The Reaction of Photo-excited Phenanthraquinone with Hydrogen Donors.[1] The Behaviors of the Resulting 1,2-Photo-adducts Studied by the CIDNP Technique

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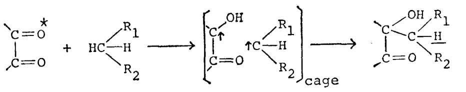
(Received March 24, 1971)

Strongly-enhanced PMR absorption signals due to the underlined proton of the 1,2-photo-adduct have been observed in the photochemical reaction of phenanthraquinone with alkyl aromatics *via* a radical in the electronic triplet state (Eq. (1)).[2]

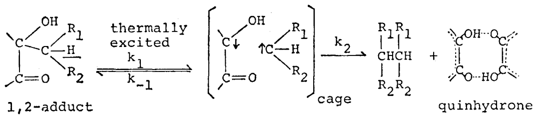


(1)

(I): R_1=R_2=C_6H_5, (II): R_1,R_2= C_6H_4-C_6H_4
(III): R_1,R_2= C_6H_4-O-C_6H_4

On the contrary, when 1,2-photo-adducts, especially those produced from the reaction of phenanthraquinone with diphenylmethane (I), fluorene (II), and xanthene (III), were heated in an NMR probe at a suitable temperature, we observed a strong, enhanced PMR emission signal at exactly the same position as was observed in the process described in Eq. (1). The optimal temperature to observe the strongest emission signal was at 150°C, 175°C, and 110°C respectively for I, II, and III (Fig. 1). Accompanying such a phenomenon, the 1,2-photo-adduct promptly decomposed to give phenanthraquinhydrone as black purple crystals and the dimer of the alkyl aromatic moiety.[4]

These exciting phenomena appear to be caused by the process described in Eq. (2); that is, the 1,2-photo-adduct is thermally activated to give the radical pair in the electronic singlet state in a solvent cage (the rate of k_1). The radical pair produced will be stabilized by the two competitive routes; the reverse reaction to the adduct, and the decomposition reaction out of the solvent cage (the rates of k_{-1} and k_2 respectively). Thus, the methine proton (underlined) of the reproduced adduct will be polarized with inversely-populated



(2)

When $k_1 \simeq 0$ and/or $k_2 \gg k_{-1}$, we were not able to observe such a strong enhanced emission signal. Although the spin states to those in the process described in Eq. (1). enhanced absorption or emission PMR spectra observed here are compatible with those predicted by the CKO theory,[5] no such typical representation as in our experiments has ever been reported.

Furthermore, when the 1,2-photo-adduct was irradiated with and without a yellow filter (Kenko L40C UV cut filter) with a 500 W high-pressure Hg lamp at a suitable temperature just before thermal decomposition takes place, for example, at 125°C for I in neat diphenylmethane, it was found that an enhanced PMR absorption signal of the same methine proton (about 10 times the normal signal intensity) can be observed. At this temperature, the signal intensity of normal signal does not change between before and after irradiation. This phenomenon seems to be explainable by taking into account the process described in Eq. (3)

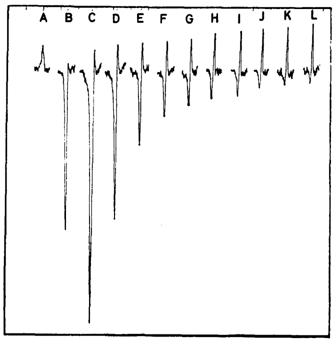
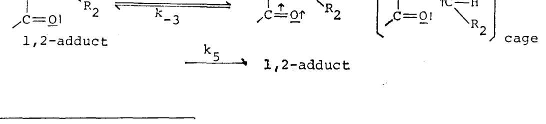


Fig. 1 Enhanced PMR emission signals (247 Hz down-field from TMS) observed in the course of thermal decomposition of 1,2-photo-adduct obtained from phenanthraquinone and xanthene (solvent:*o*-dichlorobenzene, 110°C). Signals (from **A** to **L**) were measured for every 10 sec. **A**: normal signal immediately after sample was inserted into an NMR probe. **B,C,D**……: enhanced PMR emission signal after thermal decomposition started, and the other signal due to proton of decomposition product begins to appear at a slightly upper field.



(3)

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[1] This work has been done at the Department of Chemistry, College of Liberal Arts and Science, Kyoto University.

[2] K. Maruyama, H. Shindo, and T. Maruyama, This Bulletin, **44**, 585 (1971); K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, *ibid.*, submitted for publication.

[3] In the photo-excited triplet state.

[4] This was confirmed both chemically and spectroscopically.

[5] G. L. Colss and A. D. Trifunac, *J. Amer. Chem. Soc.*, **91**, 4554 (1969); **92**, 2183, 2186 (1970); G. L. Closs, C. E. Doubleday, and R. D. Paulson, *ibid.*, **92**, 2185 (1970); R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).