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The Laser-flash Photolysis of 2-Hexanone and 5-Methyl-2-hexane for the Direct Detection of the Triplet 1,4-Biradical

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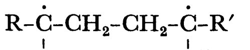
Synopsis. In the laser-flash photolysis of 2-hexanone and 5-methyl-2-hexanone (265 nm, 15 ns pulse), triplet 1,4-biradicals were detected directly. The absorption spectrum exhibits absorption maxima at $\lambda=250$ nm and at $\lambda=320$ nm. The decay-rate constant of the 1,4-biradical increases as follows: in methanol < in acetonitrile < in hexane < in dichloromethane $[(2—4)\times10^7\,\mathrm{s^{-1}}$ (2-hexanone), $(3—6)\times10^7\,\mathrm{s^{-1}}$ (5-methyl-2-hexanone)].

There have been many reports on the laser-flash photolysis of aromatic carbonyl compounds, and some transient species, *i.e.*, triplet-state and triplet 1,4-biradical intermediates on the Norrish Type-II reaction, have been identified. In the case of aliphatic caybonyl compounds, triplet 1,4-biradicals formed from 2-pentanone,[1] pentanal,[2] and 2-substituted cyclohexanone,[3] were trapped by HBr (gas phase)[1] and paraquat ions.[2,3]



$$\mathrm{R}\text{-}\underset{\mathrm{OH}}{\dot{\mathrm{C}}}\text{-}\mathrm{CH_2}\text{-}\mathrm{CH_2}\text{-}\underset{\mathrm{R''}}{\dot{\mathrm{C}}}\text{-}\mathrm{R'}$$

(Triplet 1,4-biradical)

Recently, the triplet states of propanone,[4,5] butanone,[5] and 2-pentanone[5] and the triplet 1,4-biradical formed from poly(3-buten-2-one)[5] were detected. The photolysis of 2-hexanone and 5-methyl-2-hexanone are accepted as proceeding predominantly through the Norrish Type-II mechanism.[6] The laser-flash photolysis of these compounds were carried out in order to detect the triplet 1,4-biradical, directly.

Experimental

Materials. The 2-hexanone and 5-methyl-2-hexanone were dried on anhydrous sodium sulfate and distilled three times by using a splitting-tube column.

The dichloromethane (for fluorescence spectroscopy) was washed five times with a 5% sodium carbonate solution and five times with distilled water. After drying on calcium chloride, the dichloromethane was distilled twice by using the splittingtube column.

The acetonitrile (for spectroscopy) was purified by refluxing it five times on diphosphrus pentaoxide for ten hours and was then distilled twice by using the splitting-tube column.

The hexane (for fluorescence spectroscopy) was washed five times with sulfuric acid and five times with distilled water. After drying on calcium chloride and calcium hydride, the hexane was distilled twice by using the splitting-tube column.

The methanol (for spectroscopy) was purified by refluxing on a magnesium metal for one night and distilled twice by using the splitting-tube column.

The *cis*-1,3-pentadiene was used after two distillations.

Apparatus. The Nd laser apparatus has been described before (265 nm, 15 ns pulse).[7] The output of this laser apparatus was about 100 mJ. The intensity of the laser light was determined by means of the cycloreversion reaction of *r*-1,*t*-2,*t*-3,*c*-4-tetraphenylcyclobutane in 1-chlorobutane ($\phi=0.34$). Normal flashed photons: 2.0×10^{-8} einstein per flash. By choosing an appropriate solute concentration, the optical density was kept at 0.5 (*ca.* 3.0×10^{-2} mol dm^{-3}). The measured emission and absorption spectra were calibrated by the normal number of photons per flash.

Results and Discussion

The Nd laser-flash photolysis of 2-hexanone and 5-methyl-2-hexanone were carried out in dichloromethane in order to detect the triplet 1,4-biradical intermediate. Immediately after the flash, emission (fluorescence) and transient absorption spectra were monitored in the wavelength ranges from 300 nm to 540 nm and from 230 nm to 400 nm respectively. The transient absorption spectrum exhibits absorption maxima at $\lambda=250$ nm and at $\lambda=320$ nm, as it shows in Fig. 1. The triplet absorption spectra of propanone, butanone, and 2-pentanone do not exhibit a minor absorption maximum at $\lambda=320$ nm.[4,5] The acetyl radical absorbed the light in the wavelength range from 500 nm to 600 nm.[5,8] The measured spectra do not agree with those of the triplet state and acetyl radical. The transient absorption decay obeys first order kinetics, and its decay rate (k) is constant over all the wavelength ranges monitored [$k=3.9\times10^7\mathrm{s^{-1}}$ (2-hexanone), $6.0\times10^7\,\mathrm{s^{-1}}$ (5-methyl-2-hexanone)]. Figure 2 shows the effect of absorbed photons on the transient absorption in methanol. Although the transient absorbance increases with the quantity of absorbed photons, k is independent of the quantity of absorbed photons.

The laser-flash photolysis were carried out in the presence of a triplet quencher, *cis*-1, 3-pentadiene[$(0.2-1.0)\times10^{-2}$ mol dm^{-3}]. The transient absorbance of 2-hexanone decreased with the quencher concentration. The quenching rate ($k_g\tau_T$) of 2-hexanone was de-

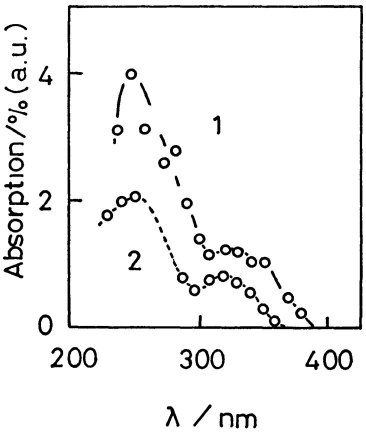


Fig. 1. Transient absorption spectra monitored in the laser flash photolysis of 2-hexanone (1) and 5-methyl-2-hexanone (2) in dichloromethane immediately at the end of the flash. Absorbed photons were normalized to 1.1×10^{-8} einstein per flash. Concentration: 3×10^{-2} mol dm^{-3}.

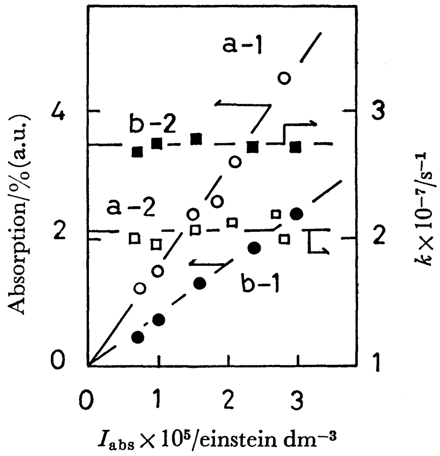


Fig. 2. Effect of absorbed photons on the transient absorption. The absorbance (1) and the decay rate (2) were plotted against the absorbed photons on the laser flash photolysis of 2-hexanone (a) and 5-methyl-2-hexanone (b) in methanol (3×10^{-2} mol dm^{-3}).

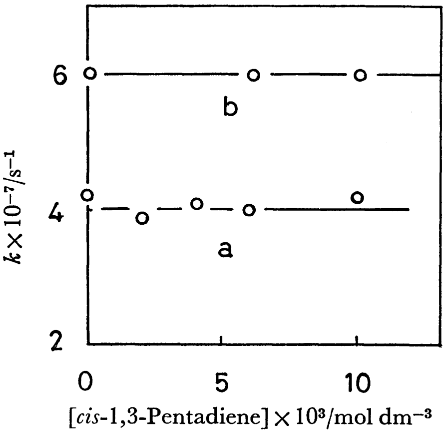


Fig. 3. Change of the decay rate (k) of the transient species in the concentration of *cis*-1,3-pentadiene on the laser flash photolysis of 2-hexanone (a) and 5-methyl-2-hexanone (b) in dichloromethane (3×10^{-2} dm^{-3}).

termined to be *ca.* 3×10 dm^3 mol^{-1} by means of the transient absorbance but the rate of 5-methyl-2-hexanone could not be determined because the results were scattered. Figure 3 shows the plots of k *vs.* the quencher concentration. The decay rates, k, did not increase with the quencher concentration. The quenching rate constant of *cis*-1,3-pentadiene in acetonitrile has been reported to be 4.4×10^9 dm^3 mol^{-1} s^{-1}.[9] If the transient species monitored were the triplet states, the k values were increased to *ca.* 8×10^7 s^{-1} (2-hexanone) and *ca.* 1×10^8 s^{-1} (5-methyl-2-hexanone) in the presence of 1×10^{-2} mol dm^{-3} of the quencher. The triplet decay rate (k_T) of 2-hexanone has been reported to be 1×10^9 s^{-1},[6] and the k_T values have been estimated to be 1×10^8 s^{-1} (2-hexanone) and 3×10^8 s^{-1} (5-methyl-2-hexanone) by means of the $K_g\tau_T$ values reported.[10] These k_T values are much larger than the k values. It can be stated that the transient species monitored is the triplet 1,4-biradical and that k is its decay-rate constant.

Table 1. Decay-rate constants of the transient species formed from 2-hexanone and 5-methyl-2-hexanone in various solvents and the reaction-rate constant of oxygen

Compound	Solvent	$k\times10^{-7}$ [a)] / s^{-1}	$k'\times10^{-7}$ [b)] / s^{-1}	$[O_2]\times10^3$ / mol dm^{-3}	$k_{O_2}\times10^{-10}$ / dm^3 mol^{-1} s^{-1}
2-Hexanone	Dichloromethane	3.0	6.8	2[c)]	1.5
	Hexane	3.3	7.8	3.9[d)]	1.5
	Acetonitrile	2.4	7.8	1.3[e)]	4.2?
	Methanol	2.06	5.1	2.12[d)]	1.4
5-Methyl-2-hexanone	Dichloromethane	6.0	8.8	2[c)]	1.4
	Hexane	5.4	9.6	3.09[d)]	1.6?
	Acetonitrile	2.9	8.0	1.3[e)]	3.9
	Methanol	2.75	6.0	2.12[d)]	1.5

a) Error limit, ±10%. b) Error limit, ±20%. c) Ref. 5. d) Ref. 12. e) Ref. 13.

These laser-flash photolyses were carried out in acetonitrile, in hexane, and in methanol. The results are listed in Table 1. The k value increased as follows:

in dichloromethane < in hexane < in acetonitrile < in methanol.

Small and Scaiano reported that the 1,4-biradical formed from the aromatic carbonyl compound was stabilized in a polar solvent for the formation of hydrogen bonding with the solvent and a heavy-atom effect was also detected.[11] The characteristics of the triplet 1,4-biradical from the aliphatic carbonyl compounds agree with the results reported by Small and Scaiano.[11] The decay rates of the 1,4-biradical in the presence of oxygen (k') were determined by means of pseudo-first-order kinetics to be as one listed in Table 1. The rate, k', can be written in the form of the following equation;

$$k' = k + k_{O_2}[O_2]$$

where k_{O_2} is the reaction-rate constant of oxygen with the 1,4-biradical. Although the k' rate contains a relatively large error, k_{O_2} is a constant for every solvent (k_{O_2}=*ca.* 1.5×10^{10} dm^3 mol^{-1} s^{-1}).

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References

1) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Am. Chem. Soc.*, **96**, 3351 (1974).

2) M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc.*, **100** 7108 (1978).

3) M. V. Encinas and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 56.

4) G. Porter, R. W. Yip, J. M. Duston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67** 3149 (1971).

5) I. Naito and W. Schnabel, in preparation.

6) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

7) S. Takamuku, G. Beck, and W. Schnabel, *J. Photochem.*, **11**, 49 (1979).

8) S. Noda, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, **49**, 3287 (1968).

9) N. J. Turro and Y. Tanimoto, *J. Photochem.*, **14**, 199 (1980).

10) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

11) R. D. Small and J. C. Scaiano, *Chem. Phys. Lett.*, **59**, 246 (1978).

12) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 89.

13) U. Grollman and W. Schnabel, private communication.