Bull. Chem. Soc. Jpn., 53, 2201—2204 (1980)

Direct Observation of the 1,4-Biradical of Benzophenone with *cis*-3-Methyl-2-pentene Excited by the Fourth Harmonic of a Nd:YAG Laser

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(Received March 18, 1980)

Intermolecular biradical formation between the benzophenone triplet state with *cis*-3-methyl-2-pentene was studied by a ns laser-photolysis technique, the fourth harmonic (266 nm) of a *Q*-switched Nd : YAG laser being used as an exciting light source. We succeeded for the first time in observing the transient absorption due to the 1,4-biradical in the 380—300 nm region. Its lifetime was determined to be 25±4 μs (in acetonitrile), 15±4 μs (in methanol), and 6±2 μs (in cyclohexane). Quenching experiments with methyl viologen dication were also carried out in order to assign the observed transient absorptions.

Photochemical reactions of benzophenone have been studied extensively as typical examples for those of carbonyl compounds.[1)] Their primary processes are composed of: (1) triplet-triplet energy transfer, (2) hydrogen-abstraction reaction, and (3) biradical formation. Many studies on the processes (1) and (2) have been carried out with the aid of the time-resolved spectroscopy technique, their reaction intermediates being detected directly.[2—4)] On the other hand, studies on the process (3) with the transient method are scanty.

Biradicals play important roles in photochemical reactions of carbonyl compounds.[1,5)] Transient absorptions due to biradicals produced by the intramolecular hydrogen-abstraction reactions of valerophenones were recently found with the aid of the laser-photolysis technique.[6,7)] Their spectra were found to resemble those of the triplet state and ketyl radical of acetophenone. The situation may be the same for the spectra of 1,4-biradicals formed from the triplet state of benzophenone with olefins.[5)] Thus they may be expected to resemble the spectra of its triplet state and ketyl radical which have a strong peak at about 320 nm. However, no transient absorption due to the biradicals has ever been observed by the laser-photolysis technique using a *Q*-switched frequency doubled ruby laser (347.2 nm) or an N_2 laser (337.1 nm) as an exciting light source.[8)] This is because it is very difficult to measure transient absorptions in the wavelength region shorter or slightly longer than that of the exciting light source.

Under these circumstances, we have undertaken to extend the measurement region to 300 nm by exciting samples by the fourth harmonic (266 nm) of a Nd: YAG laser and to detect the biradicals. Quenching experiments with methyl viologen dication (MV^{2+})[9)] have also been carried out in order to confirm the assignment of the observed transient absorptions.

Experimental

Benzophenone (**1**) and methyl viologen hydrated were purified by repeated recrystallizations from ethanol and methanol–acetone (1 : 1) mixed solvent, respectively. *cis*-3-Methyl-2-pentene (*cis*-**2**) purified by vacuum distillation was used as olefin. Spectrograde acetonitrile, methanol, and cyclohexane were used as solvents without further purification.

Laser-photolysis measurements were made for degassed solutions at room temperature by using a Molectron UV-24 N_2 laser or the fourth harmonic of a Quanta-Ray DCR-1 Nd : YAG laser as an exciting light source. The laser pulse widths were 10 ns for the former and 5 ns for the latter. The details of the laser-photolysis apparatus have been published elesewhere.[7)]

Results and Discussion

After exciting a ternary solution containing **1** and *cis*-**2** in acetonitrile with the fourth harmonic of the Nd : YAG laser, we have measured the time-dependence of its transient absorption, $I(t)$, in the 300—600 nm region. As examples the $I(t)$ curves observed at 520 and 330 nm for the solution containing **1** of 8.8×10^{-4} mol dm^{-3} and *cis*-**2** of 0.266 mol dm^{-3} are shown in Figs. 1(a) and (b). We can see from Fig. 1(a) that the decay curve at 520 nm can be represented by a single exponential function with the lifetime (τ_1) of 15±2 ns as follows:

$$I(t) = I_1 \exp(-t/\tau_1). \tag{1}$$

The decay curves at the different wavelength in the 380—600 nm region can also be represented by Eq. 1 with the same lifetime as that observed at 520 nm.

On the other hand, the decay curve at 330 nm is represented as follows:

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) + I_3. \tag{2}$$

Here τ_1 and τ_2 denote the fast and slow lifetimes, respectively, and they were determined to be 15±2 ns and 25±4 μs from Figs. 1(a) and (b), respectively. The fast lifetime is equal to that obtained at 520 nm. The third term on the right side of Eq. 2 is a constant component in the observed time range (shorter than 140 μs).[10)] The decay curves at the different wavelength in the 300—380 nm region can also be represented by Eq. 2 with the same lifetimes as those observed at 330 nm.

It is well known that the primary photochemical processes of **1** with *cis*-**2** and MV^{2+} are shown by the following scheme:[1,5,9,11)]

$$\mathbf{1} \xrightarrow{h\nu} S_1 \tag{3}$$

$$S_1 \xrightarrow{k_{ISC}} T_1 \tag{4}$$

$$T_1 \xrightarrow{k_T} \mathbf{1} \tag{5}$$

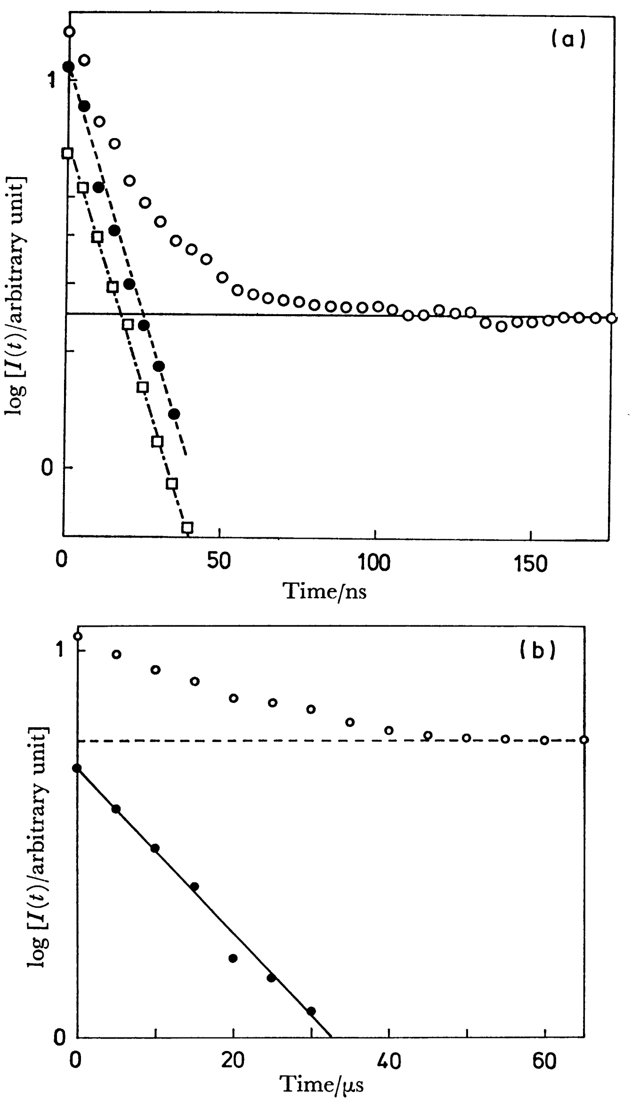
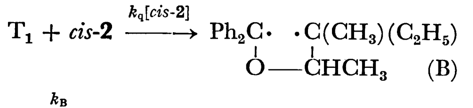


Fig. 1. Decay curves, I (t), of the transient absorption observed for the ternary solution containing benzophenone (8.8×10^{-4} mol dm^{-3}) and *cis*-3-methyl-2-pentene (0.266 mol dm^{-3}) in acetonitrile.
(a) ns region. ○: The total decay curve observed at 330 nm, ——: the constant component in this time region observed at 330 nm, ●: the difference between the total decay curve and the constant component observed at 330 nm, □: the total decay curve observed at 520 nm. (b) μs region observed at 330 nm. ○: The total decay curve ------: the constant component in this time region, ●: the difference between the total decay curve and the constant component.

$$T_1 + RH \xrightarrow{k_H[RH]} K\cdot + R\cdot \qquad (6)$$



$$T_1 + cis\text{-}\mathbf{2} \xrightarrow{k_q[cis\text{-}2]} \begin{array}{l} Ph_2\underset{|}{C}\cdot \quad \cdot\underset{|}{C}(CH_3)(C_2H_5) \\ \;\;\;O\text{—}CHCH_3 \quad (B) \end{array} \qquad (7)$$

$$B \xrightarrow{k_B} \mathbf{1} + cis\text{-}\mathbf{2},\ \mathbf{1} + trans\text{-}\mathbf{2},\ \text{oxetane} \qquad (8)$$

$$T_1 + MV^{2+} \xrightarrow{k_a[MV^{2+}]} \mathbf{1}\cdot^{+} + MV\cdot^{+} \qquad (9)$$

$$K\cdot(R\cdot) + MV^{2+} \xrightarrow{k_b[MV^{2+}]} K^{+}(R^{+}) + MV\cdot^{+} \qquad (10)$$

$$B + MV^{2+} \xrightarrow{k_c[MV^{2+}]} B\cdot^{+} + MV\cdot^{+} \qquad (11)$$

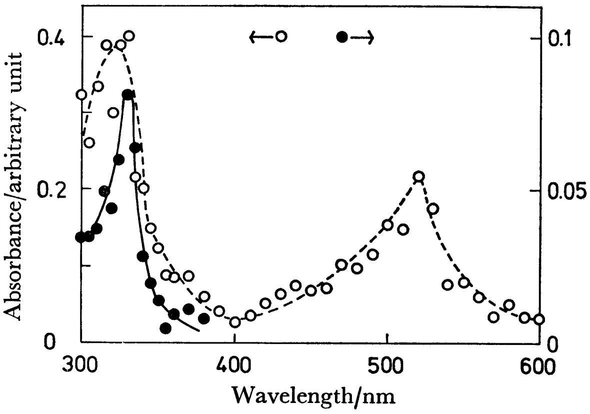


Fig. 2. Transient absorption spectra observed for the acetonitrile solution containing **1** (8.8×10^{-4} mol dm^{-3}) and *cis*-**2** (0.266 mol dm^{-3}) excited with the fourth harmonic of the Nd : YAG laser.
○: Observed immediately after excitation (Spectrum I), ●: observed 800 ns after excitation (Spectrum II).

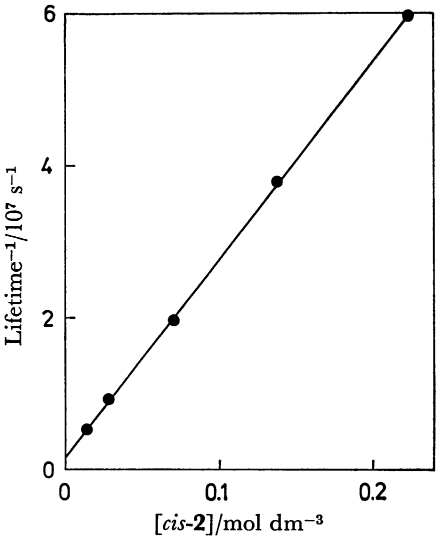


Fig. 3. Stern-Volmer relation between the inverse of the lifetime ($1/\tau_1$) observed at 520 nm and [*cis*-**2**] for the ternary solution containing **1** (8.8×10^{-4} mol dm^{-3}) and *cis*-**2** in acetonitrile

Here S_1 and T_1 are the lowest excited singlet and triplet states of **1**, respectively. RH is a hydrogen donor and K· is the benzophenone ketyl radical. The rate constants of the respective processes are represented by k_{ISC}, k_T, k_H, k_q, k_B, k_a, k_b, and k_c.

Time-resolved absorption spectra were measured before and after quenching of T_1 by *cis*-**2** with the result shown in Fig. 2. Spectrum I measured immediately after excitation of the acetonitrile solution containing **1** and *cis*-**2** is identical with that of the triplet-triplet (T_n—T_1) absorption of **1**[4] and corresponds to the spectrum before quenching of T_1, while Spectrum II measured 800 ns after excitation of the solution is a new one observed for the photochemical reaction of **1**. Thus the observed short lifetime (τ_1) corresponds to the quenching process of T_1 by *cis*-**2** and, as is shown in Fig. 3, the following Stern-Volmer relation was proved to be fulfilled for this process:[12)]

$$1/\tau_1 = k_T + k_{sv}[cis\text{-}\mathbf{2}]. \qquad (12)$$

Here k_{sv} is the slope of the $1/\tau_1$—[*cis*-**2**] plot in Fig. 3 and corresponds to either k_H or k_q. From the observed straight line in Fig. 3, the k_T and k_{sv} values were determined to be 1.4×10^6 s^{-1} and 2.7×10^8 s^{-1} mol^{-1} dm^3, respectively.

Spectrum II is not due to the triplet state of *cis*-**2** from the following reasons: (1) Upon exciting the acetonitrile solution of *cis*-**2** (0.32 mol dm^{-3}) with the fourth harmonic of the Nd : YAG laser, no transient absorption could be observed in the 300—600 nm region. (2) The energy level of its lowest triplet state is considered to be higher than that of T_1.[5)] Furthermore, Spectrum II is not due to the ketyl radical of **1** from the following reasons: (1) The ratio of the absorbance of the peak at 530 nm (P_L) to that at 320 nm (P_S) for the ketyl radical was observed to be 0.25.[4)] On the other hand, the P_L/P_S value for Spectrum II was observed to be nearly zero. (2) The k_{sv} value for this system is larger than the k_H one for the reaction of T_1 with cyclohexene in benzene (5.1×10^7 s^{-1} mol^{-1} dm^3),[12)] in spite of the fact that the hydrogen-donating ability of cyclohexene is much larger than that of *cis*-**2**.[13)] This means that Spectrum II is due to a product other than the ketyl radical. Therefore, the remaining possible assignment of Spectrum II is either due to the biradical or oxetane. But no electronic transition has been observed for 2,2-diphenyloxetanes at the wavelength longer than 300 nm.[14)] Thus Spectrum II and the observed k_{SV} may be assigned to the 1,4-biradical and k_q, respectively.

In order to obtain further support to this assignment, the electron transfer experiments with MV^{2+} were carried out. Since MV^{2+} is almost insoluble in acetonitrile, wet acetonitrile was used as a solvent. The volume ratio of water to acetonitrile was 3.5×10^{-2}. The behavior of the transient absorption observed for the wet acetonitrile solution containing **1** and *cis*-**2** excited with the fourth harmonic of the Nd : YAG laser was proved to be actually the same as that in acetonitrile solution. The decay curve of the transient absorption observed at 330 nm for the ternary solution containing **1** of 8.0×10^{-4} mol dm^{-3} and *cis*-**2** of 0.29 mol dm^{-3} in wet acetonitrile is represented by Eq. 2 with the lifetimes of 14±1 ns and 26±5 μs. The slow decay curve is shown in Fig. 4(a).

For the laser-photolysis of solutions containing MV^{2+}, the N_2 laser was used as an exciting light source to avoid direct excitation of MV^{2+} which has a strong absorption at 266 nm but not at 337.1 nm, transient absorption being measured in the 380—650 nm region. MV^{2+} withdraws an electron from T_1, K$^{\cdot}$, or the biradical forming its radical cation (MV$^{\cdot+}$) (see Eqs. 9, 10, and 11).[9,11)] MV$^{\cdot+}$ is stable in degassed solvents and has a broad absorption band at about 600 nm and a sharp one at about 390 nm.[15)]

The transient absorption was measured for the ternary solution containing **1** of 2.77×10^{-2} mol dm^{-3} and MV^{2+} of 2.4×10^{-4} mol dm^{-3} in wet acetonitrile. The T_n—T_1 absorption of **1** was found to be quenched by MV^{2+} forming MV$^{\cdot+}$ The $I(t)$ curve observed at 530 nm is shown in Fig. 4(b). It is represented by the superposition of an exponential function with the lifetime of 570±50 ns and a constant component in this time region. The decay part is due to the combination of the processes shown by Eqs. 5 and 9 and the constant corresponds to the absorption of MV$^{\cdot+}$.

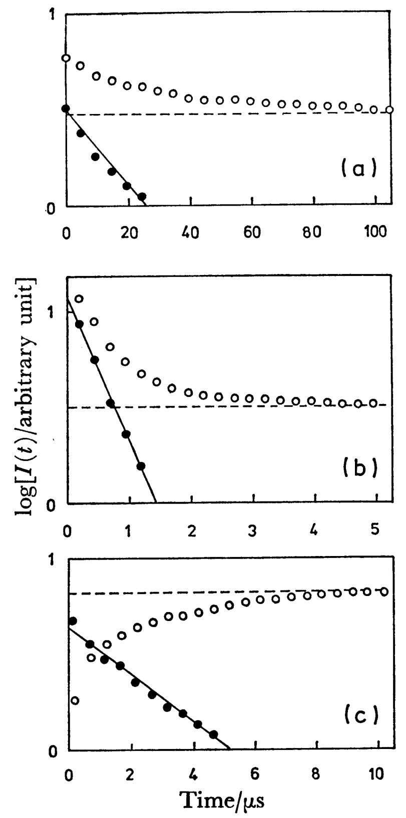


Fig. 4. Time dependence of transient absorption intensities, I (t), observed for wet acetonitrile solutions. ○: The total decay curve, ------: the constant component in this time region, ●: the difference between the total decay curve and the constant component.

(a) Decay curve observed at 330 nm for the ternary solution containing benzophenone (8.8×10^{-4} mol dm^{-3}) and *cis*-3-methyl-2-pentene (0.29 mol dm^{-3}) in wet acetonitrile. (b) Decay curve observed at 530 nm for the ternary solution containing benzophenone (2.77×10^{-2} mol dm^{-3}) and MV^{2+} (2.4×10^{-4} mol dm^{-3}) in wet acetonitrile. (c) Growth curve observed at 600 nm for the quaternary solution containing benzophenone (2.77×10^{-2} mol dm^{-3}), *cis*-3-methyl-2-pentene (0.32 mol dm^{-3}), and MV^{2+} (2.4×10^{-4} mol dm^{-3}) in wet acetonitrile.

The transient absorption was measured for the quaternary solution containing **1** of 2.77×10^{-2} mol dm^{-3}, *cis*-**2** of 0.32 mol dm^{-3}, and MV^{2+} of 2.4×10^{-4} mol dm^{-3} in wet acetonitrile. After fast quenching of the T_n—T_1 absorption of **1** by *cis*-**2** with the lifetime of 11 ns, the absorption of MV$^{\cdot+}$ appears slowly. As an example, the growth curve observed at 600 nm is shown in Fig. 4(c). It is represented by the following equation:

$$I(t) = I_4(1-\exp(-t/\tau_4)). \qquad (13)$$

The growth time (τ_4) which is determined to be 3.6±0.5

μs from the curve in Fig. 4(c) corresponds to the appearance time of the transient absorption of $MV^{\cdot +}$.

From the above-mentioned experimental results obtained with the wet acetonitrile solutions we conclude that, in the quaternary solution under study, *cis*-**2** quenches T_1 more effectively than MV^{2+} and an intermediate formed by the interaction between T_1 and *cis*-**2** transfers an electron to MV^{2+}. Generally speaking, either the ketyl radical or the biradical is the possible intermediate acting as an electron donor to MV^{2+}.[9,11] The spectrum of the intermediate (Spectrum II) is different from that of the ketyl radical as mentioned before. Thus it can be seen that the observed growth of $MV^{\cdot +}$ in Fig. 4(c) is brought about by the process represented by Eq. 11 and that Spectrum II is due to the 1,4-biradical.

From the above discussion, the obtained τ_2 value, 25±4 μs, in acetonitrile can also be considered to be the lifetime of the biradical. Similar results were also obtained for the methanol and cyclohexane solutions containing **1** and *cis*-**2** with the laser-photolysis technique using the Nd : YAG laser. The lifetime of the biradical was determined to be 15±4 μs in methanol and 6±2 μs in cyclohexane. The lifetime in the polar solvents was observed to be longer than that in the nonpolar solvent. This tendency agrees well with that observed for the biradicals formed from the intramolecular hydrogen-abstraction reaction of valerophenones.[6,7]

This is the first direct observation of the transient absorption due to the biradical as a precursor of the reactions of oxetane formation and isomerization through the Yang mechanism,[5] although it has already been observed for the biradicals produced by the intramolecular hydrogen-abstraction reactions.[6,7] The reason for failure of the previous attempts to observe it[8] may be due to the fact that its strong band locates in the wavelength region shorter than 380 nm. In fact the following relation seems to hold for the absorption intensity ratio between the longer and shorter wavelength bands observed for the triplet state of **1**, its ketyl radical, and its biradical:

$$P_L/P_S(T_1) > P_L/P_S(K\cdot) \gg P_L/P_S(B). \qquad (14)$$

Theoretical interpretation for this is a future problem. The constant component represented by the third term in Eq. 2 (I_3) was observed in all the solvents used in the present study. Its spectrum is similar to Spectrum II, but its origin is not yet clarified.

The author wishes to express his thanks to Professor Saburo Nagakura of The University of Tokyo for his continuous encouragement and fruitful discussion and Dr. Masao Kaneko of The Institute of Physical and Chemical Research for his kindness in informing the author of the purification method of methyl viologen hydrate. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 454135 from the Ministry of Education, Science and Culture.

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