species)

---

[9] N. O. Coggeshall and E. L. Saier, *J. Amer. Chem. Soc.*, **73**, 5414 (1951).

[10] The photoreduction of HOBP in ether seems to be somewhat anomalous; upon irradiation, a new absorption spectrum appears in the longer wavelength region in contrast to cyclohexane. This may be due to a trivial side reaction.

[11] Φ for the photoreduction of benzophenone in 2-propanol varies from 0.80 to 2 according to the light intensity.[5]

It follows from (6) that

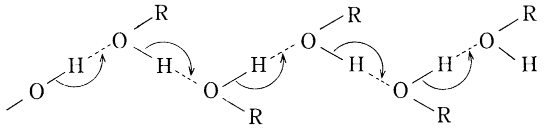
$$\frac{1-\Phi_{\mathrm{rel}}}{[\mathrm{S}]}=\alpha\Phi_{\mathrm{rel}}-\alpha\frac{\Phi_2}{\Phi_1} \qquad (7)$$

In fact the plot of $1-\Phi_{\mathrm{rel}}/[\mathrm{S}]$ *vs.* Φ_{rel} gives a good straight line and from the slope and intercept we obtain $\Phi_2/\Phi_1 \approx 0.5$ which agrees fairly well with the experimental value.

However, in view of the fact that the specific interaction between ROH and HOBP or the strength of H-bond is the weakest for methanol and ethanol next, the dielectric nature of the solvent is considered to be an important factor for determining the reactivity of H-species. Perhaps the entity consisting of $\mathrm{O{-}H\cdots O\langle^{H}_{R}}$ group and the surrounding solvation sphere of alcohol molecules may determine the reactivity.

On the other hand, the second step decrease in Φ_{rel} in methanol and ethanol and a single step decrease in other alcohols are considered to be closely related to the deprotonation of HOBP. It is regrettable that the yield of anion could not be examined as a function of ethanol concentration, since the absorption spectrum of anion was superposed by that of ketyl radical which has about ten times absorbance as that of the former. However, the approximate agreement between the two plots, Φ_{rel} and the yield of ketyl radical against [ethanol], implies that the cause of the quenching of photoreduction occurs prior to the formation of ketyl radical. It is very likely therefore, that the phenomenon is related to the proton transfer. Successful analysis by Eq. (1) also supports this view. If the decrease in Φ_{rel} were merely due to the difference in reactivity of species A and B existing in equilibrium, the decrease would not be so steep.

The result where the order of quencher participation (n) is as large as seven might be understood in the following way. For the proton transfer to suppress the reaction, the excited anion $\mathrm{O^-BP}$ produced as a result of deprotonation would be reconverted to the ground state with no chance of recombining with the proton. This may be possible only if a proton transfer occurs from one alcohol molecule to its neighbour in a successive scheme of a relay type as shown below (Grotthus mechanism).



The order of the quencher participation may then be interpreted as the average number of alcohol molecules participating in the proton transfer, required for the quenching of reaction to occur. The result where n is seven for three alcohols except for 2-propanol is also in line with this view.

If such a model is accepted the value of K may be related to the association tendency of alcohol molecules. If one assumes that this tendency is measured by an equilibrium constant of dimerization and the same equilibrium constant for the successive association

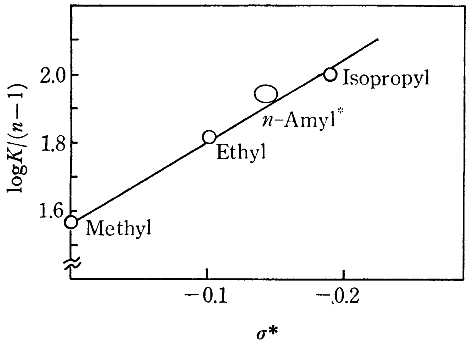


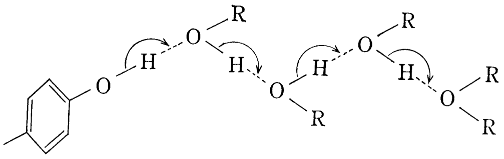
Fig. 13. A plot of log $K/(n-1)$ against σ^*.
σ^* value of n-amyl is assumed to be -0.130—-0.145.

$$k=\frac{[\mathrm{A}_2]}{[\mathrm{A}]^2}=\frac{[\mathrm{A}]^3}{[\mathrm{A}_2][\mathrm{A}]}=\frac{[\mathrm{A}_4]}{[\mathrm{A}_3][\mathrm{A}]}=\cdots$$

then k is given by $K^{1/n-1}$. In fact, the relation between $\log K/(n-1)$ and the Hammett constant[12] is approximately linear as shown in Fig. 13. That the order of quencher participation is 5.5 for 2-propanol may be due to a large electron releasing power of isopropyl group, which enhances the accepting power of proton.

Thus we might say that the proton transfer efficiency in alcohols is closely related to the specific interaction between alcohol molecules and not to the dielectric nature or the viscosity of the solvent, as was found in Table 1.

It is of interest to add that for Φ_{rel} in the mixed solvent of ether and ethanol, the same type of equation as (1) holds but with $n=3$ and $K=2.8\times10^{-2}$. The smaller values of n and K are reasonable because the proton accepting power is considered to be larger for ether than for ethanol. It is possible that the following structure has a lifetime longer than that of the excited anion $\mathrm{O^-BP}$.



Thus all the results we obtained are consistently explained by the Grotthus mechanism of proton transfer.

Our thanks are due to Dr. K. Kikuchi for his help in the flash experiments.

---

[12] R. W. Taft, Jr., in Steric Effects in "Organic Chemistry," ed. by Newman, John Wiley & Sons, New York, N. Y. (1956), p. 619.