

PHOTOENOLIZATION OF 2-METHYLBENZOPHENONE STUDIED BY PICOSECOND AND NANOSECOND LASER SPECTROSCOPY

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Summary

Picosecond and nanosecond spectroscopy methods were used to investigate the photoenolization of 2-methylbenzophenone in ethanol at room temperature. Picosecond laser photolysis revealed a $T_n \leftarrow T_1$ absorption spectrum with $\lambda_{\max} = 520$ nm and a decay time of 2.8 ns. Nanosecond laser photolysis revealed two types of transient absorption: one was observed near 400 nm and decayed with two components with lifetimes of 8.1 μ s and 8 ms which were assigned to *cis*-dienols and *trans*-dienols respectively; the other was observed near 530 nm and had a lifetime of 26 ns. Since this value is almost equal to the rise time of the absorptions of the *cis*- and/or *trans*-dienols, it is reasonable to assume that the transient absorption around 530 nm is due to the triplet states of either the dienols or the 1,4-biradicals.

1. Introduction

It is well known that 2-methylbenzophenone (0K) undergoes a photochemical intramolecular hydrogen abstraction yielding the thermally unstable *cis*- and *trans*-dienols which decay to the original ketone [1]. The existence of the dienol species has been supported by the results of a number of experiments, and Uji-Ie *et al.* [2] observed two types of transient absorption, which are due to singlet state *cis*-dienol (0E_c) and *trans*-dienol (0E_t) respectively, by conventional and nanosecond laser photolysis. These workers also found that the Stern-Volmer plots for the yields of these dienols in aerated solutions gave different quenching constants when naphthalene was used as a triplet quencher. Thus they suggested that the *cis* (3K_c) and *trans* (3K_t) conformers of the ketone triplet are produced independently through the very fast intersystem crossing from the corresponding conformers of the lowest excited singlet states, and that 0E_c and 0E_t are produced via two independent pathways from 3K_c and 3K_t as shown in Fig. 1.

The intermediates 3E_c and 3E_t were attributed to either the triplet states of the dienols or the 1,4-biradicals.

Das and Scaiano [3] have recently pointed out that the choice of the triplet quencher and experimental conditions made by Uji-Ie *et al.* is most unfortunate because the results obtained in oxygen-containing systems with naphthalene as the quencher involve side reactions that vitiate the kinetic analysis. These workers used 2,5-dimethyl-2,4-hexadiene and *trans*-1,3-pentadiene as the triplet quenchers in an examination of the yields of both enols and concluded that the mechanism proposed by Uji-Ie *et al.* (Fig. 1) is incorrect. They proposed a mechanism in which hydrogen abstraction is only expected to take place from 3K_c and very rapid interconversion exists between 3E_c and 3E_t as shown in Fig. 2.

In the present paper we report the results of picosecond and nanosecond laser photolysis. Our direct observation of the transient absorptions of the triplet ketone(s) and 1,4-biradical(s) (or triplet dienols) suggests that the scheme shown in Fig. 2 is more reliable than the scheme shown in Fig. 1.

2. Experimental details

2-methylbenzophenone (Aldrich) was purified by distillation at reduced pressure under a nitrogen atmosphere, followed by column chromatography on 200 mesh alumina (2 cm internal diameter, 30 cm long) using ethanol as the developer. Spectral grade ethanol (Nakarai) was used as the solvent without further purification.

The second harmonics (347.2 nm) from picosecond mode-locked and nanosecond *Q*-switched ruby lasers were used to excite the sample. The details of our picosecond transient absorption spectrometer have been given elsewhere [4]. The monitoring light pulse was a picosecond continuum which was generated by focusing the fundamental pulse into a 10 cm BK-7 glass block. A double-beam optical arrangement was adopted, and the absorption spectra in the 200 nm scanning region were measured using two multichannel photodiode systems. The mean pulse width (26 ps) and the zero time point $t = 0$ were determined from the overlap of exciting and probe pulses by measuring the build-up of the $T_n \leftarrow T_1$ absorption of benzophenone in *n*-heptane at 530 nm. The concentration of the sample was 8×10^{-2} M and the sample solution, which was contained in a cell of path length 2 mm, was not deaerated. The transient absorption spectra were measured at room temperature.

The *Q*-switched ruby laser used for nanosecond photolysis was constructed in this laboratory [5]. The half-peak duration of the second harmonic was 22 ns. The transient absorptions and decay times at various wavelengths were observed using an HTV R666 photomultiplier and a Tektronix 475A oscilloscope. The monitoring light pulse was obtained from a xenon flash-lamp (Nikon SD-X). The experiments were also carried out at

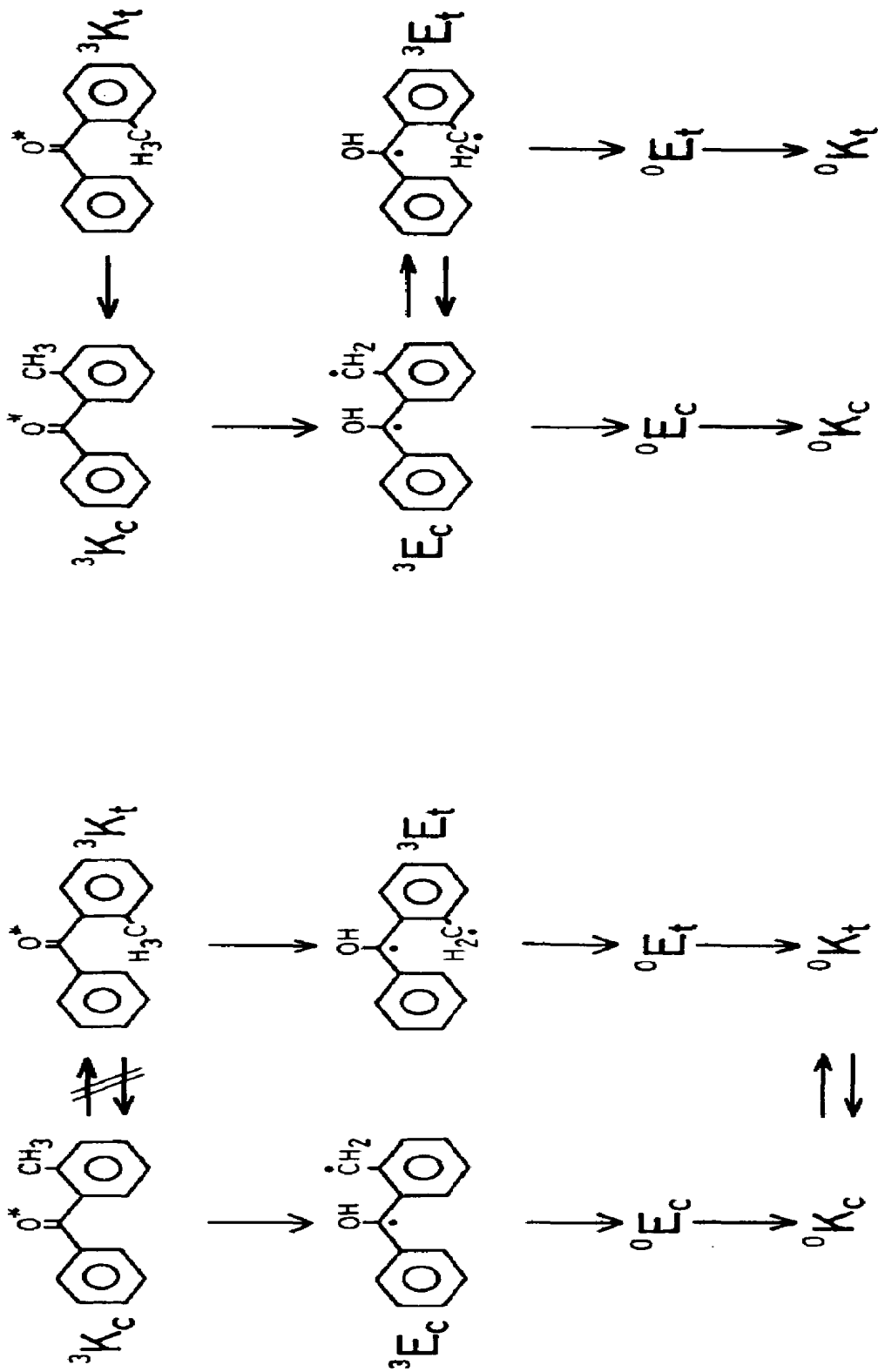


Fig. 1. Mechanism proposed by Uji-*le et al.* [2] for the photooxygenation of 2-methylbenzophenone.

Fig. 2. Mechanism proposed by Das and Scaiano [3] for the photooxygenation of 2-methylbenzophenone.

room temperature using a cell of path length 10 mm. The concentration of the deaerated sample solution was 1.6×10^{-2} M.

3. Results and discussion

Figure 3 shows the transient absorption spectra of 2-methylbenzophenone observed by picosecond laser photolysis at delay times of 100 ps (spectrum A). Spectrum B is a typical baseline spectrum for our system. The systematic deviation from zero is everywhere less than 0.02 absorbance units. The profile of spectrum A is very similar to the published $T_n \leftarrow T_1$ absorption of benzophenone [6]. The evolution of spectrum A with time was determined by measuring the absorbance ΔOD at 520 nm as shown in Fig. 4. The experimental points give the average $\Delta OD(t)/\Delta OD(\infty)$ of all shots at each delay time, and the error bars give the standard deviation from the average. $\Delta OD(\infty)$ was determined by averaging data for t in the range 60 - 330 ps. It is evident that the band growth reaches a plateau after about 60 ps and that its intensity remains constant up to 330 ps. The full curve corre-

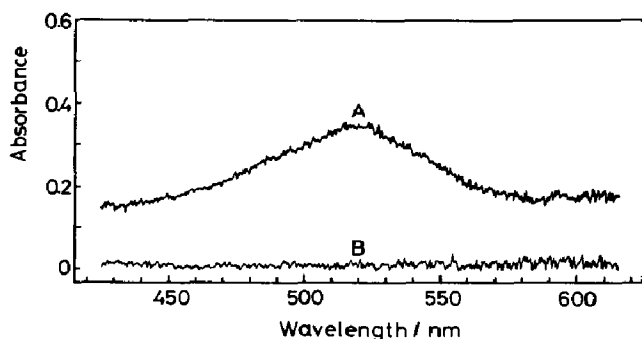


Fig. 3. Spectrum A, transient absorption spectrum of 2-methylbenzophenone in ethanol at 100 ps delay; spectrum B, baseline spectrum.

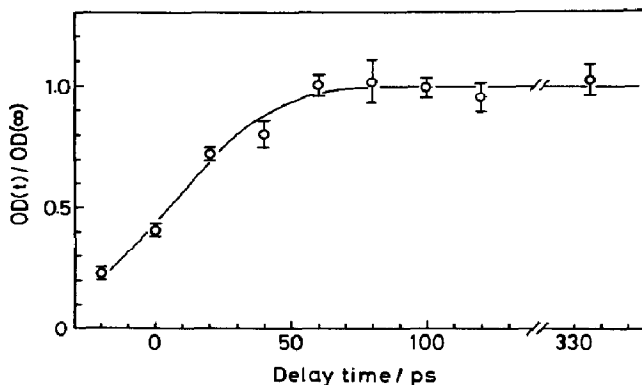


Fig. 4. Time evolution of $T_n \leftarrow T_1$ absorption of 2-methylbenzophenone in ethanol at 520 nm: —, instrumental response function assuming a 26 ps gaussian probe and excitation pulse shapes.

sponds to the instrumental response function calculated using a well-known convolution method [7] by assuming 26 ps gaussian probe and excitation pulse shapes. Since this pulse width was determined by measuring the build-up of $T_n \leftarrow T_1$ absorption of benzophenone in *n*-heptane and since the rate of intersystem crossing of benzophenone is very rapid, *i.e.* 8 ps [7], it can safely be concluded that spectrum A is due to the $T_n \leftarrow T_1$ absorption of 2-methylbenzophenone and that the rate of intersystem crossing is also rapid in this compound.

Figure 5 shows the decay of the $T_n \leftarrow T_1$ absorption of 2-methylbenzophenone on the relatively longer time scale; this decay can be expressed by a single-exponential function with a lifetime of 2.8 ns. This value is almost equal to that estimated from the Stern–Volmer plots for the yields of the dienols by Das and Scaiano [3], *i.e.* 3.5 ns for 3K_c ; Uji-Ie *et al.* [2] estimated lifetimes of 2.2 ns for 3K_c and 7.0 ns for 3K_t in ethanol solution.

Figure 6 shows the transient absorption spectrum of 2-methylbenzophenone at 8 ns delay. Comparison with spectrum A in Fig. 3 shows that this spectrum has new absorptions below 450 nm. The decay of the absorbance at 420 nm is shown in Fig. 7 (open circles). Since the spectral growth of the

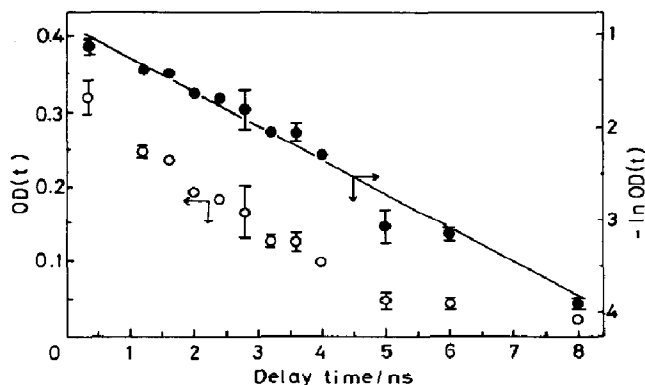


Fig. 5. The decay of the $T_n \leftarrow T_1$ absorption of 2-methylbenzophenone in ethanol at 520 nm.

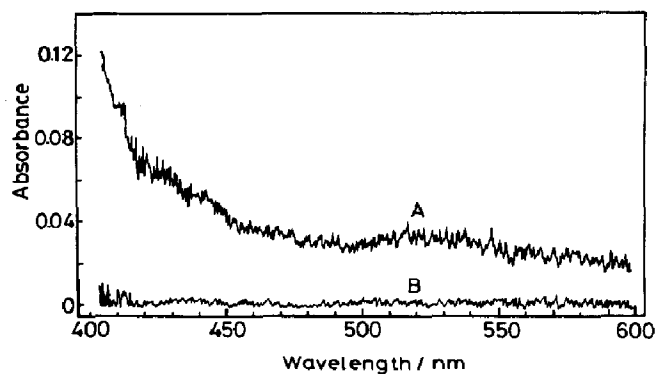


Fig. 6. Spectrum A, transient absorption spectrum of 2-methylbenzophenone in ethanol at 8 ns delay; spectrum B, baseline spectrum.

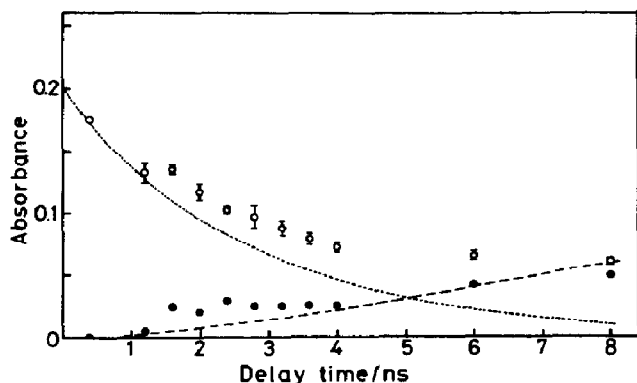


Fig. 7. Time variation in the 420 nm absorbance of 2-methylbenzophenone in ethanol: \circ , observed absorbance; - · - ·, calculated absorbance due to 3K with a lifetime of 2.8 ns; \bullet , difference between \circ and - · - ·; - - - -, calculated build-up of the formation of 0E assuming consecutive reactions.

triplet state of 2-methylbenzophenone reached a plateau after about 60 ps delay and the spectral intensity remained constant up to 330 ps, we estimated the maximum absorbance due to the $T_n \leftarrow T_1$ absorption of 2-methylbenzophenone at 420 nm from that at 520 nm. Assuming that this estimated value is a measure of the initial concentration of the ketone triplet 3K and that it decays according to a single-exponential function with a lifetime of 2.8 ns, we calculated the time variation in the 420 nm absorbance due to 3K . The result is also shown in Fig. 7 (dotted curve). When the difference between the open circles and the dotted curve is plotted (full circles), it can be seen that the difference increases with increasing time.

Spectra A and B in Fig. 8(a) show the results obtained by nanosecond laser photolysis at 1 μ s and 15 μ s delays respectively. The difference spectrum (spectrum C) is essentially the same as spectra A and B. However, the oscilloscope traces of the transmittance at 420 nm (Fig. 8(b)) decayed with two components with lifetimes of 8.1 μ s and 8 ms.

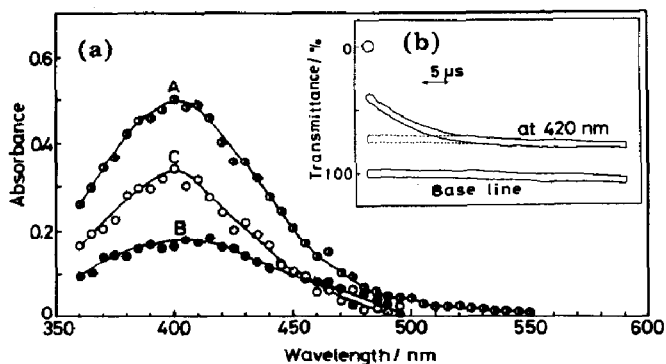


Fig. 8. (a) Transient absorption spectra (spectrum A, at 1 μ s; spectrum B, at 15 μ s; spectrum C, the difference between spectra A and B) and (b) oscilloscope trace of the transmittance of 2-methylbenzophenone.

On irradiation of 2-methylbenzophenone with steady state 366 nm light in ether-isopentane-ethanol (5:5:2 by volume) at 77 K, a new absorption band identical with the spectra in Fig. 8(a) was observed around 400 nm. Ullman and Huffman [8] also observed the formation of this species on irradiation of the isopropanol solution at -80°C and assigned the photo-product to the dienol(s) of 2-methylbenzophenone. All these results are consistent with those of Uji-Ie *et al.* [2] who assigned the short-lived and long-lived species to ${}^0\text{E}_c$ and ${}^0\text{E}_t$ respectively.

Although the ground state dienols decay in the microsecond and millisecond regions, their formation can be observed on the nanosecond time scale as shown in Fig. 9. As can be seen from the spectra obtained at 25 ns and 1.0 μs delays, the absorption with $\lambda_{\text{max}} \approx 400$ nm increases while that with $\lambda_{\text{max}} = 530$ nm decreases. The oscilloscope traces of the transmittance at 420 and 530 nm are shown in Fig. 9(b). The trace at 420 nm can be expressed by a single-exponential build-up function with a rise time of 28 ns. In contrast, the trace at 530 nm reaches a maximum value within the duration of a laser pulse (half-peak duration of about 22 ns) and decays by a single-exponential function with a lifetime of 26 ns. Since the rise time of the absorption at 420 nm is almost equal to the lifetime of the absorption at 530 nm and since the latter value is very long compared with that of ${}^3\text{K}$, it is reasonable to suggest that the transient absorption at 530 nm is different from that of ${}^3\text{K}$ and is due to the precursor of ${}^0\text{E}_c$ and/or ${}^0\text{E}_t$. Assuming that spectrum A is due to pure ground state dienols at 1.0 μs , we calculated the corresponding spectrum at 25 ns and subtracted it from spectrum B. The difference spectrum (spectrum C) is also shown in Fig. 9(a). (Since the absorbance due to ${}^3\text{K}$ at 25 ns is estimated to be the order of 10^{-2} of that of spectrum B, the contribution of the ketone triplet absorption may be negligible.)

Haag *et al.* [9] observed an absorption at 535 nm by the nanosecond laser photolysis of 2,4-dimethylbenzophenone. Since the decay of this absorption (lifetime, 30 ns) was accompanied by a rate matching increase in the absorption at 420 nm which was due to *cis*- and/or *trans*-dienols, they assigned the absorption at 535 nm to the triplet states of dienols. Thus it can

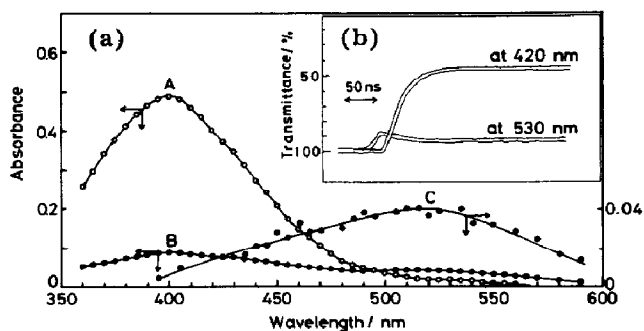
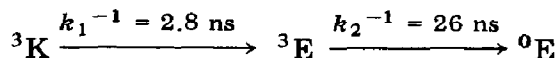


Fig. 9. (a) Transient absorption spectra (spectrum A, at 1 μs ; spectrum B, at 25 ns; spectrum C, difference between spectrum B and the spectrum calculated from spectrum A) and (b) oscilloscope traces of the transmittance of 2-methylbenzophenone.

be concluded that our spectrum C in Fig. 9(a) is also due to the triplet states of the dienols (^3E) or 1,4 biradicals.

Since we did not observe any differences between the absorption spectra of the *cis* and *trans* forms of ^3K , ^3E and ^0E , we calculated the build-up of the formation of ^0E by assuming the following consecutive reactions on a time scale of a few nanoseconds:



The absorbance A of ^0E at 420 nm at delay time t is given by

$$A = \frac{\epsilon A_T}{\epsilon_T} \left[1 - \frac{k_2 \exp\{-k_1(t - 0.33)\}}{k_2 - k_1} + \frac{k_1 \exp\{-k_2(t - 0.33)\}}{k_2 - k_1} \right]$$

where A_T is the absorbance of ^3K at 420 nm and at 0.33 ns delay, and ϵ_T and ϵ are the extinction coefficients of the absorptions of ^3K and ^0E respectively at 420 nm. We determined $\epsilon A_T/\epsilon_T$ from the observed value of A at 6 ns and then calculated A for various delay times. The result is given in Fig. 7 (broken curve) and shows a qualitative agreement with the experimental values.

We have presented the results of the picosecond and nanosecond laser photolysis of 2-methylbenzophenone. Our conclusion is essentially the same as that of Das and Scaiano [3].

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