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PHOTODIMERIZATION OF 2,6-DIPHENYLPYRYLIUM SALT IN THF SOLUTION

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Abstract: By the photoillumination of 2,6-diphenylpyrylium tetrafluoroborate (DPP) in tetrahydrofuran (THF), its dimer is confirmed to be formed through the pyranyl radical which is produced by one electron reduction of DPP.

In the preceding paper,[1] we treated the photoreaction of various pyrylium salts and reported that 2,4,6-triphenylpyrylium salt is subject to one electron reduction by irradiation and converts to pyranyl radical, which is in equilibrium with its dimer. In this equilibrium, the dimer predominates at lower temperature. The dimer is stable for photoirradiation and can dissociate into pyranyl radical only by thermal process. In this letter, we report the mechanism of photodimerization of DPP studied by using a conventional flash photolysis.

The change in the absorption spectra is observed on irradiating a deaerated THF solution of DPP by a 100 W high pressure mercury lamp (Toshiba-SHL-100UV) with a Toshiba L-39 filter, as shown in Fig.1. The solvent THF stocked on a sodium-potassium alloy in an ampoule connected to a vacuum line was used. The photoproduct has the absorption maxima at 231 and 330 nm and the band extends to the wavelength longer than that of the original DPP.

Thus, the conjugation of π electrons in the photoproduct is considered to be rather long. It exihibits no ESR signal. The quantum yield for the disappearance of DPP was determined to be 0.49. This value is relatively large compared with those of other pyrylium salts. It may be due to the fact that DPP molecule has no large substituent at the position of reactive carbon.

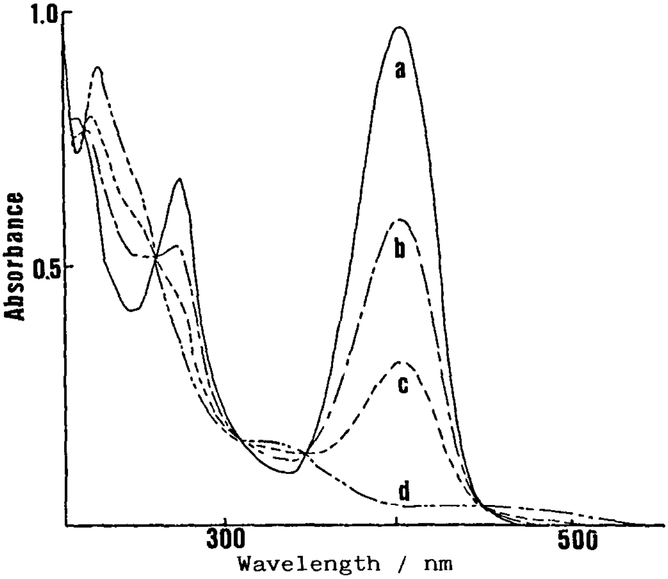


Fig.1. Spectral change of DPP (1.0×10^{-4}mol·dm^{-3}) in deaerated THF solution on irradiation for various times: curve a, 0 min; curve b, 1 min; curve c, 2 min; curve d, 5 min.

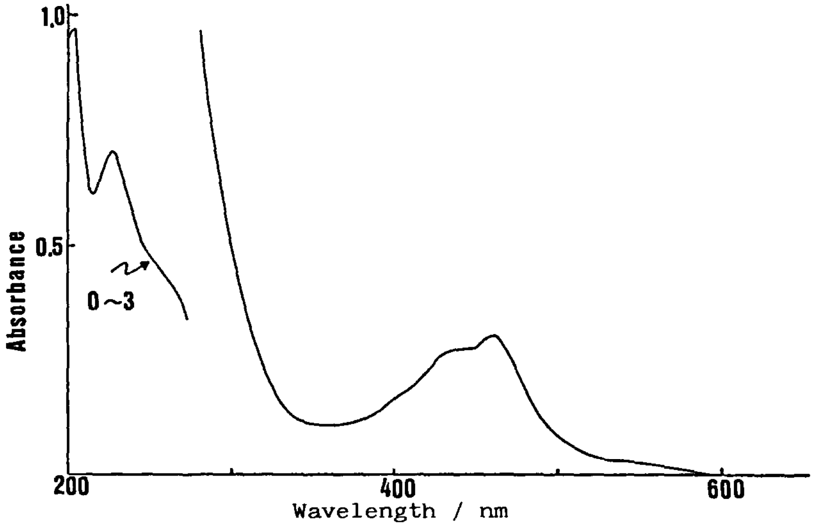
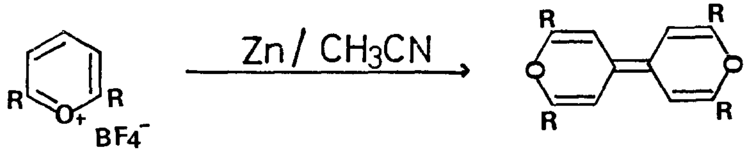


Fig.2. Absorption spectrum of Zn-reduction product in deaerated THF solution (~1×10^{-4}mol·dm^{-3}).

The irradiation of deaerated DPP in THF was carried out in large scale. The mass spectrum of the photoproduct was measured immediately after removing the solvent in deaerated system. The strong peak at 466 (M^+) corresponds to the molecular weight of dimer of DPP. In order to confirm the structure of the photoproduct, we tried to synthesize DPP-dimer chemically by reducing a DPP salt with zinc in acetonitrile bubbling N_2 gas. A mass spectrum of the zinc-reduction product has a peak at 464 (M^+). The absorption spectrum of the product in deaerated THF solution is shown in Fig.2. The absorption has its maxima at 434 and 458 nm and extends to a wavelength longer than that of the original DPP just like the case of the photoproduct. It decomposes by the introduction of air. Thus, the structure of the zinc-reduction product is similar to but a little different from that of the photoproduct and is considered to be 1.[2] On the other hand, we infer the structure of the photoproduct is a DPP-dimer 2, taking the difference in the data of mass spectra into account.



DPP ($R=C_6H_5$) 1

By flashing the deaerated THF solution, a transient absorption was observed in the wavelength region of 460-530 nm, as shown in Fig.3. The photoproduct also has the absorption band in this wavelength region to a lesser extent. The decay of this transient is second order. We can estimate its rate constant as $(1.2 \pm 0.5) \times 10^9\ dm^3 \cdot mol^{-1} \cdot s^{-1}$ from the analysis of the initial part of the decay curve, assuming the molar extinction coefficient of DPP radical as $1.3 \sim 3.2 \times 10^3\ dm^3 \cdot mol^{-1} \cdot cm^{-1}$ in the light of the data on 2,4,6-triphenylpyrylium and 2-t-butyl-4,6-diphenylpyrylium radicals.[1] Pyranyl and thiopyranyl radicals usually have the absorption band in the wavelength region of 460-570 nm. It should be added that the formation process of DPP-dimer was not followed by flash photolysis because the absorption of DPP-dimer was hidden behind that of the pyranyl radical in the course of the process.

By flashing the deaerated acetonitrile solution of DPP, no signal was detected in the wavelength region of 460-750 nm and no photoreaction was observed by steady light irradiation. Thus, the photodimerization in THF arises from the abstraction of an electron from the solvent molecule.

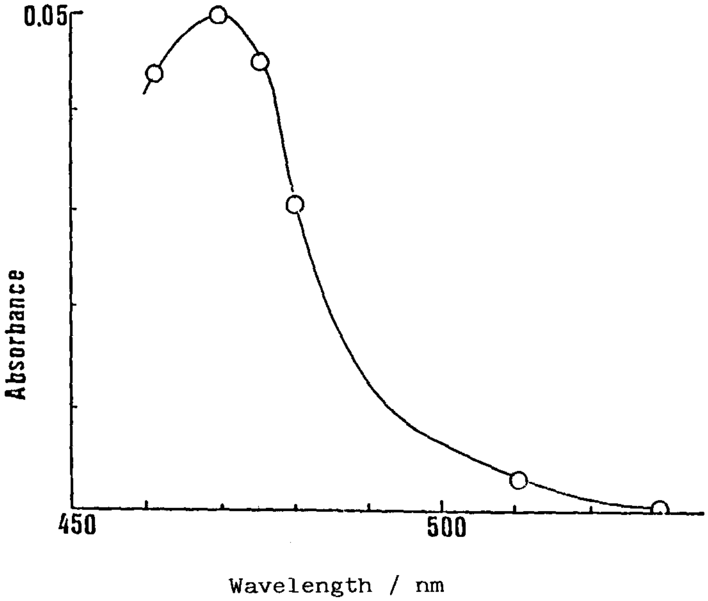
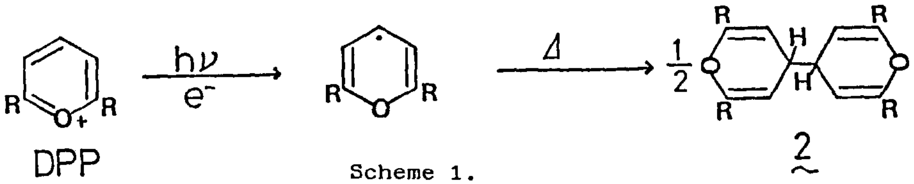


Fig.3. Transient absorption spectrum observed immediately after flashing the deaerated THF solution of DPP.

These results can be summarized in the following way: the transient observed in flash photolysis is pyranyl radical formed by electron transfer from THF and then this pyranyl radical dimerizes thermally, as shown in Scheme 1.



Scheme 1.

References

1. S.Niizuma, N.Sato, H. Kawata, Y.Suzuki, T.Toda and H.Kokubun, Bull. Chem. Soc. Japan., 58, 2600 (1985).
2. J.Alizon, J.Gallice, H.Robert, G.Delplanque, C.Weyl, C.Fabre and H.Strzelecka, Mol. Cryst. Liq. Cryst., 33, 91 (1976).

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