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Photochemical Reaction of 4-Hydroxy-diphenylamine with Polychloromethane

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The main photochemical reaction of 4-hydroxy-diphenylamine (R) in the aerated cyclohexane was photocyclization. In the presence of polychloromethane (Q), however, photooxidation to *N*-phenyl-*p*-benzoquinone monoimine (PBQI) took place instead of the photocyclization. The formation of PBQI was in parallel with the quenching of fluorescence by Q, and it was proposed that both PBQI formation and fluorescence quenching by Q proceed *via* exciplex, $(R^+Q^-)^*$, which is nonfluorescent. The kinetic analysis based on this reaction mechanism gives the fluorescence quenching constant, which is in good agreement with the value obtained directly from the fluorescence quenching study. This agreement strongly supports the validity of the proposed reaction mechanism.

The electron donor and acceptor system involves the electron transfer as the deactivation process of the electronically excited state of the donor or acceptor and forms a resultant pair of radical cation and anion which participates in various types of reactions.[1] The aromatic amine and polychloromethane (Q) system can be regarded as one electron donor–acceptor system. Latowsky and Zelent have made systematic studies on the photochemistry of monophenylamines–Q systems and have pointed out that the primary process may be an electron transfer from the excited amine to Q, however, the final products were not simple enough to allow them to analyze the over-all reaction completely.[2] Diphenylamine and its *N*-substituted derivatives have been known to photocyclize to give carbazoles.[3,4] This photocyclization has been proposed to proceed *via* triplet state.[5] In the presence of Q, however, photolysis of diphenylamines furnishes a variety of products which are quite different from the photocyclization product.[6–9] These new products are considered to arise from the electron transfer from the excited amine to Q. The present authors extended the treatment to 4-substituted diphenylamines because the effect of substituent in the benzene nucleus on the photochemical path ways of diphenylamine has rarely been reported.

In this paper, the identification of the photolysis product from 4-hydroxy-diphenylamine and Q system together with the discussion on the mechanism of the reaction will be presented.

Experimental

Materials. 4-Hydroxy-diphenylamine was obtained commercially and purified by repeated recrystallization. Polychloromethanes and solvents were the spectroscopic grade reagents and were used without further purification.

Light Source and Actinometry. The high pressure mercury lamp was used with an interference filter for 313 nm light source. The intensity of the incident light was measured by the method of potassium trioxalatoferrate(III) actinometer.

Analysis. Measurement of the quantum yield of the reaction was carried out spectroscopically by monitoring the increase in characteristic absorption of the reaction product. The absorption spectra were measured by Hitachi EPS-2-model spectrophotometer and emission spectra were taken with a Hitachi MPE-3-model fluorescence spectrophotometer.

Results and Discussion

The progressive spectral changes of 4-hydroxy-diphenylamine (AH_2) in aerated cyclohexane solution caused by irradiation of 313 nm light in the absence and presence of Q are given in Fig. 1 (a) and Fig. 1 (b), respectively. The spectral changes under the absence of Q are characteristic for the well-known photocyclization. The final spectrum obtained under the presence of Q shown in Fig. 1 (b), however, is quite different from that shown in Fig. 1 (a), and is identical with that of *N*-phenyl-*p*-benzoquinone monoimine (PBQI) reported by Teuber.[10] Further confirmation of the reaction product was carried out as follows: The crude product separated from the irradiated solution was submitted to the alumina chromatography using benzene as a solvent. The red fine crystal was separated from benzene. The melting point of this crystal coincided with that reported for PBQI,[11] and the mixed melting point with the synthesized PBQI showed no depression. Since the irradiation of *p*-aminophenol in the presence of Q gave complicated reaction products other than *p*-benzoqui-

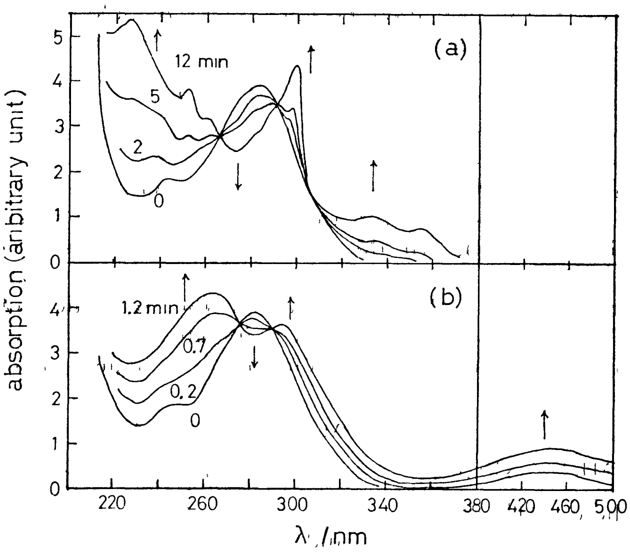


Fig. 1. Spectral changes of 4-hydroxy-diphenylamine in aerated cyclohexane caused by irradiation of 313 nm light in the absence (a), and in the presence (b) of $CHCl_3$.

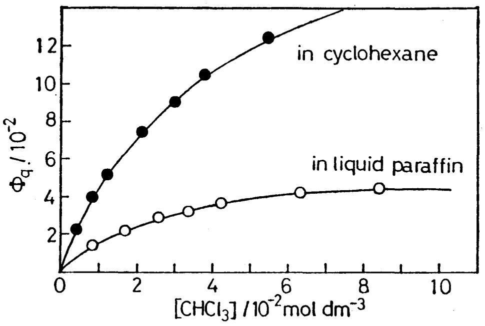


Fig. 2. Dependence of the quantum yield on the concentration of $CHCl_3$ in cyclohexane and in liquid paraffin.

TABLE 1. QUANTUM YIELDS (Φ_q) AND FLUORESCENCE QUENCHING CONSTANTS (k_Q)

	CH_2Cl_2	$CHCl_3$	CCl_4
Φ_q	0.01	0.04	0.43
k_Q[a]	6.0	23.5	79.2
k_Q[b]	7.3	20	75
$1/(k_0k_1\tau)$	0.91	0.20	0.013
$k_Q/(k_0k_1\tau)$	6.6	4.0	1.0

a) Obtained from the fluorescence quenching experiment. b) Obtained from the reaction kinetics.

none monoimine, the photooxidation by Q giving benzoquinone monoimine-type product is the characteristic reaction for AH_2.

The quantum yield of PBQI formation (Φ_q) in cyclohexane increased with increasing the concentration of Q, as shown in Fig. 2. Polychloromethane acts as a quencher on the fluorescence of AH_2 and the Stern-Volmer plots give a straight line. Values of Φ_q, obtained under the condition where the concentration of Q is 0.01 mol dm^{-3}, and values of the fluorescence quenching constant (k_Q) are listed in Table 1. It may be seen in the Table that the effect of Q on PBQI formation becomes more notable as the fluorescence quenching ability of Q increases. This result suggests that the process of fluorescence quenching by Q leads to the formation of PBQI. To make sure of this assumption, the mechanism of the reaction and fluorescence quenching by Q were studied. The photochemical reaction of aromatic amine with Q has been known to result in the formation of hydrogen chloride (HCl). In the present case, the formation of HCl was confirmed from the increase in the concentration of hydrogen ion under the irradiation of AH_2–Q–ethanol–water system. Similar to the case of aniline derivatives,[2] the following mechanism may be presented:

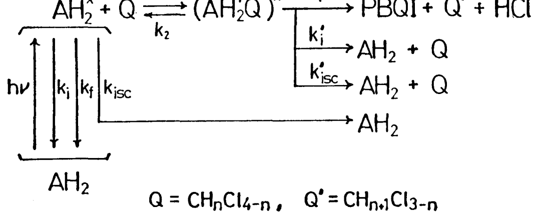
$$AH_2^* + CH_nCl_{4-n} \longrightarrow AH_2^+ + (CH_nCl_{4-n})^-, \qquad (1)$$

$$AH_2^+ + (CH_nCl_{4-n})^- \longrightarrow A + CH_{n+1}Cl_{3-n} + HCl, \quad (2)$$

where AH_2^* and A are the excited AH_2 and PBQI, respectively. CH_nCl_{4-n} and $CH_{n+1}Cl_{3-n}$ denote polychloromethane, where $n=0$, 1, 2.

It has been reported that the aromatic amine forms a stable complex with Q in their ground state.[12,13] On the other hand, Sharpe[14] reported that the amine forms a complex with Q only in the excited state. The fluorescence spectrum of AH_2 was sensitively affected by the addition of Q, while the absorption spectrum was almost unchanged. The quantum yield (Φ_q) was found to be markedly reduced in liquid paraffin compared with that in cyclohexane, as shown in Fig. 2. These results clearly indicate that the diffusion controlled encounter process is involved in the reaction between the excited amine and Q and the role of the stable complex is not important.

The results described above can be accounted for by the following reaction scheme. Polychloromethane forms a exciplex, $(AH_2^+Q^-)^*$, *via* the encounter complex with the excited amine. As for the relaxation process of the exciplex, the reaction leading to PBQI (rate constant: k_r), nonradiative relaxation (k_i'), and intersystem crossing (k'_{isc}) are taken into account. The stability of the exciplex depends on the nature of Q. Using the steady state approximation, the following equations are obtained for Φ_q and Φ_f°/Φ_f:



Reaction scheme.

$$\Phi_q = \frac{k_0k_1\tau[Q]}{1+k_Q[Q]}, \qquad (3)$$

$$\Phi_f^\circ/\Phi_f = 1 + k_Q[Q], \qquad (4)$$

where

$$k_Q = k_1\tau/(1+k_2\tau), \quad \tau = 1/(k_i+k_f+k_{isc}),$$

$$\tau' = 1/(k_i'+k_r+k'_{isc}),$$

and

$$k_0 = k_r\tau'/(1+k_2\tau).$$

Equation 3 is rewritten as follows:

$$\Phi_q^{-1} = k_Q/k_0k_1\tau + (1/k_0k_1\tau)[Q]^{-1}.$$

Then, the reciprocal of the quantum yield is expected to have a linear relation with the reciprocal of the concentration of Q. The experimental results meet with this expectation, and the value of k_Q is obtained from the intercept ($k_Q/k_0k_1\tau$) and slope ($1/k_0k_1\tau$) of the straight line. This value of k_Q can be compared with that obtained directly from the fluorescence quenching and these are summarized in Table 1. The good agreement of the values obtained by reaction kinetic analysis and by the fluorescence quenching experiment strongly supports the validity of the proposed reaction scheme.

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