

THE PHOTOENOLIZATION MECHANISM OF 2-METHYLBENZOPHENONE

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Summary

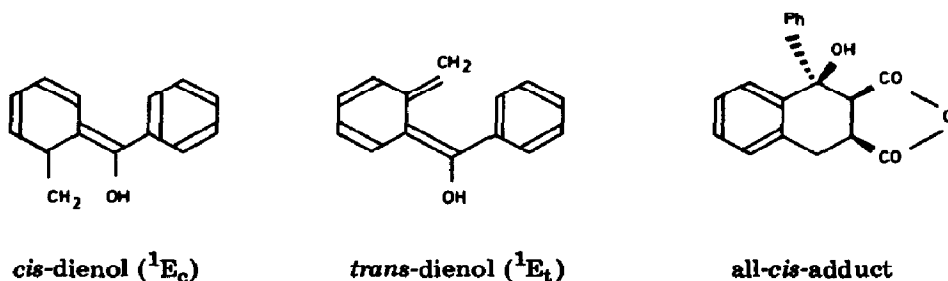
The photoenolization of 2-methylbenzophenone was investigated by conventional and laser flash photolysis. Two kinds of transient absorption were distinctly observed in the ethanol and the dioxane solutions. The short lived transient was assigned to the *cis*-dienol and the long lived transient to the *trans*-dienol. The Stern-Volmer plots for the yields of these dienols gave different quenching constants when naphthalene was used as a triplet quencher. It was concluded that the *cis*-dienol is produced from the $n-\pi^*$ triplet state of 2-methylbenzophenone with *s-cis* conformation and the *trans*-dienol from the triplet state with *s-trans* conformation.

1. Introduction

Since Yang and Rivas [1] reported the photoenolization of ortho-alkyl-substituted benzophenones in 1961, it has been established that 2-methylbenzophenone undergoes a photochemical intramolecular hydrogen abstraction, yielding the corresponding dienol. The existence of the dienol species has been supported by several experiments such as Diels-Alder trapping [1 - 3], deuterium exchange [4, 5] and dienol oxidation reactions [6]. The occurrence of the intramolecular reaction was verified by the fact that the photochemical pinacol reduction is completely suppressed and no ketyl radical formation is detected even in hydrogen-donating solvents [1, 7].

Beckett and Porter [7] observed a yellow transient with a lifetime of several hours by conventional flash photolysis in the degassed isopropanol solution of 2-methylbenzophenone. Ullman and Huffman [8] assigned this colored species to a dihydroanthrone structure. They found that a deep yellow transient was formed by the irradiation of the degassed isopropanol solution at -80°C . The deep yellow species, which is rapidly diminished upon warming to 25°C , was assigned to the dienol of 2-methylbenzophenone.

Porter and Tchir [9, 10] observed five transient absorptions for 2,4-dimethylbenzophenone and the other alkyl substituted benzophenones by conventional and laser flash photolysis. In the cases of 2-methyl and 2,4-dimethylbenzophenone, the first transient species (A, lifetime $\tau = 28 - 38$ ns) was assigned to the $n-\pi^*$ triplet state of the ketone, the second transient (B, $\tau = 0.067 - 1.7 \mu\text{s}$), which is produced from A, presumably to the 1,4-biradical, the third transient (C, $\tau = 0.02 - 250$ s) to the *trans*-dienol, the fourth transient (D, $\tau = 0.0095 - 3.9$ s) to the *cis*-dienol and the fifth transient (E, τ of the order of hours) to the dihydroanthrone structure. In previous work [11], we assigned B to the *cis*-dienol and D to the *trans*-dienol and suggested that B and D are separately produced from the different triplet states of the ketone. Haag *et al.* [12] supported our assignment of B. Moreover, they assigned A to the enol excited triplet state which might be produced from the $n-\pi^*$ triplet state of the ketone on the basis of the quenching experiment by *cis*-piperylene.



Nerdel and Brodowski [3] found that the irradiation of 2-methylbenzophenone in the presence of 0.1 M maleic anhydride in dioxane gives the all-*cis* adduct with an 80% yield. On the basis of Alder's rule, Sammes and coworkers [13, 14] pointed out that the result of Nerdel and Brodowski is explained by the Diels-Alder reaction of the *trans*-dienol alone.

Recently Wagner and coworkers [5, 15] have suggested, on the basis of the kinetic analysis of the *cis-trans* photoisomerization of 1,3-pentadiene, that two $n-\pi^*$ triplet states with different structural conformations exist for 2-methylbenzophenone as well as for 2-methylacetophenone.

In the present paper, we report further evidence for our assignment of B and D. A photoenolization mechanism of 2-methylbenzophenone which explains all the findings is proposed.

2. Experimental

2-Methylbenzophenone was prepared and purified by the method of Reiding and Nauta [16]. Benzophenone (G. R. grade, Wako Junyaku) was recrystallized twice from ethanol. Naphthalene (E. P. grade, Kanto Kagaku) was recrystallized twice from ethanol and sublimed in vacuum. Ethanol

(G.R. grade, Wako Junyaku) was used without further purification. All the other solvents were purified by ordinary methods [17].

Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. Phosphorescence spectra were recorded on a modified Hitachi EPU spectrophotometer. A passive Q-switched ruby laser provided a 15 ns pulse of about 0.15 J, and its second harmonics were used for excitation. The output fluctuation of the ruby laser was found to be less than 5% in the fundamental pulse. Three analysing light sources were used: (i) a xenon flash for the usual transient absorption spectroscopy, (ii) an Ushio USH-102D super high pressure mercury lamp for the quenching experiment of the *cis*-dienol and (iii) an Ushio UXL-150D arc lamp for the direct measurement of the formation quantum yield of the *trans*-dienol. An RCA 1P28 photomultiplier and a Tektronix 7904 oscilloscope were used for monitoring the transient signal. A detailed description of the experimental set-up has been given elsewhere [18]. A conventional flash apparatus has also been reported [19]. A quartz cell, 10 mm in diameter and 100 mm in length, was used for conventional and laser flash experiments.

For conventional flash experiments the concentration of 2-methylbenzophenone and the filter used were as follows: about 1×10^{-4} M Toshiba UV-D25 and about 9×10^{-3} M Hoya UVP for the transient absorption spectroscopy, about 5×10^{-6} M Toshiba UV-D25 for the determination of the molar extinction coefficient of the *trans*-dienol and about 2×10^{-2} M Toshiba V-V40 for the quenching experiment to obtain the formation quantum yield of the *trans*-dienol. For laser flash experiments the concentration of the ketone was about 2×10^{-3} M. The transient absorption spectra were obtained by means of a point-by-point (5 nm) plot.

The pH of the sample solution in the range 0 - 4.1 was adjusted by the addition of H_2SO_4 and in the range 5.6 - 9.8 by phosphate buffer. The pH of the solution was measured with a TOA Model HM-18B pH meter. Ethanol solutions were degassed by repeating bulb-to-trap distillation. The other solutions were degassed by the freeze-pump-thaw method. All measurements were made at 23 °C.

3. Results and discussion

Figure 1(a) shows the transient absorption spectrum obtained immediately after laser flashing of 2-methylbenzophenone in ethanol. The decay of spectrum (a) is of first order and its decay constant is $2.2 \times 10^5 \text{ s}^{-1}$ both in the aerated and deaerated solutions. After spectrum (a) disappeared, a long lived transient absorption spectrum (Fig. 1(b)) remained. Spectrum (b) was also obtained by a conventional flash photolysis. The decay of spectrum (b) is of first order, but its decay constant varies from sample to sample in the range $3 - 10 \text{ s}^{-1}$ for the aerated solution. The decay rates of spectra (a) and (b) were not effectively affected by the presence of oxygen or by the addition of 1.3×10^{-2} M ferrocene which is an excellent triplet quencher

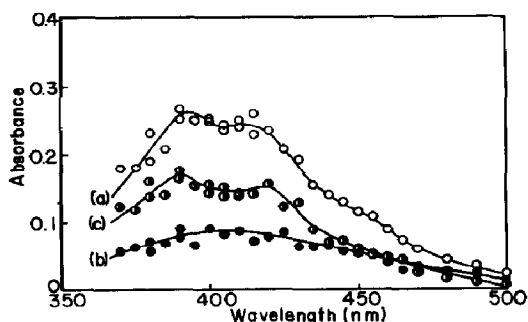


Fig. 1. Transient absorption spectra obtained (a) immediately and (b) about 20 μ s after laser flashing of the ethanol solution. Spectrum (c) was obtained by subtracting (b) from (a).

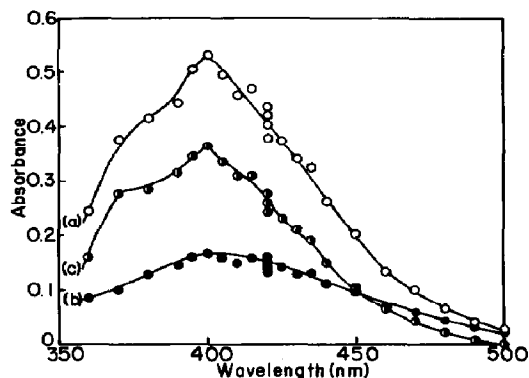


Fig. 2. Transient absorption spectra obtained (a) immediately and (b) about 20 μ s after laser flashing of the dioxane solution. Spectrum (c) was obtained by subtracting (b) from (a).

[20]; therefore, these spectra cannot be attributed to the triplet state of 2-methylbenzophenone. After spectrum (b) disappeared, a much longer lived transient absorption was observed in the wavelength range 300 - 400 nm. However, it is not discussed hereafter because of its very weak absorption. After these transient absorptions disappeared, the absorption spectrum of 2-methylbenzophenone was almost completely recovered.

Two kinds of transient absorption similar to those obtained in ethanol were observed in dioxane (Fig. 2 (a), (b)). The decay of spectrum (a) is of first order and its decay constant is $2.9 \times 10^5 \text{ s}^{-1}$ both in the aerated and deaerated solutions. The decay of spectrum (b) is of first order and its decay constant is about 0.3 s^{-1} in the aerated solution and $0.1 - 0.3 \text{ s}^{-1}$ in the deaerated solution.

TABLE 1

The lifetimes of B in various solvents

| Solvent | Viscosity (cP) | Dielectric constant | Lifetime (μ s) |
|-----------------|----------------|---------------------|---------------------|
| Ethanol | 1.078 (25 °C) | 24.55 (25 °C) | 4.5 |
| Dioxane | 1.087 (30 °C) | 2.209 (25 °C) | 3.4 |
| Cyclohexane | 0.898 (25 °C) | 2.023 (20 °C) | 0.05 |
| Benzene | 0.603 (25 °C) | 2.275 (25 °C) | 0.05 |
| Ether | 0.242 (20 °C) | 4.335 (20 °C) | 1.3 |
| Acetonitrile | 0.325 (30 °C) | 37.5 (20 °C) | 1.2 |
| Pyridine | 0.884 (25 °C) | 12.4 (21 °C) | 21 |
| Liquid paraffin | — | — | 0.04 |

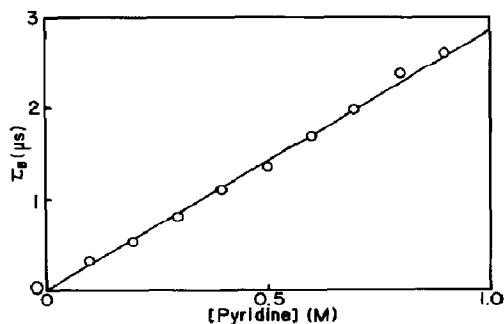


Fig. 3. The relation between the lifetime of B and pyridine concentration in the cyclohexane solution.

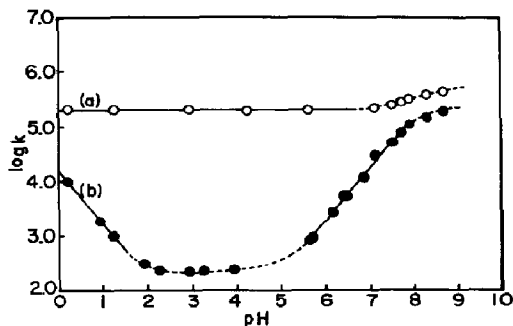
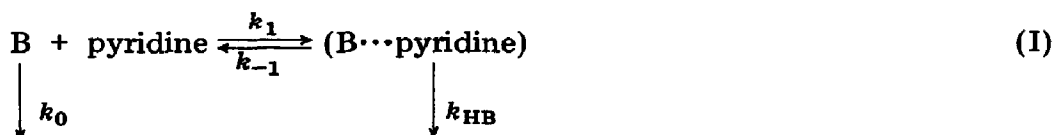


Fig. 4. The pH dependences of the decay constants of B (—○—) and D (—●—) in ethanol-water (1:1 in volume).

The short lived transient corresponds to B and the long lived transient to D in Porter's notation. The lifetimes of B in various solvents are summarized in Table 1. The lifetime is not correlated with the solvent polarity and viscosity, but it is longer in proton-accepting solvents.

When pyridine was added to the cyclohexane solution, the lifetime τ_B of B becomes longer in proportion to the pyridine concentration as shown in Fig. 3. If it is assumed that B forms a hydrogen bond with pyridine, the decay processes of B may be expressed by



The equilibrium is maintained throughout the decay process for pyridine concentrations above 0.1 M because the decay curve is a single exponential at any pyridine concentration studied. The lifetime of the equilibrium mixture is expressed by [21, 22]

$$\tau = \frac{1 + K[\text{pyridine}]}{k_0 + k_{\text{HB}}K[\text{pyridine}]} \quad (1)$$

where $K = k_1/k_{-1}$. The result shown in Fig. 3 requires the relation

$$k_0 \gg k_{\text{HB}}K[\text{pyridine}] \quad (2)$$

Accordingly, we obtain

$$\tau = \frac{K}{k_0} [\text{pyridine}] + \frac{1}{k_0} \quad (3)$$

The slope of the plot in Fig. 3 is $K/k_0 = 2.8_4 \times 10^{-6} \text{ M}^{-1} \text{ s}$ at 23 °C. Using $k_0 = 2 \times 10^7 \text{ s}^{-1}$, we obtain $K = 57 \text{ M}^{-1}$ at 23 °C which is close to the equilib-

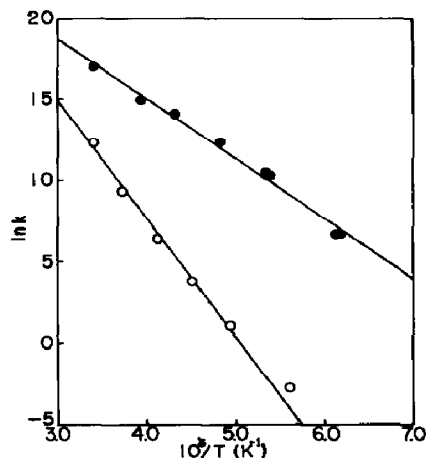


Fig. 5. Arrhenius plots for the decay constant of B in the aerated ethanol (\circ) and methylcyclohexane (\bullet) solutions.

rium constant of the hydrogen bond between phenol and pyridine [23]. Since relation (2) holds at a pyridine concentration of 1 M, k_{HB} in cyclohexane is estimated as $k_{\text{HB}} \leq 3.5 \times 10^5 \text{ s}^{-1}$ which is consistent with the lifetime in pyridine. Therefore it may be concluded that the lifetime of B is prolonged by hydrogen-bond formation in proton-accepting solvents.

Figure 4 shows the pH dependence of the decay constants of B and D in ethanol-water (1:1 in volume). In the pH range 0 - 2, the decay constant of D decreases with increasing pH value (Fig. 4 (b)) but that of B hardly changes (Fig. 4 (a)). The decay constants of B and D increase gradually in the pH ranges above 7 and 5 respectively. The slopes of Fig. 4 (b) are -1.0 in the pH range 0 - 2 and 1.0 in the pH range 5 - 8. These results suggest that the decay process of D is associated with protonation in the pH range 0 - 2 and deprotonation in the pH range above 5, and that the decay process of B is associated with deprotonation in the pH range above 7 but not with protonation in the pH range 0 - 7.

Figure 5 shows the Arrhenius plots for the decay constant of B in the aerated ethanol and methylcyclohexane solutions. From the slopes and the intercepts, we obtain the apparent activation energy $E_{\text{app}} = 14.0 \text{ kcal mol}^{-1}$ and the apparent frequency factor $A_{\text{app}} = 3.5 \times 10^{15} \text{ s}^{-1}$ for the ethanol solution, and $E_{\text{app}} = 7.3 \text{ kcal mol}^{-1}$ and $A_{\text{app}} = 1.0 \times 10^{13} \text{ s}^{-1}$ for the methylcyclohexane solution. It should be noticed that the values of E_{app} and A_{app} for the ethanol solution are much larger than those for the methylcyclohexane solution. Since ethanol is a proton-accepting solvent, this result can be explained by the hydrogen-bond interaction between B and ethanol as in the case of B and pyridine.

The excitation energy of the $n-\pi^*$ triplet state of 2-methylbenzophenone was determined to be $24\,400 \text{ cm}^{-1}$ in ethanol and $24\,100 \text{ cm}^{-1}$ in methylcyclohexane from the measurements of the phosphorescence

TABLE 2

The initial absorbances of the naphthalene triplet at various naphthalene concentrations

| [naphthalene] (10^{-2} M) | A_Q |
|------------------------------|-------|
| 1.01 | 0.105 |
| 2.14 | 0.210 |
| 2.81 | 0.270 |
| 3.96 | 0.320 |
| 5.10 | 0.353 |
| 5.95 | 0.379 |
| 7.08 | 0.423 |
| 8.19 | 0.449 |
| 8.81 | 0.468 |

spectra in these solvents at 77 K. In order to clarify whether or not B and D are produced from the $n-\pi^*$ triplet state, naphthalene (triplet energy, $21\,320\text{ cm}^{-1}$ [24]) was used as a triplet quencher. When naphthalene was added to the aerated ethanol solution, the decay rates of B and D did not change but both yields of B and D decreased. Moreover, the triplet-triplet absorption of naphthalene appeared under the condition that naphthalene was not directly excited, and its absorbance A_Q increased with increasing naphthalene concentration as shown in Table 2. It is obvious that B is produced from the $n-\pi^*$ triplet state. However, it is still not known whether D is produced from the triplet state or from B, because the absorption spectra of B and D lie in the same spectral range. The absorbance A_0 of B at the end of the laser pulse and the absorbance A_∞ of D $50\ \mu\text{s}$ after the laser pulse at various naphthalene concentrations are given in Table 3. It is expected that the ratio of A_∞ to A_0 does not depend on naphthalene concentration if D is produced from B. These ratios are listed in Table 3. Since A_∞/A_0 depends on naphthalene concentration, it is clear that B is not the precursor of D. Accordingly, the correct spectrum of B is obtained by subtracting A_∞ from A_0 (Fig. 1, curve (c) and Fig. 2, curve (c)).

Figure 6 shows the Stern-Volmer plots for the yields of B and D. From these plots the quenching constants were obtained as $11 \pm 3\text{ M}^{-1}$ for B and $35 \pm 2\text{ M}^{-1}$ for D. On the assumption that the quenching reactions are diffusion controlled ($k_{\text{diff}} = 5 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$), the lifetimes of the precursor triplets of B and D are estimated to be 2.2 and 7.0 ns respectively. Therefore it is suggested that B is produced from the short lived triplet state and D from the long lived triplet state.

As regards the assignments of B and D, Porter and Tchir [10] have suggested that B is the 1,4-biradical and D is the *cis*-dienol or the equilibrium mixture of the *cis*-dienol and the *trans*-dienol. Findlay and Tchir [25] have reported that B is presumably the dienol triplet rather than the 1,4-biradical. If B is the 1,4-biradical or the dienol triplet, D must be the *cis*-dienol or the equilibrium mixture of the *cis*-dienol and the *trans*-dienol, and

TABLE 3

The values of A_0 , A_∞ and A_∞/A_0 at various naphthalene concentrations

| [naphthalene] (10^{-2} M) | A_0 | A_∞ | A_∞/A_0 |
|------------------------------|-------|------------|----------------|
| 0 | 0.535 | 0.178 | 0.333 |
| 1.15 | 0.401 | 0.112 | 0.279 |
| 1.96 | 0.384 | 0.106 | 0.276 |
| 3.08 | 0.359 | 0.081 | 0.226 |
| 4.33 | 0.297 | 0.062 | 0.209 |
| 4.84 | 0.293 | 0.063 | 0.215 |
| 6.05 | 0.257 | 0.053 | 0.206 |
| 7.22 | 0.240 | 0.044 | 0.183 |

The observed wavelength was 406 nm.

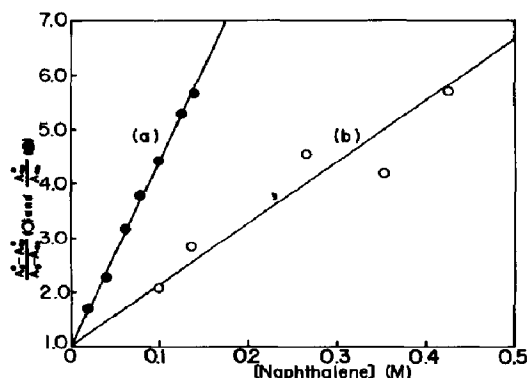
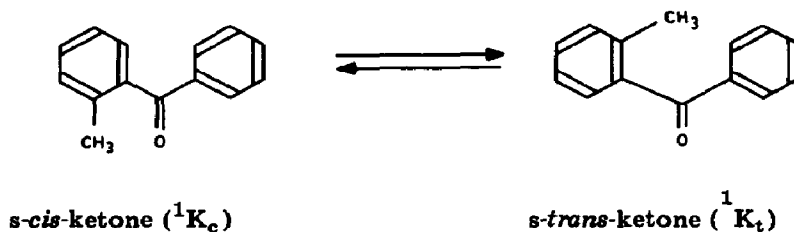


Fig. 6. Stern-Volmer plots for the yields of B (—○—) and D (—●—) in the ethanol solution; A_0^0 and A_∞^0 are the absorbances in the absence of naphthalene.

D must be produced from B. If this is the case, the effects of naphthalene concentration on the yields of B and D should be the same in disagreement with the results shown in Fig. 6. Therefore B is neither the 1,4-biradical nor the dienol triplet. On the basis of the facts that (i) the lifetimes of B and D depend on the pH of the solution, (ii) the lifetime of B is longer in proton-accepting solvents than in the other solvents and is shorter than that of D and (iii) 2-methylbenzophenone is reproduced at the expense of B and D, it is concluded that B is the *cis*-dienol 1E_c and D is the *trans*-dienol 1E_t .

The above assignment appears to contradict the conclusion of Sammes and coworkers [13, 14] for the result obtained by Nerdel and Brodowski [3]. However, since the lifetime of 1E_c may be too short to allow the Diels-Alder reaction, only 1E_t might be trapped with maleic anhydride.

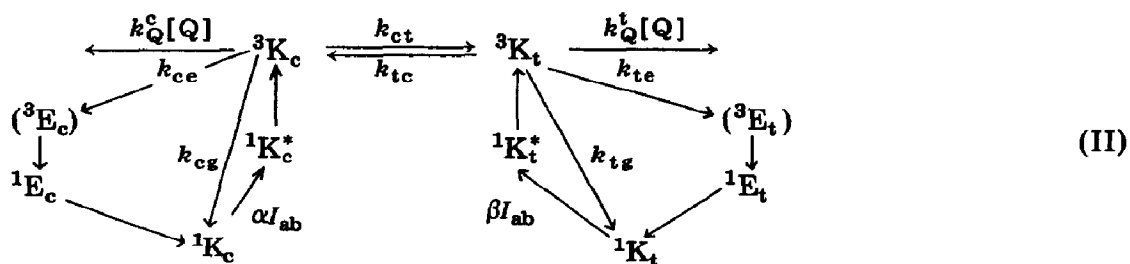
Grimaud *et al.* [26] suggested the existence of the following conformational equilibrium in the ground state of 2-methylbenzophenone from the depolarization experiment for Rayleigh scattering:



Recently, Wagner [5] has reported the existence of two $n\text{-}\pi^*$ triplet states having different conformations, *i.e.* the $s\text{-cis}$ (3K_c) and the $s\text{-trans}$ (3K_t) excited triplet ketone, and estimated the quantum yield of 3K_t formation to be 0.38 in benzene. This agrees with the fact that the quenching constants for 1E_c (B) and 1E_t (D) differ from each other.

Porter and Tchir [9, 10] and Haag *et al.* [12] have observed a short lived transient absorption ($\tau = 28 - 38$ ns) in the solutions of 2,4-dimethylbenzophenone and found that the decay of this transient (A) is accompanied by the rise of the absorption of B. Porter and Tchir attributed A to the $n\text{-}\pi^*$ triplet state, but Haag *et al.* attributed it to the dienol excited triplet state 3E , the excitation energy of which is smaller than that of the triplet *cis*-piperylene (triplet energy, $19\,900\text{ cm}^{-1}$ [27]). In the case of 2-methylbenzophenone we could not observe this transient. However, it was found that the precursor triplet states of 1E_c (B) and 1E_t (D) are quenched by the addition of naphthalene and the lifetimes of their triplet states are much shorter than that of A of 2,4-dimethylbenzophenone. It is required by the spin selection rule that the enolization of the ketone in the triplet state produces the enol triplet state. Therefore it is more probable to assign A to 3E which is produced from the triplet ketone.

Since the rate of the intersystem crossing of benzophenone is very rapid [28], the following reaction scheme is adequate for the photoenolization of 2-methylbenzophenone:



where $[Q]$ is the concentration of naphthalene, I_{ab} the total quantity of photons absorbed during one flash and α and β the fractions of the photons absorbed by 1K_c and 1K_t respectively, *i.e.* $\alpha + \beta = 1$.

According to scheme II, we obtain the following relations for the yields Φ_c and Φ_t of 1E_c and 1E_t respectively:

$$\frac{1}{\Phi_c} = \frac{(k_{tc} + k_{te} + k_{tg} + k_Q^t[Q])(k_{ct} + k_{ce} + k_{cg} + k_Q^c[Q]) - k_{tc}k_{ct}}{k_{ce}\{k_{tc} + \alpha(k_{te} + k_{tg} + k_Q^t[Q])\}} \quad (4)$$

$$\frac{1}{\Phi_t} = \frac{(k_{tc} + k_{te} + k_{tg} + k_Q^t[Q])(k_{ct} + k_{ce} + k_{cg} + k_Q^c[Q]) - k_{tc}k_{ct}}{k_{te}\{k_{ct} + \beta(k_{ce} + k_{cg} + k_Q^c[Q])\}} \quad (5)$$

The linearity of the Stern–Volmer plot shown in Fig. 6(a) requires that either $k_{ct} \ll \beta(k_{ce} + k_{cg} + k_Q^c[Q])$ or $k_{ct} \gg \beta(k_{ce} + k_{cg} + k_Q^c[Q])$ at any naphthalene concentrations examined. The latter condition is insignificant, because both absorptions of 1E_c and 1E_t were observed. Similarly the linearity of the plot in Fig. 6(b) requires that $k_{tc} \ll \alpha(k_{te} + k_{tg} + k_Q^t[Q])$. Accordingly, we obtain the following relations which are consistent with the results shown in Fig. 6:

$$\frac{\alpha}{\Phi_c} \approx \left(\frac{1 + k_Q^c[Q]}{k_{ce} + k_{cg}} \right) \frac{k_{ce} + k_{cg}}{k_{ce}} \quad (6)$$

$$\frac{\beta}{\Phi_t} \approx \left(\frac{1 + k_Q^t[Q]}{k_{te} + k_{tg}} \right) \frac{k_{te} + k_{tg}}{k_{te}} \quad (7)$$

The quantum yield Φ_Q of the naphthalene triplet produced by the energy transfer from 3K_c and 3K_t is expressed as

$$\Phi_Q = \alpha \frac{k_Q^c\tau_c[Q]}{1 + k_Q^c\tau_c[Q]} + \beta \frac{k_Q^t\tau_t[Q]}{1 + k_Q^t\tau_t[Q]} \quad (8)$$

where $\tau_c \approx (k_{ce} + k_{cg})^{-1}$ and $\tau_t \approx (k_{te} + k_{tg})^{-1}$. Using $\alpha + \beta = 1$, we obtain

$$\frac{\Phi_Q}{[Q]} \left(\frac{1}{k_Q^c\tau_c} + [Q] \right) \left(\frac{1}{k_Q^t\tau_t} + [Q] \right) = \frac{1-\alpha}{k_Q^c\tau_c} + \frac{\alpha}{k_Q^t\tau_t} + [Q] \quad (9)$$

Φ_Q is related to the absorbance A_Q of the triplet–triplet absorption of naphthalene at 415 nm immediately after flashing 2-methylbenzophenone:

$$\Phi_Q = A_Q/\epsilon_Q d I_{ab} \quad (10)$$

where ϵ_Q is the molar extinction coefficient of the triplet–triplet absorption of naphthalene at 415 nm, the optical path length $d = 100$ mm and A_Q is listed in Table 2. From eqns. (9) and (10) we obtain

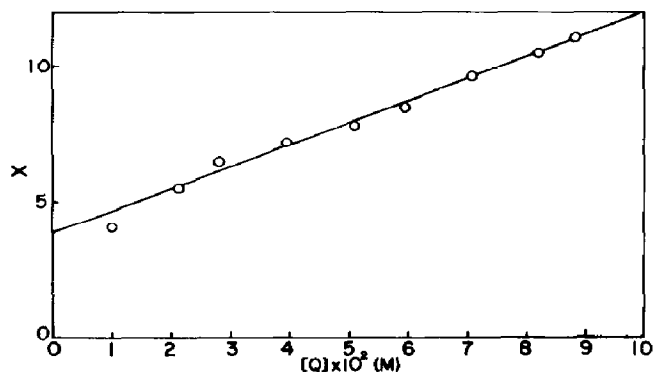
$$\begin{aligned} X &\equiv \frac{A_Q}{[Q]} \left(\frac{1}{k_Q^c\tau_c} + [Q] \right) \left(\frac{1}{k_Q^t\tau_t} + [Q] \right) \\ &= \epsilon_Q d I_{ab} \left(\frac{1-\alpha}{k_Q^c\tau_c} + \frac{\alpha}{k_Q^t\tau_t} + [Q] \right) \end{aligned} \quad (11)$$

where $k_Q^c\tau_c$ and $k_Q^t\tau_t$ have already been determined as 11 M^{-1} and 35 M^{-1} respectively. The plot of X versus $[Q]$ is shown in Fig. 7. From the ratio

TABLE 4

The values of A_B , A_∞ and Φ_t^0

| [benzophenone] (10^{-3} M) | [2-methylbenzophenone] (10^{-3} M) | A_B | A_∞ | Φ_t^0 |
|----------------------------------|--|-------|------------|------------|
| 1.04 | 1.26 | 0.317 | 0.144 | 0.347 |
| 1.04 | 1.26 | 0.304 | 0.183 | 0.459 |
| 2.08 | 2.51 | 0.383 | 0.148 | 0.295 |
| 2.08 | 2.51 | 0.333 | 0.144 | 0.330 |
| 3.12 | 3.77 | 0.387 | 0.142 | 0.280 |
| 3.12 | 3.77 | 0.333 | 0.157 | 0.360 |
| 4.15 | 5.02 | 0.317 | 0.167 | 0.402 |
| 4.15 | 5.02 | 0.270 | 0.119 | 0.336 |
| 5.19 | 6.28 | 0.292 | 0.151 | 0.395 |
| 5.19 | 6.28 | 0.281 | 0.139 | 0.377 |

Fig. 7. The plot of X vs. $[Q]$.

of the intercept and the slope, we obtained $\alpha = 0.6 - 0.8$ and hence $\beta = 0.4 - 0.2$.

In order to obtain further information for scheme II we determined the quantum yield Φ_t^0 of 1E_t at $[Q] = 0$ M by using triplet actinometry [29]. A deaerated benzene solution of benzophenone was used as a standard solution. The aerated ethanol solution of 2-methylbenzophenone and the standard solution, which have the same absorbance at 347 nm, were irradiated by a frequency-doubled Q-switched ruby laser. The initial absorbance A_B due to the benzophenone triplet and the absorbance A_∞ due to 1E_t were measured at 532.5 nm and 410 nm respectively and are listed in Table 4. The triplet yield Φ_B of benzophenone is 1.00 [30] and the molar extinction coefficient ϵ_B of the triplet-triplet absorption of benzophenone is $7630 \text{ M}^{-1} \text{ cm}^{-1}$ at 532.5 nm [31]. The molar extinction coefficient ϵ_t of 1E_t was found to be $1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 410 nm according to the method of Pavlopoulos [32]. The laser intensity was maintained at a constant value, so that Φ_t^0 could be evaluated by the equation

$$\Phi_t^0 = \Phi_B \frac{A_\infty/\epsilon_t d}{A_B/\epsilon_B d} = \frac{A_\infty}{A_B} \times 0.763 \quad (12)$$

The results are listed in Table 4. Averaging the results, we obtain $\Phi_t^0 = 0.36 \pm 0.05$. From eqn. (7) we obtain $\Phi_t^0 = \beta k_{te}/(k_{te} + k_{tg})$. Since $\beta = 0.2 - 0.4$ and $\Phi_t^0 = 0.36 \pm 0.05$, it may be concluded that the deactivation of 3K_t to 1K_t is negligible: $k_{te} \gg k_{tg}$. If the shorter lifetime of 3K_c compared with that of 3K_t is due to the fact that the rate of photoenolization of 3K_c is faster than that of 3K_t , the deactivation of 3K_c to 1K_c is also negligible: $k_{ce} \gg k_{cg}$.

The difference between the lifetimes of 3K_c and 3K_t can be attributed to the differences in structural conformation between these triplet states, *i.e.* the enolization does not require structural distortion in 3K_c but it does in 3K_t . The difference between the lifetimes of 1E_c (B) and 1E_t (D) can also be interpreted in terms of the differences in the structural conformations of these dienols. The result shown in Fig. 4(b) suggests that the protonation on the $=CH_2$ group and the deprotonation from the $-OH$ group enhance the reketonization of these dienols. The prolongation of the lifetime of 1E_c by the addition of pyridine can be attributed to hydrogen-bond formation between 1E_c and pyridine which suppresses the intramolecular proton transfer of 1E_c , *i.e.* the reketonization.

References

- 1 N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83** (1961) 2213.
- 2 N. D. Heindel, E. W. Sarver and M. A. Pfau, *Tetrahedron Lett.*, (1968) 3579.
- 3 F. Nerdel and W. Brodowski, *Chem. Ber.*, **101** (1968) 1398.
- 4 K. R. Huffman, M. Loy and E. F. Ullman, *J. Am. Chem. Soc.*, **87** (1965) 5417.
- 5 P. J. Wagner, *Pure Appl. Chem.*, **49** (1977) 259.
- 6 N. D. Heindel, J. Molnar and M. Pfau, *Chem. Commun.*, (1970) 1373.
- 7 A. Beckett and G. Porter, *Trans. Faraday Soc.*, **58** (1963) 2051.
- 8 E. F. Ullman and K. R. Huffman, *Tetrahedron Lett.*, (1965) 1863.
- 9 G. Porter and M. F. Tchir, *Chem. Commun.*, (1970) 1372.
- 10 G. Porter and M. F. Tchir, *J. Chem. Soc. A*, (1971) 3772.
- 11 K. Uji-ie, K. Kikuchi and H. Kokubun, *Chem. Lett.*, (1977) 499.
- 12 R. Haag, J. Wirz and P. J. Wagner, *Helv. Chim. Acta.*, **60** (1977) 2595.
- 13 B. J. Arnold, S. M. Mellows, P. G. Sammes and T. W. Wallace, *J. Chem. Soc. Perkin Trans. 1*, (1974) 401.
- 14 P. G. Sammes, *Tetrahedron*, **32** (1976) 405.
- 15 P. J. Wagner and C.-P. Chen, *J. Am. Chem. Soc.*, **98** (1976) 239.
- 16 D. J. Reiding and W. Th. Nauta, *Recl. Trav. Chim. Pays-Bas*, **80** (1961) 399.
- 17 A. Weissberger, J. A. Riddick and W. B. Bunger, *Technique of Organic Chemistry*, Vol. II, *Organic Solvents* (3rd edn.), Interscience, New York, 1970.
- 18 S. Kobayashi, K. Kikuchi and H. Kokubun, *Chem. Phys. Lett.*, **42** (1976) 494.
- 19 K. Kikuchi, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **41** (1968) 1545.
- 20 M. Kikuchi, K. Kikuchi and H. Kokubun, *Bull. Chem. Soc. Jpn.*, **47** (1974) 1331.
- 21 J. B. Birks, *Photophysics of Aromatic Molecules*, Interscience, New York, 1970, p. 304.
- 22 D. M. Rayner and P. A. H. Wyatt, *J. Chem. Soc. Faraday Trans. 2*, **70** (1974) 945.

- 23 N. Fuson, P. Pineau and M. L. Josien, *J. Chim. Phys.*, 55 (1958) 454.
- 24 J.-P. Grivet and M. Ptak, *C.R. Acad. Sci., Ser. B*, 265 (1967) 972.
- 25 D.M. Findlay and M. F. Tchir, *J. Chem. Soc. Faraday Trans. 1*, 72 (1976) 1096.
- 26 M. Grimaud, M. Loudet, R. Roger and G. Pfeister-Guillougo, *Bull. Soc. Chim. Fr.*, (1974) 1161.
- 27 A. A. Lamola, in P. A. Leermakers and A. Weissberger (eds.), *Technique of Organic Chemistry*, Vol. 14, Interscience, New York, 1969, p. 102.
- 28 R. W. Anderson, Jr., R. M. Hochstrasser, H. Lutz and G. W. Scott, *Chem. Phys. Lett.*, 28 (1974) 153.
- 29 L. Lutz and L. Lindquist, *Chem. Commun.*, (1971) 493.
- 30 A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43 (1965) 2129.
- 31 R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, 67 (1971) 1904.
- 32 T. G. Pavlopoulos, *J. Opt. Soc. Am.*, 63 (1973) 180.