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Direct Observation of the Type II Biradical and Triplet State of Valerophenone Excited by the Fourth Harmonic of a Nd:YAG Laser

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The Norrish type II reaction of valerophenone was studied by the ns-laser photolysis technique, the fourth harmonic (266 nm) of a Q-switched Nd: YAG laser being used as an exciting light source. Transient absorptions due to the triplet state and 1,4-biradical of valerophenone were observed in both polar and nonpolar solvents. Quenching experiments with *cis*-1,3-pentadiene were also carried out. Transient absorptions due to the biradical were observed in the 350—300 nm region with the lifetimes of 103 ns (in methanol), 99 ns (in 2-propanol), 71 ns (in acetonitrile), and 31 ns (in 1,2-dichloroethane). Transient absorptions due to the triplet state were also observed in the 440—300 nm region.

Biradicals produced by the Norrish type II reaction of carbonyl molecules[1] have been regarded as important reaction intermediates in organic photochemistry. However, their existence had not been proved directly before the studies of Small and Scaiano with the aid of the ns-laser photolysis technique were carried out.[2–4] They used an N_2 laser (337.1 nm) as an exciting light source and observed the lifetimes of some type II biradicals through the rise curves of the absorptions of transient specimens produced by the electron transfer from the biradicals to some electron acceptors.

They also succeeded in observing directly transient absorptions due to the biradicals with a laser photolysis apparatus of very high sensitivity using a Q-switched frequency doubled ruby laser (347.1 nm) as an exciting light source.[5] They observed the transient absorptions of the biradicals in the 500—370 nm region, the spectra of which resembled that of the acetophenone ketyl radical.[6,7] Besides these weak bands, the ketyl radical has a much stronger band in the region below 370 nm.[6,7] From a similarity in the electronic structures of both specimens, the biradical might also be expected to have a strong band in the shorter wavelength region. However, it is very difficult to measure the transient absorption in the wavelength region shorter than that of the exciting light source. We recently constructed a ns-laser photolysis apparatus, the fourth (266 nm), third (355 nm), or second (532 nm) harmonics of a Q-switched Nd: YAG laser being used as an exciting light source. We have undertaken to measure the transient absorption due to the type II biradical of valerophenone extending the measurement region to 300 nm exciting the sample by the fourth harmonic of the laser.

The triplet-triplet (T_n-T_1) absorption of acetophenone overlaps the absorption of its ketyl radical.[7] A similar overlap is expected for the T_n-T_1 absorption of valerophenone and the absorption of the biradical, although Small and Scaiano did not consider the overlap.[5] In the present study, we have tried to measure the biradical absorption separately from the T_n-T_1 absorption by quenching experiments with *cis*-1,3-pentadiene.

Experimental

Valerophenone (Tokyo Kasei) was purified by distillation under reduced pressure. All solvents of spectrograde (Wako or Tokyo Kasei) were used without further purification. *cis*-1,3-Pentadiene (Tokyo Kasei Ultra Pure) purified by vacuum distillation was used for quenching studies. The samples contained in quartz cells with an optical length of 10 mm were degassed by four freeze-pump-thaw cycles. The concentration of valerophenone was 0.0065 mol dm^{-3}.

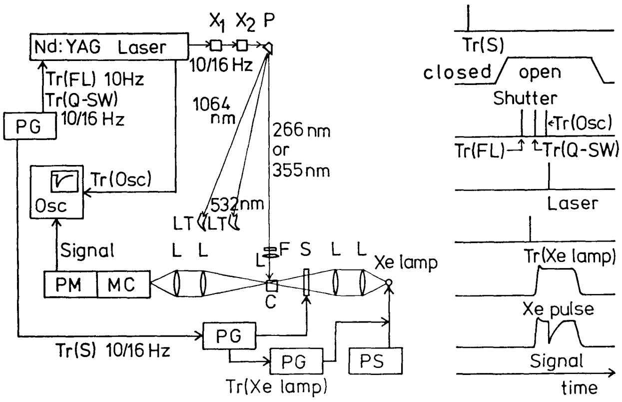


Fig. 1. Laser photolysis apparatus and time profiles of shutter, laser, and Xe pulse.
C: Sample cell, S: Electric shutter, L: Lenses, F: Filter (Toshiba UV-D33S), MC: Monochromator, PM: Photomultiplier, Osc: Oscilloscope, Tr(X): Trigger for X, PS: Power supply, PG: Pulse generator, FL: Flash lamps, Q-SW: Q-switching, X_1: Second harmonic generator, X_2: Third or fourth harmonic generator, P: Prism, LT: Light traps.

A block diagram of the laser photolysis apparatus is shown in Fig. 1. A Q-switched Quanta-Ray DCR-1 Nd: YAG laser was used as an exciting light source, a Quanta-Ray HG-1 harmonic generator providing the second, third, or fourth harmonics of the laser. The fourth harmonic was used as exciting light source, pulse width being 5 ns and maximum power 30 mJ. In order to avoid thermal lensing effects, the actual power was reduced as much as possible. Flash lamps for exciting the laser were discharged at 10 Hz, the maximum power being obtained. Its Q-switching was operated every 16 shots of the flash lamps (0.625 Hz) in order to prevent photochemical changes of the samples. The monitoring light with pulse width of 300 μs was obtained from a pulsed xenone arc (Ushio 150 W), irradiating the sample synchronously with the laser (0.625 Hz). Laser and monitoring light beams were crossed at right angles to each other. The monitoring light intensity was detected with an HTV-R636 photomultiplier through a grating monochromator (Nikon G-250). An electronic shutter (Vincent 225L0A25X5[8] or Copal EMS #0[9]), opening synchronously with the laser pulse was used in order to protect the sample and the photomultiplier from continuous irradiation by the xenon arc. The time profiles of the shutter, monitoring light, and laser are also shown in Fig. 1. The transient signals were recorded by taking the photographs of the images on a Tektronix 7904 oscilloscope.

Results and Discussion

We have measured the transient absorption caused by the excitation of valerophenone in both polar and nonpolar solvents, in the region 440—300 nm. As examples, time-resolved absorption spectra were observed for the methanol and cyclohexane solutions (Fig. 2), the decay curve of the transient absorption being observed for these solutions (Fig. 3). We see that the decay curve for the methanol solution consists of two components:

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \qquad (1)$$

where τ_1 and τ_2 are the lifetimes of the fast and slow components, respectively, and I_1 and I_2 are the corresponding pre-exponential factors. The observed τ_1 and τ_2 values are given in Table 1.[10]

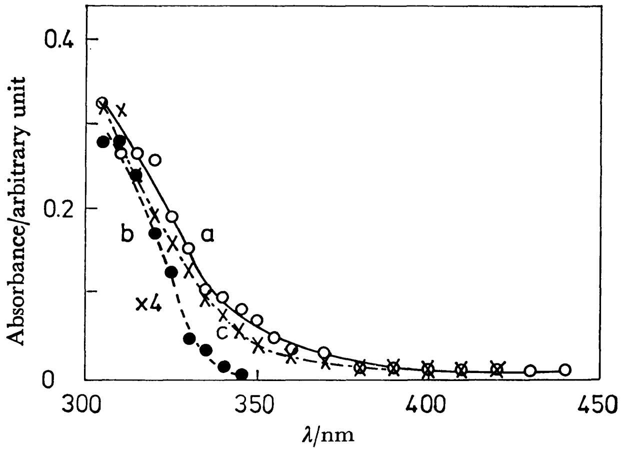


Fig. 2. Transient absorption spectra observed with valerophenone excited by the fourth harmonic of the Nd: YAG laser.
Curve a, observed with the methanol solution immediately after excitation: Curve b, observed with the methanol solution 100 ns after excitation: Curve c, observed with the cyclohexane solution immediately after excitation.

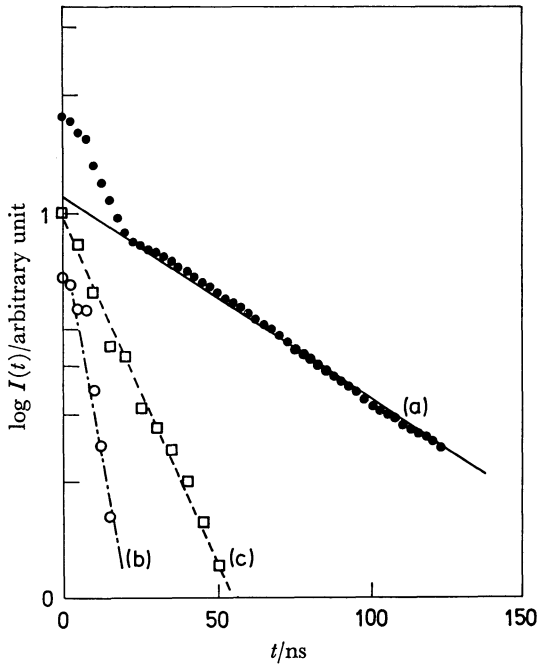
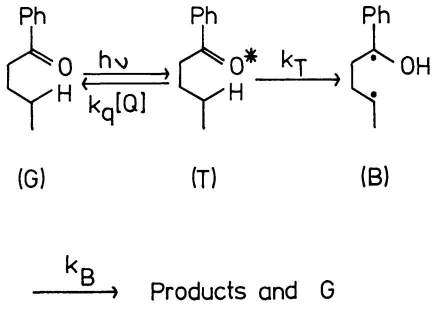


Fig. 3. Decay curves, $I(t)$, of the transient absorptions of valerophenone.
Curve a, the total decay curve observed at 318 nm in methanol: Curve b, the differnce between the observed curve in methanol and the fitted line for the slow decay component: Curve c, the decay curve observed at 320 nm in cyclohexane.

In order to assign the observed absorptions, we carried out quenching experiments with *cis*-1,3-penta-



Scheme 1.

TABLE 1. LIFETIMES OF THE BIRADICAL AND TRIPLET STATE OF VALEROPHENONE

Solvent	Dielectric constant	η/cp	This work			Ref. 5	Ref. 3	
			τ_1/ns[a]	τ_2/ns[a]	τ/ns[a]	τ_B/ns[b]	τ_B/ns[b]	τ_T/ns[b]
Methanol	32.7[c]	0.5445[c]	12	103±7		93	102±15	16
2-Propanol	19.92[c]	1.765[d]	<9	99±10		—	—	—
Acetonitrile	37.5[e]	0.325[d]	<9	71±3		70	71±10	8.7
1,2-Dichloroethane	10.36[c]	0.730[d]	<9	31±6		—	—	—
Heptane	1.924[e]	0.3967[c]			30±6	—	—	—
Cyclohexane	2.023[e]	0.898[c]			23±3	38	—	—

a) See text. b) τ_B and τ_T are represented by the lifetimes of the biradical and triplet state of valerophenone, respectively. c) Values at 25 °C.[f] d) Values at 30 °C.[f] e) Values at 20 °C.[f] f) J. A. Riddick and W. B. Bunger, "Organic Solvents," John Wiley and Sons Inc., New York (1970).

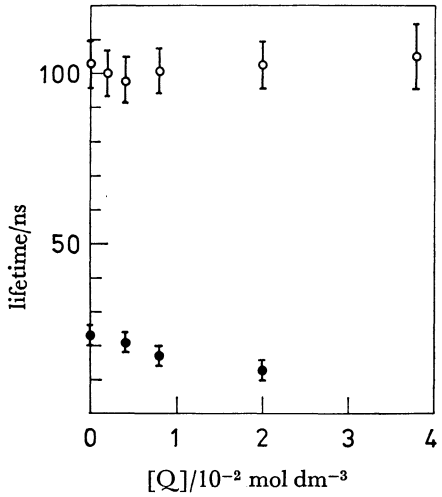


Fig. 4. Dependence of the lifetimes of the transient absorptions on [Q].
(○), For the slow lifetime, τ_2, observed with the methanol solution: (●), for the lifetime observed with the cylohexane solution.

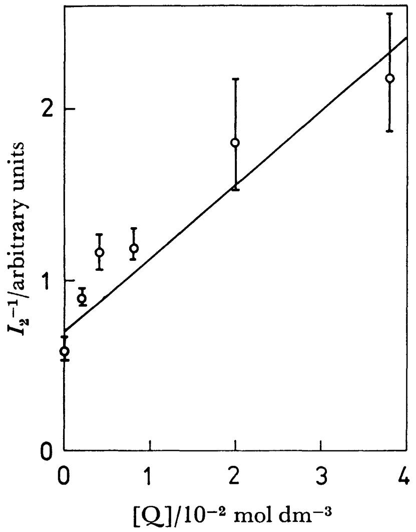


Fig. 5. Plot of $1/I_2$ observed for the methanol solution against [Q].

diene. The primary photochemical process of valerophenone in the ns-region is shown by Scheme 1, where G, T, and B denote the ground and triplet states of valerophenone and its biradical, respectively,[1] [Q] is the concentration of *cis*-1,3-pentadiene and k_T, k_B, and k_q are the respective rate constants. From measurement of the [Q] dependence of τ_1, τ_2, and I_2 (Figs. 4 and 5), we see that τ_2 is independent of [Q] and the inverse of the pre-exponential factor of the slow component, $1/I_2$, increases with increasing [Q]. This indicates that the slow component is safely assigned to the biradical and that curve b (Fig. 2) corresponds to its spectrum.[11] On the other hand, the fast component can be assigned to the triplet state, the only observable precursor of the biradical. Thus curve a (Fig. 2) can be considered to be a combination of curves due to the triplet state and the biradical. However, its 440—350 nm region may be mainly due to the triplet state, since the absorption intensity of the biradical is weak in this region.

When $k_T > k_B$, $1/I_2$ can be represented by (See Appendix)

$$1/I_2 = c[(k_T - k_B)/k_T + k_q[Q]/k_T] \tag{2}$$

where c is a constant. The following result is obtained from the $1/I_2$—[Q] line (Fig. 5):

$$k_q = (61 \pm 24) \times (k_T - k_B) \text{ mol}^{-1} \text{ dm}^3 \tag{3}$$

Since k_B and k_T were determined to be 0.97×10^7 s^{-1}, larger than 0.83×10^8 s^{-1}, respectively, k_q was calculated to be larger than $(4.5 \pm 1.8) \times 10^9$ s^{-1} mol^{-1} dm^3. This value is reasonable compared with the assumed one (5.5×10^9 s^{-1} mol^{-1} dm^3).[5]

We observed similar two component transient absorptions in acetonitrile, 2-propanol, and 1,2-dichloroethane. The observed fast and slow lifetimes are given in Table 1. The time-resolved spectra for these systems observed immediately and 100 ns after excitation are similar to those observed in methanol.

The cyclohexane solution also has a transient absorption in the region 420—300 nm (curve c, Fig. 2). Its decay curve, however, unlike that of the methanol solution, has only one component (Fig. 3). The lifetime, τ, for the cyclohexane solution was found to be 23±3 ns. The [Q] dependence of τ is also shown in Fig. 4. Since the observed τ values are not corrected, they are the upper limits of the real lifetimes, but we can conclude that τ decreases with increasing [Q]. Therefore, the observed transient absorption can be considered to be mainly due to the triplet state. Thus the spectrum obtained with the cyclohexane solution may be due to the triplet state, although possibility of contamination of the biradical absorption still remains.

We observed a similar one component decay curve of the transient absorption for the heptane solution (Table 1). The transient spectrum in heptane is similar to that in cyclohexane.

From the results, we conclude that the transient spectrum observed for valerophenone in the polar solvents in the 350—300 nm region can be assigned to the 1,4-biradical. It resembles that of the acetophenone ketyl radical.[7] Small and Scaiano observed the transient absorption spectra of the biradicals produced from γ-methylvalerophenone and valerophenone in the 500—370 nm region.[5] They are also similar to the spectrum of the acetophenone ketyl radical. The biradical absorption in this region is weak. We extended the wavelength region of the measurement to 300 nm, making it much easier to carry out such precise mechanistic works as quenching experiments.

As is shown in Table 1, the observed lifetimes for the biradical of valerophenone in polar solvents in this work agree with those obtained by Small and Scaiano with the indirect[3] and direct[5] methods. However, they could not observe the fast component in their transient absorption of valerophenone, and estimated the lifetime of the triplet state of valerophenone in methanol to be 16 ns through the indirect method.[3] This value is somewhat longer than the present result (less than 12 ns). The disagreement might be due to their underestimation of the k_q value.

In nonpolar solvents, Small and Scaiano also observed transient absorptions for γ-methylvalerophenone and valerophenone in the 500—370 nm region and assigned them to the biradical.⁵⁾ For example, the lifetimes of the biradicals of γ-methylvalerophenone and valerophenone in cyclohexane were reported to be 37 ns and 38 ns, respectively. The assignment for the former can be considered to be correct, since its triplet lifetime was confirmed to be much shorter than 37 ns,⁵⁾ but the assignment for the latter should be reexamined.

Appendix

The rate equations for [T] and [B] can be written as follows:

$$d[T]/dt = -k_T[T] - k_q[Q]\cdot[T], \qquad (A\text{-}1)$$

$$d[B]/dt = k_T[T] - k_B[B]. \qquad (A\text{-}2)$$

From Eq. (A-1), we get

$$[T] = [T]_0 \exp(-kt), \qquad (A\text{-}3)$$

where $[T]_0$ is the initial concentration of [T] and k is given by

$$k = k_T + k_q[Q]. \qquad (A\text{-}4)$$

When $t=0$, $[B]=0$. Thus [B] can be expressed by

$$[B] = A[\exp(-k_Bt) - \exp(-kt)], \qquad (A\text{-}5)$$

where A is a constant. When $k > k_B$, I_2 is proportional to A. Introducing Eqs. (A-3) and (A-5) into Eq. (A-2) we get

$$A = k_T[T]_0/(k-k_B). \qquad (A\text{-}6)$$

Thus we can derive Eq. 1.

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10) The obtained τ_1 may be the upper limit of the real lifetime, since no correction due to the laser pulse shape and the time delay of the measuring system were made.

11) Small and Scaiano observed the transient absorption spectra for the type II biradical in the 500—370 nm region. We also observed very weak transient absorption corresponding to the slow component in the 450—400 nm region.