© 1992 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 65, 3186—3188 (1992) [Vol. 65, No. 11

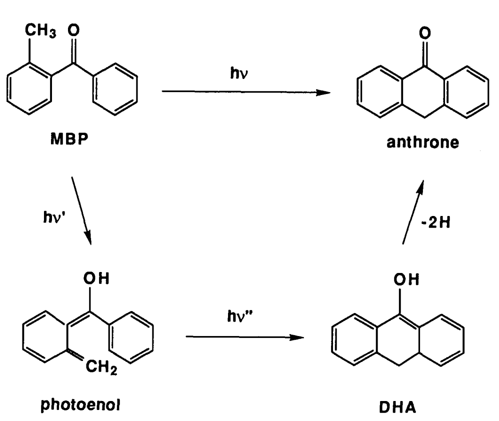
Electron-Laser Dual Beam Irradiation of 2-Methylbenzophenone

Akito Ishida,* Kazuki Yamamoto, and Setsuo Takamuku
The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka 8-1, Ibaraki 567

(Received June 29, 1992)

Synopsis. Pulse radiolysis of 2-methylbenzophenone (MBP) in benzene gave the triplet excited state (^{3}MBP*) which rapidly decayed by intramolecular hydrogen abstraction resulting in the photoenol. Successive laser flash photolysis elucidated the photochemical formation of dihydroanthrone from the photoenol.

Photochemical reactivity of *o*-substituted benzophenones has been studied with interest concerning the formation of the photoenol via the triplet states.[1-6] For example, photolysis of 2-methylbenzophenone (MBP) affords anthrone as final product, and the mechanism has been assumed to be the sequential two-photon process. The intramolecular hydrogen abstraction of the excited triplet state (^{3}MBP*) gives the unstable photoenol, and successive photoexcitation of the resulting photoenol affords the precursor of anthrone, that is dihydroanthrone (DHA).[2,3] However, the sequential two-photon process was not confirmed by direct spectral measurement. Recently, we have improved our pulse radiolysis system for electron–photon dual beam irradiation.[7] In the present paper, we have investigated the photoexcited triplet states of MBP and the resulting photoenol by combination of pulse radiolysis and laser flash photolysis.



(1)

Experimental

2-Methylbenzophenone was obtained from Aldrich Co. and purified by distillation. Spectral grade benzene was dried by distillation over CaH$_2$. Product determination was carried out by GLC, GC-MS, and UV. Transient absorption measurements were carried out by the electron-laser dual beam irradiation system of ISIR. The details have been reported elsewhere[7] and the outline is as follows. A sample solution was saturated with Ar and sealed in a Suprasil cell (light path 10 mm). A linear accelerator of Osaka University supplied an electron pulse for pulse radiolysis, and the beam properties for the present experiments were as follows; the energy, 28 MeV; the pulse width, 8 ns; the dose, 0.7 kGy/pulse. A coaxial flashlamp dye laser (Phase-R, DL-1100) provided a light pulse of 460 nm with the energy of 60 mJ and the pulse width of 150 ns. The delay time was controlled by the synchronous trigger unit[8] and a digital delay (Stanford, DG-535). The optical alignment is shown in Fig. 1. The analyzing light from a Xe-lamp (Osram XBO-450) passing through a sample cell was focused to a computer-controlled monochromator (CVI Digikrom-240) by two lenses and four mirrors. The output light of monochromator was monitored by a photomultiplier tube (PMT; Hamamatsu Photonix, R1417). The signal from a PMT was recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). Total system control and date processing were carried out with a microcomputer (Sharp, X-68000) which was connected to the measurement components with a GP-IB interface.

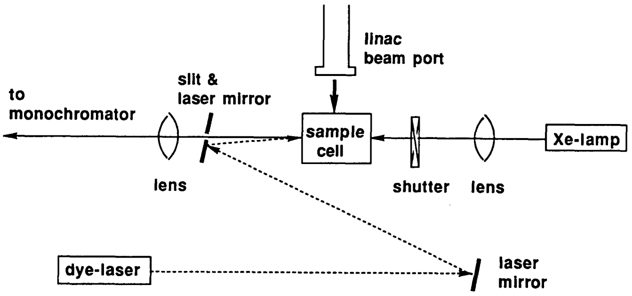


Fig. 1. Optical alignment of the pulse radiolysis system for electron-laser dual beam irradiation.

Results and Discussion

Radiolysis of benzene induces excitation and ionization of benzene. Since ionic species here-formed rapidly recombine to generate the excited states of benzene, main active species becomes a triplet state of benzene. Thus, radiolysis of a benzene solution efficiently provides the excited triplet state of a solute by energy transfer from the benzene triplet. Upon pulse radiolysis, the dynamic behavior of the triplet state is clearly followed by the observation of the T_1-T_n absorption spectrum. This method has been applied to a substrate which insufficently provides the excited triplet states by direct photoexcitation because of the low intersystem crossing yield.[9]

The pulse radiolysis of a 20 mmol dm^{-3} MBP in benzene gave transient absorption spectra as shown in Fig. 2. The observed spectra are summarized as follows in their order of formation; the initially observed weak band in the wavelength region between 480 and 600 nm (I), the sharp and intense absorption with a maximum at 330 nm (II), the absorption with a broad maximum around 390 nm and a shoulder at 300 nm (III), the finally remained stable absorption with two maxima at 300 nm and 420 nm and with a shoulder at 390 nm (IV). The spectrum I is similar to the T_1-T_n absorption spectrum of benzophenone triplet state, and we assigned I to the triplet state of MBP (^{3}MBP*). The time profile at 530 nm shows very rapid decay with a rate constant of 1.4×10^8 s^{-1}, which is consistent with the lifetime predicted by the quenching experiment.[6] Wagner et al. have assigned the spectrum II to the enol triplet (^{3}E*) which is in the equilibrium of two conformers.[4] However, their measurement system gave an absorption spectrum of ^{3}E* (II) overlapped with ^{3}MBP* (I) because of the long excitation pulse, and they supposed that ^{3}E* has two absorption bands at 320 and 535 nm.[4] The time profile at 330 nm is quite different from the 530 nm as shown in Fig. 2, and the fact clearly indicates that I and II are independent species. MBP is known to have *syn* and *anti* conformers and the fraction of the *syn*-MBP is greater than 70%.[10] It is clear that only the *syn*-^{3}MBP* adiabatically leads to ^{3}E* by intramolecular hydrogen abstraction.[6] Thus, the lifetime of *syn*-^{3}MBP* will be considerably shorter than that of *anti*-^{3}MBP*. The decay rate of *anti*-^{3}MBP* is mainly attributed to the rate of *anti*→*syn* interconversion and has been estimated to be very slow, ca. 10^7 s^{-1}.[6] The present result indicates the very rapid decay of ^{3}MBP*, which suggests that the observed absorption spectrum of ^{3}MBP* mainly due to *syn*-^{3}MBP*. The ^{3}E* decayed with simultaneous formation of the spectrum III, and the formation rate constant at 390 nm was 7.3×10^7 s^{-1}. The spectrum III has been assigned to the mixture of the short-lived (*Z*)-enol and the long-lived (*E*)-enol, the former shows a maximum at 390 nm and the latter shows a maximum at 420 nm, respectively.[4,5] The time profile at 390 nm indicates that (*Z*)-enol decayed with a rate constant of 1.3×10^7 s^{-1}. The spectrum IV is consistent with the reported absorption spectrum of the (*E*)-enol,[4,5] and the

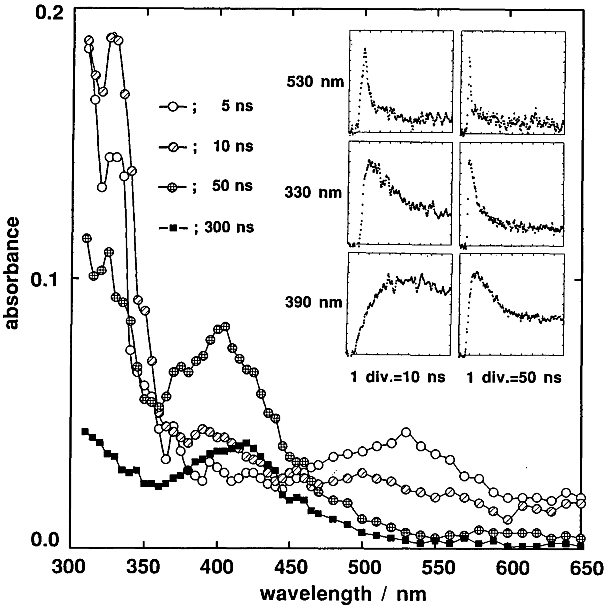
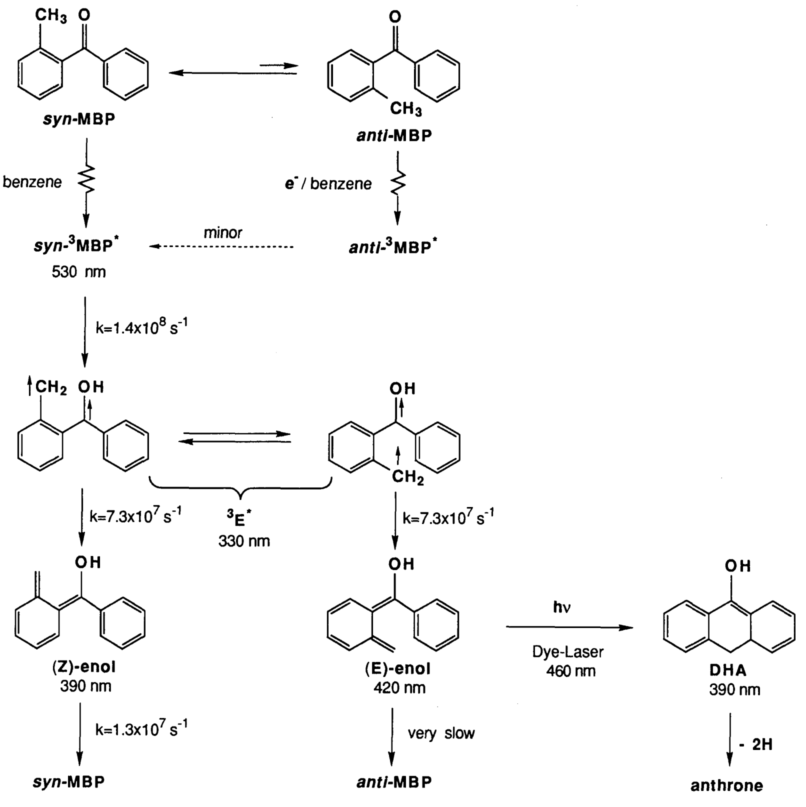


Fig. 2. Pulse radiolysis of 20 mmol dm^{-3} MBP in benzene at room temperature; transient absorption spectra were observed 5 ns (–○–), 10 ns (–⊘–), 50 ns (–⊕–), and 300 ns (–■–) after the electron pulse (28 MeV, 8 ns, 0.7 kGy/pulse) irradiation; insets show time profiles of the absorbances at 530, 330, and 390 nm in the different time scales.



Scheme 1.

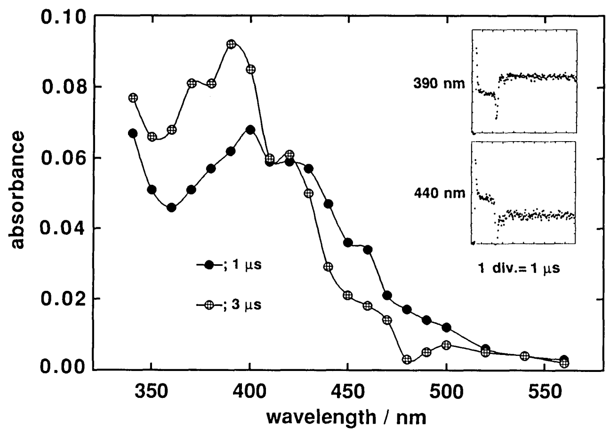


Fig. 3. Pulse radiolysis and successive laser flash photolysis of 10 mmol dm^{-3} MBP in benzene at room temperature; dye-laser pulse (460 nm, 60 mJ, 150 ns) was irradiated 2 μs after the electron pulse irradiation; transient absorption spectra were observed 1 μs (—●—) and 3 μs(—⊕—) after the electron pulse irradiation; insets show time profiles of the absorbances at 390 and 440 nm.

intensity was almost flat over than 100 μs which is the limit of our measurement system.

To confirm the formation of dihydroanthrone via the sequential two-photon process, we tried laser flash photolysis of the (*E*)-enol by successive irradiation of an electron pulse and a dye-laser pulse. The delay time was 2 μs, which is considered to be sufficient for decay of the short-lived transient species such as (*Z*)-enol. The laser pulse induced a remarkable change of the absorption spectrum as shown in Fig. 3, which is characterized by decay of the absorption around 450—500 nm and by simultaneous formation of new absorption band with a maximum at 390 nm. The resulting absorption band at 390 nm has the lifetime over than 100 μs. Dihydroanthrone has been reported to show an absorption maximum at 383 nm,[2] and the authentic dihydroanthrone, which was prepared by steady state photoirradiation in cyclohexane, has absorption maximum at 387 nm and the half-life of 45 min. These results clearly indicate that photoexcitation of the (*E*)-enol efficiently gives dihydroanthrone. Unfortunately, the pulsewidth of the laser is too long (150 ns) for determination of the reaction intermediate. Thus, the properties of the photoexcited state of the (*E*)-enol were not clarified. However, present study proved the sequential two-photon mechanism for the anthrone formation by direct observation of the reaction intermediates. Reaction of MBP triplet and absorption maxima of the observed intermediates are summarized in Scheme 1.

References

1) G. Porter and M. F. Tchir, *J. Chem. Soc., Chem. Commun.*, **1970**, 1372; *idem, J. Chem. Soc. A*, **1971**, 3772.

2) E. F. Ullman and K. R. Huffman, *Tetrahedron Lett.*, **1965**, 1863.

3) N. D. Heindel, J. Molnar, and M. Pfau, *J. Chem. Soc., Chem. Commun.*, **1970**, 1373.

4) R. Hagg, J. Wirz, and P. J. Wagner, *Helv. Chim. Acta*, **60**, 2595 (1977).

5) K. Uji-ie, K. Kikuchi, and H. Kokubun, *Chem. Lett.*, **1977**, 499; *idem, J. Photochem.*, **10**, 145 (1979).

6) P. K. Das and J. C. Scaiano, *J. Photochem.*, **12**, 85 (1980).

7) A. Ishida and S. Takamuku, Proc. of the International Conference on Evolution in Beam Applications, 1991, Abstr., p. 656.

8) K. Tsumori, A. Ishida, and S. Takamuku, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **48**, 39 (1991).

9) K. Nakabayashi, S. Toki, and S. Takamuku, *Chem. Lett.*, **1986**, 1889.

10) M. Grimarud, M. Loudet, R. Royer, and G. Pfister-Guillouzo, *Bull. Soc. Chim. Fr.*, **1974**, 1183.