Hydrogen Abstraction of Excited Benzophenone in *N*,*N*-Dimethylaniline and 2-Methyltetrahydrofuran Solution at Low Temperature

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Photochemical reactivities of aromatic ketones have been studied extensively,[1–5] Porter and his co-workers found that photoreduction of benzophenone in isopentane does not occur at temperatures 77°K—108°K, but proceeds above 108°K.[4] We wish to report that it occurs easily in a mixed glass of aromatic amine and ether at 77°K. Benzophenone (5×10^{-3} M) in a degassed mixture of *N*,*N*-dimethylaniline (DMA) and 2-methyltetrahydrofuran (2MTHF), about 1 : 3 by volume, at 77°K was photolysed in the region 350—400 nm through a glass filter with a high pressure mercury lamp for 10—30 sec. The results are shown in Fig. 1. The spectrum (appearing from 500 to 570 nm in curve d) is nearly in agreement with that of the ketyl radical at room temperature (curve e).[3,4] No ketyl radical was found by the photolysis of benzophenone in a 2MTHF matrix at 77°K.

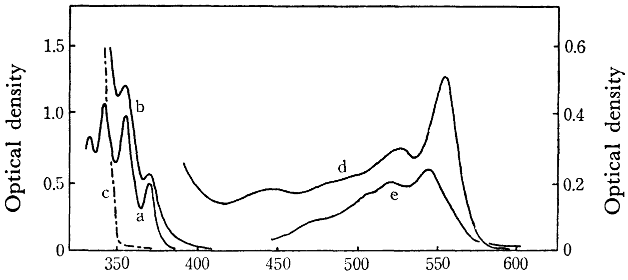

Fig. 1. a) Absorption spectrum of benzophenone in 2MTHF at 77°K. b) Absorption spectrum of benzophenone in DMA and 2MTHF at 77°K. c) Absorption of DMA and 2MTHF at 77°K. d) Absorption of sample used in b) after irradiation. e) Absorption of the ketyl radical obtained by flash illumination of a solution at room temperature.

The electronic spectrum of benzophenone in the DMA-2MTHF matrix shown by curve b suggests that an electron donor-acceptor complex is formed between benzophenone as an electron acceptor and DMA as a donor at 77°K. Therefore, it is suggested that the photochemical reactivity of benzophenone is activated significantly in the excited state of benzophenone-DMA complex. The ketyl radical appears also in a mixed matrix of DMA and trichlorotrifluoroethane, the latter having no hydrogen atom to abstract. This result definitely indicates that the ketyl is produced as a result of intermolecular hydrogen transfer from DMA to benzophenone. Thus, the absorption band at near 445 nm can be ascribed to DMA radical $\left(\phi\text{-N}\langle{}^{\dot{\mathrm{C}}\mathrm{H}_2}_{\mathrm{CH}_3}\right)$.[6]

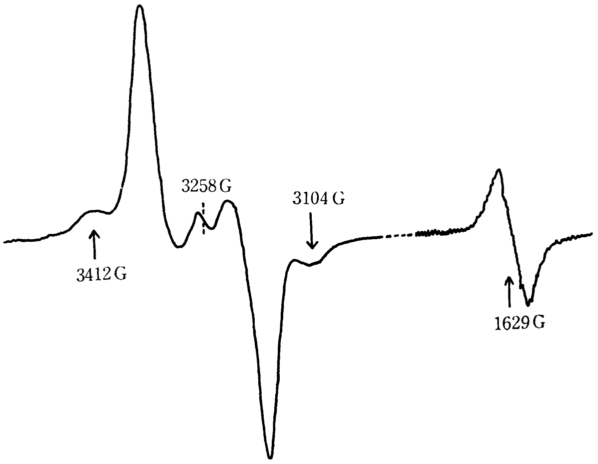

Fig. 2. ESR spectrum of benzophenone in DMA-2MTHF irradidiated at 77°K: (ν=9136 MHz.).

When benzophenone in a DMA-2MTHF matrix was irradiated at 77°K, an ESR spectrum was obtained as shown in Fig. 2. A weak absorption ascribable to the $\Delta m=2$ transition of a radical pair in a triplet state was found at 1629 gauss. A stronger spectrum which consists of two pairs of lines with a separation of 176 and 308 gauss appeared symmetrically with respect to the magnetic field strength of 3258 gauss. From the ESR spectrum we can immediately estimate the D value or the fine structure constant of the radical pair to be 154 gauss, and the average distance between the interacting radical 5.6_4 Å by using a point-spin-density approximation.[7] This result might be the first one indicating the presence of two photo-chemically formed unstable radicals which lie close to each other and form a combined triplet (S=1) state.

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