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LASER-PHOTOLYSIS STUDY OF BIRADICAL FORMATION FROM THE TRIPLET STATE OF 2,4,6-TRIISOPROPYLBENZOPHENONE

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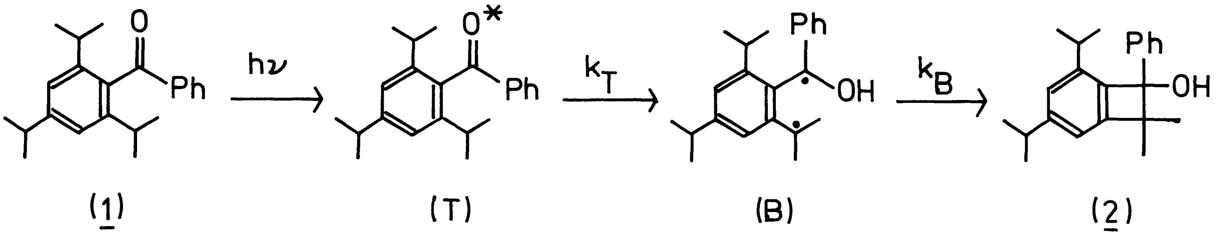
Intramolecular biradical formation from the triplet state of 2,4,6-triisopropylbenzophenone was studied by the ns laser-photolysis technique. The transient absorption spectra of the triplet state and the biradical were measured and their lifetimes were determined to be 225 ± 13 ns and 17 ± 2 μs in acetonitrile, respectively.

The photochemical conversion of 2,4,6-triisopropylbenzophenone (1) into its benzocyclobutanol (2) was studied by Kitaura and Matsuura for the purpose of developing a new system useful for the chemical storage of solar energy.[1)] The primary process of the reaction has been predicted to be the triplet state (T) formation with very high quantum yield followed by the 1,4-biradical (B) formation through intramolecular hydrogen-abstraction reaction:[2)]



The transient absorptions of T and B, however, have not yet been observed. We have undertaken to study the reaction by the ns laser-photolysis technique, which uses the fourth harmonic (266 nm, 5 ns width) of a Q-switched Nd:YAG laser as an exciting light source and has been successfully applied to the measurement of some 1,4-biradicals produced from the triplet states of carbonyl compounds.[3,4)]

Time-resolved absorption spectra were observed at room temperature with the degassed acetonitrile solution of 1 (3.3×10^{-3} mol dm^{-3}) in the 300 - 800 nm region and the result is shown in Fig. 1. Spectrum I observed immediately after excitation has two peaks at 305 and 750 nm. Spectrum II observed 1.5 μs after excitation has only one peak at 340 nm. The time dependences of the transient absorption intensities (I(t)) at 320, 375, and 600 nm were also measured and the results are shown in Fig. 2. The decay curve (◑) of a single exponential function with the lifetime of 228 ± 10 ns, the decay curve (○) of a combination of two exponential functions with the lifetimes of 225 ± 10 ns (●) and 17 ± 2 μs (— - —),

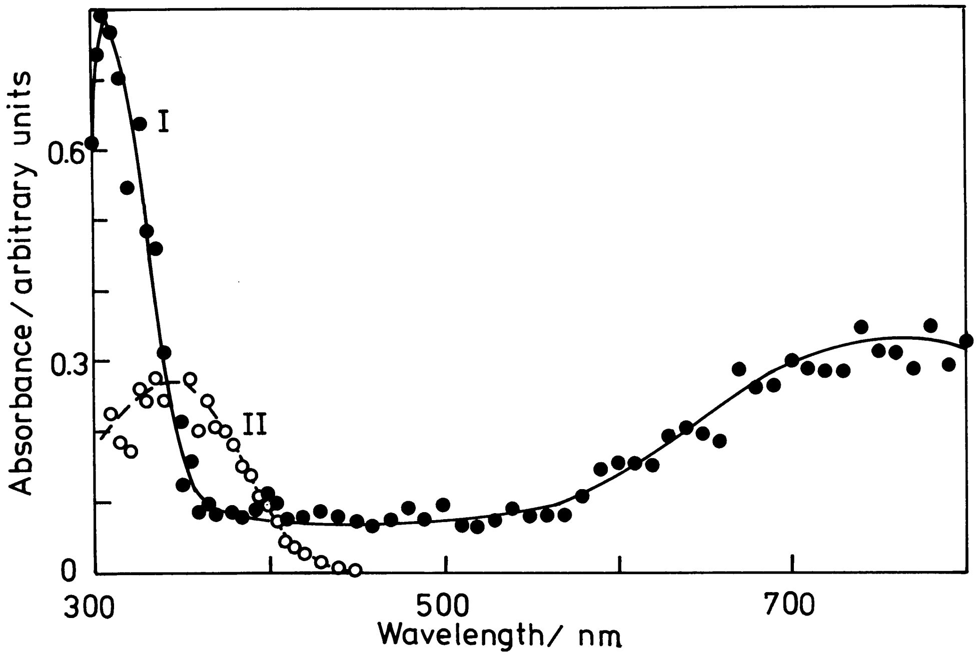
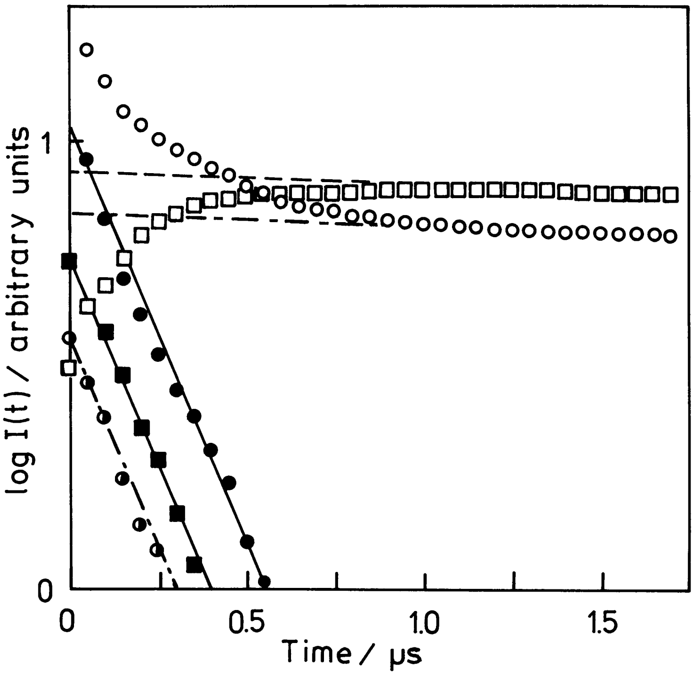


Fig. 1. Transient absorption spectra observed with the acetonitrile solution of 1 excited with the fourth harmonic of the Nd:YAG laser:
●, observed immediately after excitation (Spectrum I);
○, observed 1.5 μs after excitation (Spectrum II).

Fig. 2.
Time dependence of transient absorption intensities (I(t)) observed with the acetonitrile solution of 1:
○ , the total I(t) curve observed at 320 nm;
—·—, the slow decay part observed at 320 nm;
● , the difference between the total I(t) curve and the slow decay part observed at 320 nm;
□ , the total I(t) curve observed at 375 nm;
— —, the slow decay part observed at 375 nm;
■ , the difference between the slow decay part and the total I(t) curve observed at 375 nm;
◑ , the total I(t) curve observed at 600 nm.



and a combination (□) of the rise curve with the rise time of 223 ± 10 ns (■) and the decay curve with the lifetime of 17 ± 2 μs (— — —) were observed at 600, 320, and 375 nm, respectively. Therefore, it is concluded that Species I which gives Spectrum I changes to Species II which gives Spectrum II with the transformation time of 225 ± 13 ns and that Species II has the lifetime of 17 ± 2 μs and converts into the final product, 2.

From the comparison of the present results with the above-mentioned reaction scheme predicted from the chemical view-point, Species I and II may be assigned to T and B, respectively. In order to support the assignment, we have made the following two experiments. (a) When cis-1,3-pentadiene of 9.4×10^{-4} mol dm^{-3} was added to the acetonitrile solution of 1 as a triplet quencher, the lifetime of Species I was found to be shortened to 191 ± 5 ns, but that of Species II unaltered. This means that Species I is assigned to the triplet state (T). (b) Transient absorptions were measured with an N_2 laser as an exciting light source for the ternary solution containing 1 of 7.8×10^{-2} mol dm^{-3} and methyl viologen dication (MV^{2+}) of 5×10^{-5} mol dm^{-3} in acetonitrile.4) MV^{2+} is well known to withdraw an electron from triplet states and biradicals forming its radical cation ($MV^{\cdot +}$)5) which has a strong absorption band at 400 nm and a weak one at 600 nm.6) Actually, transient absorption with very long lifetime (longer than 100 μs) due to $MV^{\cdot +}$ was observed after quenching of T and Species II by MV^{2+}. The I(t) curves for this system were measured at 600 (○) and 400 (□) nm and the results are shown in Fig.3. From analysis of the kinetics for this system, the decay component with the life-

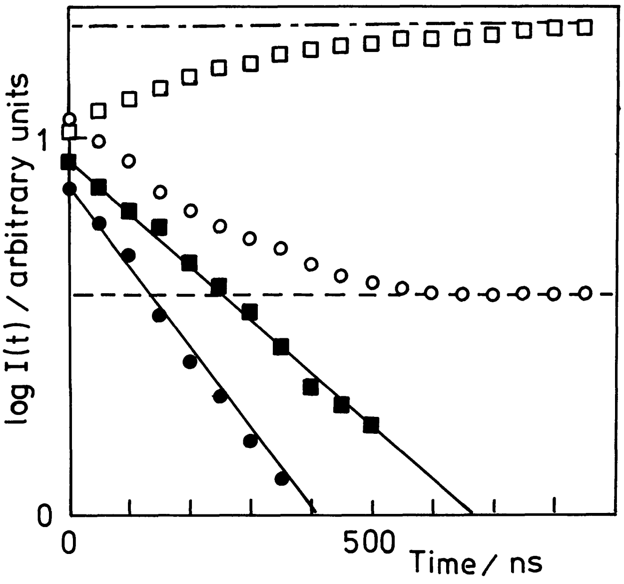


Fig.3.
Time dependence of transient absorption intensities (I(t)) observed with the ternary solution containing 1 and MV^{2+} in acetonitrile:
○ , the total I(t) curve observed at 600 nm;
– –, the constant part observed at 600 nm;
● , the difference between the total I(t) curve and the constant part observed at 600 nm;
□ , the total I(t) curve observed at 400 nm;
–·–, the constant part observed at 400 nm;
■ , the difference between the constant part and the total I(t) curve observed at 400 nm.

time of 196 ± 5 ns observed at 600 nm (●) is concluded to correspond to the decay curve of T which represents a combination of the transformation process from T to Species II and the quenching one of T by MV^{2+}, and the rise component with the rise time of 302 ± 10 ns observed at 400 nm (■) is also concluded to correspond to the rise curve of $MV^{\cdot +}$ which represents the electron transfer process from Species II to MV^{2+}. Thus Species II was proved to be quenched by MV^{2+} and may be assigned to the biradical. From the above-mentioned facts, the lifetimes of T and B ($1/k_T$ and $1/k_B$) were determined to be 225 ± 13 ns and 17 ± 2 μs in acetonitrile, respectively.

We carried out similar laser-photolysis experiments with the methanol and heptane solutions of 1, and measured the spectra of T and B which are almost the same as those in acetonitrile. Their lifetimes were also measured as follows: $1/k_T$(methanol) = 175 ± 15 ns, $1/k_T$(heptane) = 191 ± 20 ns, $1/k_B$(methanol) = 17 ± 2 μs, and $1/k_B$(heptane) = 3.1 ± 0.5 μs. Accordingly, the triplet lifetime was proved to be nearly independent of solvent polarity, but the biradical one in the polar solvents was proved to be longer than that in the nonpolar solvent. The latter tendency is parallel to that observed in some other 1,4-biradicals formed through the triplet states of carbonyl compounds.[3,4]

The rise time of the transient absorption due to T was too fast to be measured with the laser-photolysis apparatus. This means that the time is shorter than its time resolution (9 ns) and may fall into the ps region as in the case of the benzophenone triplet state (10 ps).[7] The fast intersystem crossing rate from the lowest excited singlet state to the triplet one for 1 is one of the reasons why the quantum yield of the formation of T is so high.[2] The fast intersystem crossing rate together with the high conversion efficiencies from T to B and from B to 2 may be very important for efficient solar energy conversion.

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