BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3075—3077 (1972)

Order of Quencher Participation in Photochemistry. II. Quenching Action of Ethanol on the Photoreduction of *p*-Aminobenzophenones

Mikio Hoshino and Masao Koizumi

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba, Sendai

(Received March 21, 1972)

The effect of the addition of ethanol (quencher of the reaction) on the photoreduction of *p*-aminobenzophenone (NH_2BP) and dimethyl-*p*-aminobenzophenone in cyclohexane and in ether has been studied. The order of quencher participation for ethanol has been found to be two for the former and one for the latter. The results were interpreted to be due to the formation of intramolecular C–T state during excitation, promoted by the attachment of one ethanol (or ether) molecule to the NH_2-group and one ethanol molecule to O=C of NH_2BP.

We previously reconfirmed[1] the view that proton transfer is a cause of the quenching action of ethanol on the photoreduction of *p*-hydroxybenzophenone (HOBP). This was in line with the work of Porter *et al.*[2] It was found, however, from the measurement of relative quantum yields in the mixed solvents of cyclohexane and alcohols, that the participation of several alcohol molecules is required for the eventual proton transfer to occur from HOBP in cyclohexane. An approach of the same type will enable us to attain a dynamic aspect of the quenching action not obtained with pure solvents. We have extended similar sutdies to the quenching action of alcohols on the photoreduction of *p*-aminobenzophenone (H_2NBP) and dimethyl-*p*-aminobenzophenone ($(CH_3)_2NBP$).

H_2NBP is photoreduced in cyclohexane with a quantum yield of 0.2 but not at all in ethanol.[3] The difference was explained to be due to the different character of the lowest triplet state. Thus in cyclohexane, the lowest triplet is $T(n-\pi^*)$ whereas in ethanol it is an intramolecular C–T state. However, from analogy of HOBP, the quenching action of ethanol in the case of H_2NBP is also expected to be dynamic in nature, and studies in the mixed solvents should give more detailed information. In particular, we thought it possible that in cyclohexane containing a suitable amount of ethanol, intramolecular C–T state of H_2NBP might be stabilized during the lifetime of the excited state by a suitable reorientation of alcohol molecules around $^+NH_2$ and $C=O^-$ group, notwithstanding the lack of C–T type absorption spectrum. Our results indicate that this is actually the case.

Experimental

H_2NBP was prepared by the reduction of 4-nitrobenzophenone with zinc powder and glacial acetic acid. $(CH_3)_2$-NBP was obtained by the hydrolysis of 4-dimethylaminobenzophenone anil. These aminobenzophenones were recrystallized twice from ethanol. Mp=97—98°C (lit,98°C) for $(CH_3)_2NBP$ and 123°C (lit, 123∼124°C) for H_2NBP. Cyclohexane and ethanol were purified by the usual method. Ether was refluxed on sodium metal for 24 hrs before dis-

---

1) M. Hoshino and M. Koizumi, *Chem. Lett.*, **1972**, 189. M. Hoshino and M. Koizumi, This Bulletin, **45**, 2731 (1972).

2) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1164 (1965). T. S. Godfrey, G. Porter, and P. Suppan, *Discuss. Faraday Soc.*, **39**, 194 (1965).

3) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038, 2051 (1963). J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

tillation. The spectral change was followed with a Hitachi EPS-3T spectrophotometer. A 6W germicidal lamp was used as a light source of 2537 Å.

Results and Discussion

p-*Aminobenzophenone* *(H_2NBP)*. The peak of the absorption at 303 nm in cyclohexane shifts to 335 nm in ethanol. The spectral change with the increase in ethanol concentration is shown in Fig. 1.

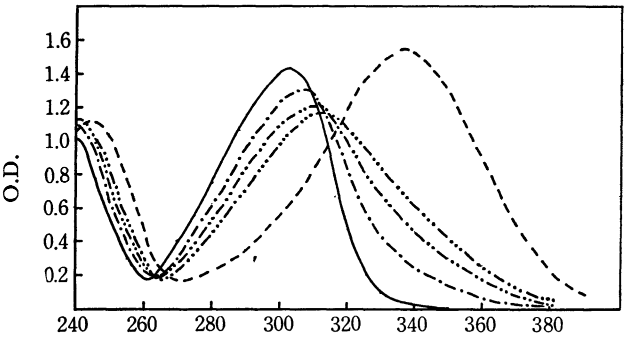
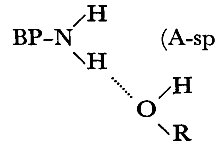


Fig. 1. Spectral change of H_2NBP (8.0×10^{-5} M) in cyclohexane with the addition of ethanol.
—— in cyclohexane
concentration of ethanol:
—·— 1.72×10^{-1} M, —··— 3.44×10^{-1} M, —···— 5.16×10^{-1} M, ---- in pure ethanol

A gradual *red* shift with no isosbestic point suggests that the interaction between NH_2-group and ethanol is hydrogen bonding of the type

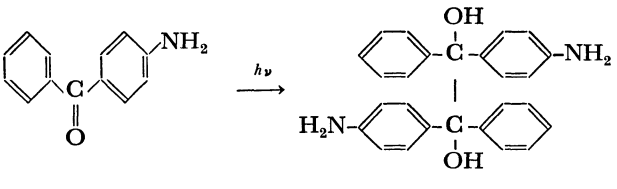


(A-species) (1)

which the general solvent effect is superposed. By analogy with a similar H-bonding species in the case of HOBP the photoreactivity of A-species was not expected to be reduced remarkably as compared with free H_2NBP.

It was found on the contrary that the relative quantum yield Φ_{rel} of the photoreduction decreases with the addition of ethanol much more rapidly than the spectral change.

The spectral change of H_2NBP in cyclohexane upon irradiation by 2357 Å is shown in Fig. 2. The change is due to the reaction



(2)

The analysis was made by the equation

$$-\frac{dC_A}{dt} = \Phi I_0(1-10^{-D})\frac{D_A}{D} \tag{3}$$

where D and D_A are the optical density of the irradiated solution and that due to H_2NBP at 2537 Å, respectively.

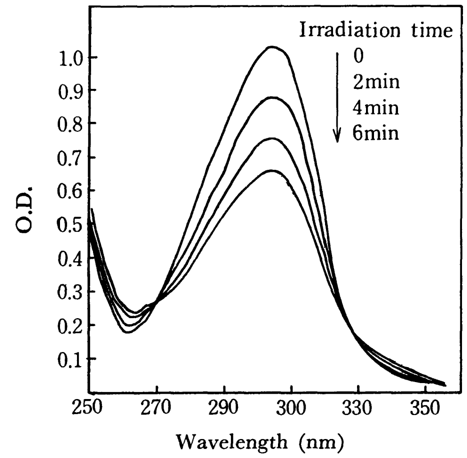


Fig. 2. Spectral change of H_2NBP containing ethanol (5.16×10^{-2} M) upon UV irradiation.

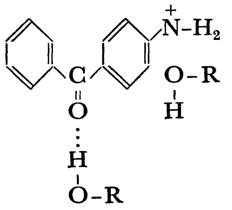
The other notations are the usual ones. Integrating we have

$$-\frac{1}{\varepsilon}\ln C_A = \Phi I_0\int\frac{(1-10^{-D})}{D}dt \tag{4}$$

Because of a small change in optical density at 2537 Å, C_A was determined from the change at ~303 nm. The values of Φ_{rel} thus obtained at various ethanol concentrations [S] can be reproduced by the equation

$$\Phi_{rel} = \frac{1}{1+K[S]^n} \tag{5}$$

where $n=2$ and $K=3.03\times10^2\,M^{-2}$. The plot of $1/\Phi_{rel}$ against $[S]^2$ gives a very good straight line as shown by curve a in Fig. 3. The value of 2 as the order of quencher participation suggests that another ethanol molecule is attached to C=O by H-bonding thus stabilizing the C–T state.



(6)

This is reasonable since the electron donating power of amino-group is much greater than that of the hydroxy

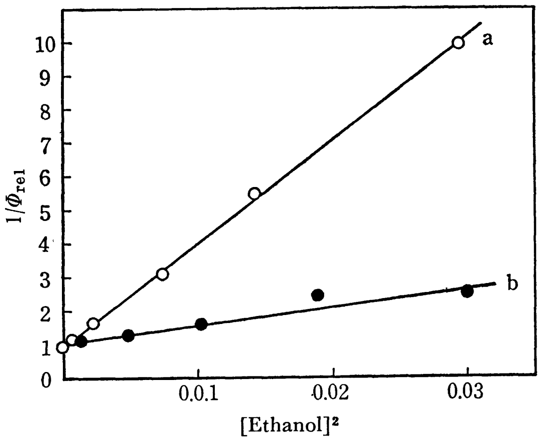


Fig. 3. Plots of $1/\Phi_{rel}$ *vs.* [ethanol]², ○: H_2NBP, ●: $(CH_3)_2NBP$.

group, for which such an electronic configuration is not so prominent. The interaction between $^{+}NH_2$ and ethanol in this state would be mainly due to a dipole-dipole one instead of H-bonding.

p-*Dimethylaminobenzophenone* (*$(CH_3)_2NBP$*). The absorption spectrum of $(CH_3)_2NBP$ has a peak at 332 nm in cyclohexane and at 358 nm in ethanol, but it scarcely changes upon addition of ethanol up to about 1.7×10^{-1}M. However, the relative quantum yield of photoreduction obtained by the above analysis decreased to 40% at this ehtanol concentration.

$(CH_3)_2NBP$ with no amino-hydrogen cannot form a H-bonded species as in the case of H_2NBP and it is quite natural that no spectral change occurs. Thus it is concluded that the decrease in Φ_{rel} in H_2NBP as well as in $(CH_3)_2NBP$ is not related to the spectral change and accordingly the hydrogen bonding between NH_2 and alcohol.

The polt of $1/\Phi_{rel}$ against $[S]^2$ ($S=C_2H_5OH$) is linear as shown by curve b in Fig. 3 and the value of K was evaluated as $0.61\times10^2\,\text{M}^{-2}$. All the results are similar to those of H_2NBP at least qualitatively and the mechanism of quenching is considered to be the same.

It is interesting that the K-value of $(CH_3)_2NBP$ is much smaller than that of H_2NBP. Judging from a larger electron releasing power of dimethyl-group than hydrogen, structure (6) is expected to be more stable for $(CH_3)_2NBP$ than for H_2NBP. The opposite result might be due to the kinetics of the phenomenon. Thus for H_2NBP, an ethanol molecule is in intimate interaction with H_2NBP molecule by H-bonding already in the ground state while no such an interaction takes place in $(CH_3)_2NBP$. However, there is a possibility that the structure itself is more stabilized by H-bonding in H_2NBP than in $(CH_3)_2NBP$.

The order of quencher participation of two could be interpreted by structure (6). It is conceivable that the quenching is caused by a dimeric ethanol molecule although this is less likely. The following experiment was carried out to clarify the mechanism.

Effect of the Addition of Ethanol on the Quantum Yield of the Photoreduction of H_2NBP in Ether. Ether is expected to interact with the amino group of H_2NBP in a similar way to ethanol, acting as a H-acceptor of H-bonding, but differing from ethanol in that no hydrogen bond formation occurs with carbonyl of H_2NBP. If by analogy to HOBP, a hydrogen bonded species of the type ${}^{R}_{R}\!\!>\!O\cdots{}^{H}_{H}\!\!>\!N\text{-BP}$ and ${}^{H}_{R}\!\!>\!O\cdots{}^{H}_{H}\!\!>\!N\text{-BP}$ (A-species (1)) is reactive, then the photoreduction of H_2NBP is expected to occur in pure ether as in HOBP. But when a small amount of ethanol is added, formation of species (6) becomes possible and the reaction may be suppressed. If this is the actual mechanism for the quenching of reaction, the order of quencher participation is now expected to become one. On the other hand, the mechanism due to ethanol dimer should result in the order of quencher participation of two. Thus it will be easy to discriminate the two mechanisms experimentally. From such a viewpoint, we have investigated the photoreduction of H_2NBP in ether.

The absorption peak of H_2NBP in ether lies at 320 nm compared with 303 nm in cyclohexane and 337 nm in alcohol. It was established that the photoreduction occurs in pure ether with a quantum yield about the same as or a little larger than in cyclohexane. This indicates that A-species (1) itself is reactive. The plot of Φ_{rel} and $1/\Phi_{rel}$ aganist the concentation of ethanol is shown in Fig. 4. It is evident that the quenching action of ethanol occurs according to the equation

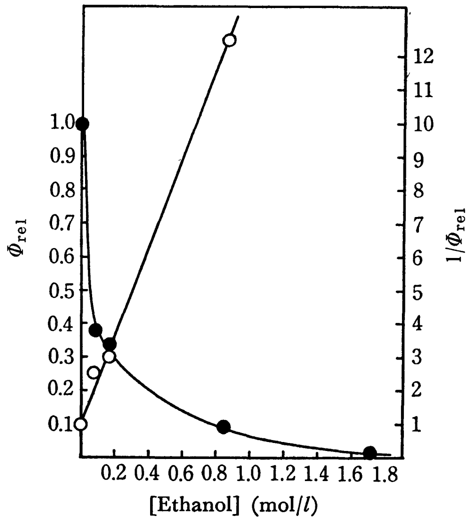


Fig. 4. Plots of Φ_{rel} *vs.* [ethanol] (●) and $1/\Phi_{rel}$ *vs.* ethanol (○) in ether.

$$\Phi_{rel}=\frac{1}{1+K[S]} \tag{7}$$

where [S] is the concentration of ethanol. The value of K evaluated from the solpe of $1/\Phi_{rel}$ *vs.* [S] plot is $13.2\,\text{M}^{-1}$. The absorption spectrum of H_2NBP in ether changes gradually to longer wavelength with the addition of ethanol, but the magnitude of change is very small at the ethanol concentration where the value of Φ_{rel} becomes about 1/10. This is reasonable in view of the fact that the effect of the hydrogen bond of this type on the π–π absorption spectra is rather small.[4]

It is thus concluded that the formation of intramolecular C–T state during the excitation by a solvent interaction as written in (6) is a cause for the quenching of reaction.

---

[4] M. Ito, M. Inuzuka, and S. Imanishi, *J. Amer. Chem. Soc.*, **82**, 1317 (1960).