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Further study on intramolecular hydrogen-atom transfer originating from the lowest excited triplet state of 2-methylbenzophenone

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Abstract

Sub-picosecond to nanosecond laser photolysis of the title compound (MBP) at room temperature reveals that its lowest excited triplet state probably with the form *cis*-^{3}MBP*, undergoes intramolecular hydrogen atom transfer from the methyl group to the carbonyl oxygen. The lowest excited triplet *cis*-^{3}BR* and then *trans*-^{3}BR* 1, 4-radicals thus generated convert to the ground-state *cis*-DE and *trans*-DE, respectively. At room temperature, both the dienols revert to MB but extremely rapid reversion of *trans*-DE in ethanol compared with that in acetonitrile or benzene is tentatively ascribed to double-proton transfer through ethanol-bridged two hydrogen bonds (cf. Scheme 2). At 77 K, steady-state photolysis of MBP yields *trans*-DE as a stable product but its nanosecond excitation gives rise to the appearance of no emission and transient absorption spectra responsible for the lowest excited singlet or triplet state of *trans*-DE. This indicates that *trans*-^{3}BR* (generated from *cis*-^{3}MBP* via *cis*-^{3}BR* → *trans*-^{3}BR* conversion) is different from the lowest excited triplet state of *trans*-DE. By measurements of the phosphorescence and its excitation spectra after steady-state photolysis of MBP or *trans*-DE at 77 K, it is proposed that the non-emissive lowest excited singlet or triplet state of *trans*-DE yields the keto form of dihydroanthrone (DHA); at a higher temperature than 77 K, this keto form reverts to MBP via DHA and then *trans*-DE.

Keywords: Intramolecular hydrogen-atom transfer; 2-Methylbenzophenone

1. Introduction

For photoinduced formation of the thermally unstable *cis* and *trans*-dienols (DE) of 2-methylbenzophenone (MBP) [1–6], Uji-Ie et al. [7] proposed that both the lowest excited triplet states (^{3}MBP*) with *cis* and *trans* forms underwent intramolecular hydrogen-atom transfer (from the methyl group to the carbonyl oxygen) generating the corresponding lowest excited triplet 1, 4-biradicals (^{3}BR*) or dienols (^{3}DE*) as the intermediates. In contrast, Das and Scaiano [8] proposed that only *cis*-^{3}MBP* generated *cis*- and *trans*-^{3}BR* (or ^{3}DE*) in equilibrium. About 14 years ago [9], we thus performed picosecond-nanosecond laser photolysis of MBP and concluded that the scheme proposed by Das and Scaiano [8] was more reliable than that proposed by Uji-Ie et al. [7].

The transient absorption spectra obtained at that time by nanosecond laser photolysis were recorded traditionally by separate measurements of absorptions at a number of desired wavelengths, each following a single laser shot, i.e. point-to-point measurements. The probing light intensity transmitted by the sample was detected by a photomultiplier and the trace of the resulting electrical waveform on the screen of an oscilloscope was recorded photographically. A hand-drawn plotting of the calculated absorbance at a given wavelength was then performed and these operations had to be repeated at each monochromator setting. Since some inaccuracy and arbitariness were unavoidable for the absorption spectra recorded by such a conventional handmade work, and since the transient absorption spectra ascribed to the super-position of absorptions responsible for the *cis* and *trans* forms of ^{3}BR* and those responsible for the corresponding ground-state dienols were very weak and not well resolved, the point-to-point measurements were not satisfactory enough for the detailed spectroscopic discussion.

As a further study on the excited-state dynamics of MBP, therefore, the present paper deals with the following subjects: (1) measurements of the singlet–singlet absorption band due to the lowest excited singlet state (^{1}MBP*) of MBP and determination of the ^{1}MBP$^* \rightarrow ^3$ MBP* intersystem crossing time by sub-picosecond laser photolysis, because our previous picosecond laser photolysis revealed that the triplet–triplet absorption band due to ^{3}MBP* appeared

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within a duration (30 ps) of excitation pulse; (2) re-investigation of intramolecular hydrogen-atom transfer originating from ^{3}MBP* using a nanosecond laser photolysis system equipped with a multichannel analyzer; (3) excitation of the *trans*-dienol (*trans*-DE) formed by steady-state photolysis of MBP at 77 K in order to find out whether *trans* ^{3}BR* is identical with the lowest excited triplet state of *trans*-DE or not.

2. Experimental details

MBP (Aldrich) and GR-grade benzophenone (Wako) were recrystallized three times from ethanol (at 196 K) and ligroin (at room temperature), respectively. The solvents used were acetonitrile, benzene, ethanol, methylcyclohexane, 2-methyltetrahydrofuran and a mixed solvent (EPA) of diethyl ether : isopentane (2-methylbutane) : ethanol = 5 : 5 : 2, in volume ratio. Although spectral-grade benzene (Dojin) and methylcyclohexane (Dojin), and Uvasol diethyl ether (Merck) were used without further purification, GR-grade 2-methylbutane (Wako) was purified by passing it through an alumina column, and spectral-grade acetonitrile (Dojin) and ethanol (Nacalai) were dried using a molecular sieve 3A (Wako); under a nitrogen atmosphere, GR-grade 2-methyltetrahydrofuran (Wako) was refluxed in the presence of calcium hydride and then distilled. The sample solution used for sub-picosecond laser photolysis in a flow cell of 2 mm path length was deoxygenated by bubbling of AR gas, while those used for nanosecond laser photolysis and steady-state photolysis in a cell of 10 mm path length were degassed by several freeze-pump-thaw cycles.

Sub-picosecond laser photolysis was performed by a pump-probe method using a laser photolysis system comprising a femtosecond mode-locked Ti:sapphire oscillator (Tsunami, model 3960) and a regenerative amplifier (model TSA-50) from Spectra-Physics [10]. The third harmonic light pulse (267 nm) was used for sample excitation and the white-light continuum generated by focusing the fundamental light pulse (800 nm) into water was used as the probing and reference light pulses. The former light pulse (after passing through the sample cell) and the latter light pulse were imaged separately onto the entrance slits of the corresponding polychromator-image sensor detector systems. In practice, 100-times accumulated intensity spectra of the probing and reference light pulses were recorded at various delay-line settings for calculation of the transient absorption spectra, i.e. the absorbance spectra corrected for the group velocity dispersion of the probing light pulse. The time-zero point and the instrumental time constant ($\tau_I = 0.25$ ps) were determined by 620 nm absorbance measurements of the singlet–singlet absorptions originating from the lowest excited singlet state of 9,10-dibromoanthracene in cyclohexane at various delay-line settings; τ_I was a full width at the half-maximum intensity (FWHM) of a Gaussian function (an instrumental response function) assumed for both the excitation and probing light pulses.

Nanosecond laser photolysis was carried out using the 355 nm third harmonic (FWHM = 5 ns) from a Nd^{3+}:YAG laser (Continuum Surelight I) and the transient absorption spectra were recorded using a multichannel analyzer composed of a polychromator (Unisoku M200), an image intensifier (Hamamatsu V3347U) and a linear position-sensitive detector (Unisoku USP501) controlled by a personal computer [11]; the decay curves of transient absorptions and phosphorescences were analyzed by means of a combination of a photomultiplier (Hamamatsu R329 or R666) with a storage oscilloscope (Iwatsu TS-8123).

Steady-state photolysis at 77 K was performed using the 313 or 405 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp, and the absorption and phosphorescence (and its excitation) spectra were recorded using a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 spectrophosphorimeter, respectively.

3. Results and discussion

Fig. 1 shows the absorption spectral change upon 313 nm steady-state photolysis of MBP at 77 K in EPA, i.e. not only the absorption band (P) due to the photoproduct but also that (R) due to the reactant increases with increasing photolysis time; identical results are also obtained in methylcyclohexane and 2-methyltetrahydrofuran, and the increment of band R upon photolysis can be ascribed to the superposition of band R and the tail of band P. After photolysis, elevation of temperature up to room temperature causes the disappearance of band P as well as decrement of band R and the absorption spectrum recorded after re-cooling the sample solution down to 77 K is found to be completely identical with that recorded before photolysis of MBP at 77 K[1]. The behavior of band P stated above is very similar to that of the absorption band due to 9-hydroxy-1,10-anthraquinone-1-methide [14] or 9-hydroxy-4-methyl-1,10-anthraquinone-1-methide [15] formed by intramolecular hydrogen-atom transfer originating from both the lowest excited singlet and triplet states of 1-methylanthraquinone or 1,4-dimethylanthraquinone, respectively. We thus believe that the photoproduct responsible for band P is the ground-state dienol (with the *trans* form as discussed later) reverting to the original ketone (MBP) at a higher temperature than 77 K. In fact, Ullman and Huffman [3] also observed a similar absorption spectral change upon steady-state photolysis of MBP in 2-propanol at 193 K and concluded that the photoproduct(s) was the ground-state dienol(s).

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[1] In accordance with these results, no band P can be seen upon steady-state photolysis of MBP at room temperature and the resulting absorption spectral change is similar to that observed for benzophenone. Since its lowest excited triplet state is well known to abstract a hydrogen atom from the solvent yielding benzpinacol as the final product [12,13], we believe that the lowest excited triplet state of MBP at room temperature yields a small amount of dimethylbenzpinacol; a similar result was also reported by Heindel et al. [4].

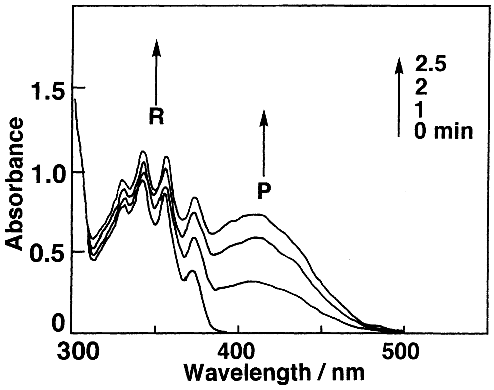


Fig. 1. Absorption spectral change upon 313 nm steady-state photolysis of MBP at 77 K in EPA.

The emission spectrum shown in Fig. 2(a) is obtained for MBP at 77 K in EPA. This spectrum can safely be attributed to the phosphorescence originating from the lowest excited triplet state (^{3}MBP*) of MBP, because the spectral profile is very similar to that of the phosphorescence spectrum obtained for the lowest excited triplet state (^{3}BP*) of benzophenone (BP) with a typical $n\pi^*$ character and a lifetime of 5.6 ms [16]; however, this lifetime is somewhat longer than that ($\tau_P = 3.0$ ms) determined from the single-exponential phosphorescence decay curve shown in Fig. 2(b). As shown in Fig. 2(c), nanosecond laser photolysis of MBP at 77 K in EPA gives rise to the appearance of a transient absorption spectrum similar to the triplet–triplet ($T_n \leftarrow T_1$) absorption spectrum reported for ^{3}BP* [16]. Furthermore, Fig. 2(d) indicates that the transient absorption monitored at 520 nm appears within a duration of nanosecond pulse excitation and then decreases following a single-exponential function with a lifetime ($\tau_T = 3.0$ ms) equal to the phosphorescence lifetime ($\tau_P = 3.0$ ms). The spectrum shown in Fig. 2(c) can thus be attributed to the $T_n \leftarrow T_1$ absorption due to ^{3}MBP*.

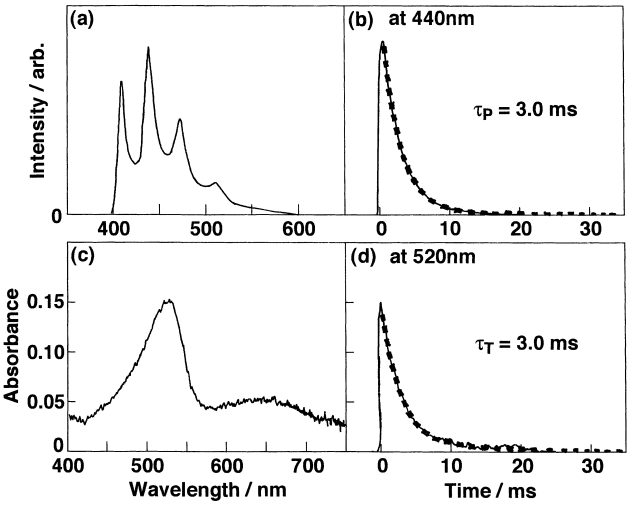


Fig. 2. (a) The phosphorescence spectrum and (b) its decay curve (—), and (c) the $T' \leftarrow T_1$ absorption spectrum and (d) its decay curve (—) obtained for MBP at 77 K in EPA. In (b) and (d), the dashed curves are the single-exponential functions with a life time of $\tau_P = \tau_T = 3.0$ ms.

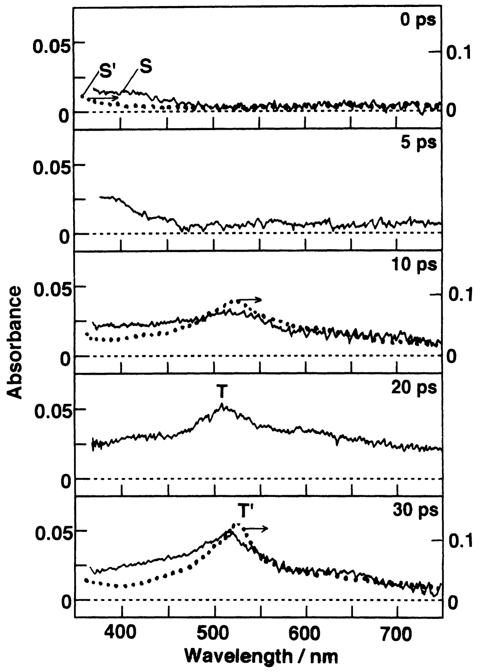


Fig. 3. Transient absorption spectra at short delay times obtained by sub-picosecond laser photolysis of MBP (—) and BP (···) at room temperature in ethanol.

Fig. 3 shows the transient absorption spectra at short delay times (solid lines) obtained by sub-picosecond laser photolysis of MBP at room temperature in ethanol. Clearly, band S appears at first and then decreases accompanied with the appearance of band T which is identical with the $T_n \leftarrow T_1$ absorption band due to ^{3}MBP* (cf. Fig. 2 (c)). Furthermore, the time-dependent absorbance changes of bands S and T (open circles monitored at 390 and 520 nm, respectively) shown in Fig. 4 indicate that band S appears within a duration of pulse excitation and its single-exponential decrease (with a decay time of $\tau_D = 5$ ps) is accompanied with the rate matching increase (with a rise time of $\tau_R = 5$ ps) of band T. For comparison, sub-picosecond laser photolysis of BP at room temperature in ethanol are also performed and the typical transient absorption spectra obtained are shown by the dotted lines in Fig. 3. In this case, it is found that the decay time of band S′ is equal to the rise time of band T′, i.e. 9 ps which is almost equal to the rise time (8 ps) of $T_n \leftarrow T_1$ absorption obtained for ^{3}BP* at room temperature in heptane by Anderson et al. [17] using a picosecond laser photolysis system. In Fig. 3, however, no absorption maximum of band S′ can be seen owing to the weak probing light intensities at wavelengths shorter than 360 nm, but the result of sub-picosecond laser photolysis obtained by Asahi et al. [18] revealed that the lowest excited singlet state (^{1}BP*) of BP at room temperature in 2,2,4-trimethylpentane had the singlet–singlet ($S_n \leftarrow S_1$) absorption band with an absorption maximum at 340 nm and a

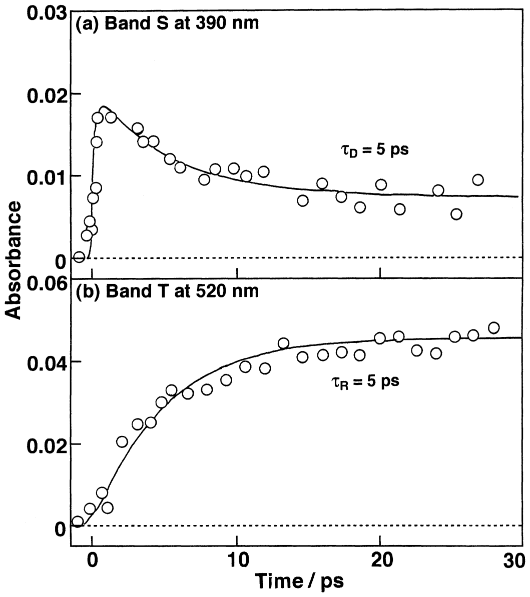


Fig. 4. (a) Decay of band S and (b) rise of band T with time (○) monitored at 390 and 520 nm, respectively. The solid curves are single-exponential functions with a decay (τ_D) or rise (τ_R) time of 5 ps.

lifetime of ≈10 ps. Hence, band S shown in Fig. 3 can safely be attributed to the $S_n \leftarrow S_1$ absorption originating from the lowest excited singlet state ($^1MBP^*$) of MBP. Although both the lowest excited singlet and triplet states of 1-methylanthraquinone [14], 1,4-dimethylanthraquinone [15] or [6]-1,4-cyclophaneanthraquinone [19] underwent intramolecular hydrogen-atom transfer, no transient absorption band reflecting intramolecular hydrogen-atom transfer originating from $^1MBP^*$ can be seen in Fig. 3. As shown in Fig. 5, however, a comparison of the transient absorption spectrum obtained at 0.9 ns delay with those obtained at delay times longer than 2 ns reveals that the decrement of band T (the $T_n \leftarrow T_1$ absorption band of $^3MBP^*$) is accompanied by the increment of band X. In fact, Fig. 6 indicates that the absorbance changes of bands X and T with time (open circles monitored at 410 and 520 nm, respectively) can be reproduced by the single-exponential functions (solid curves) with a rise (τ_R) or decay (τ_D) time of 2.5 ns.

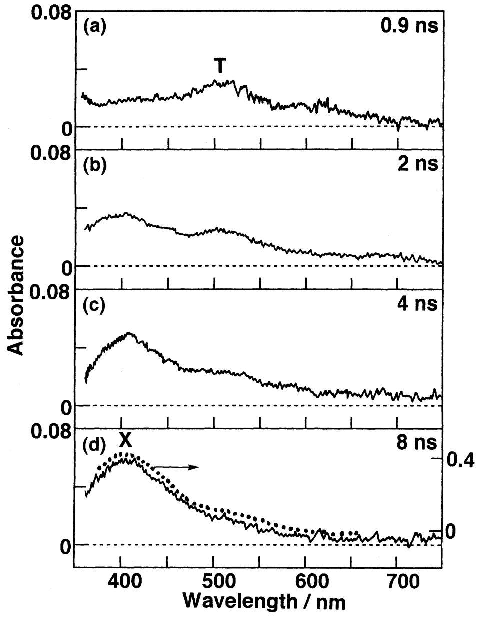


Fig. 5. Transient absorption spectra at long delay times (—) obtained by sub-picosecond laser photolysis of MBP at room temperature in ethanol. In (d), the dotted line is the normalized spectrum (spectrum A) obtained by nanosecond laser photolysis of MBP at 12 ns delay.

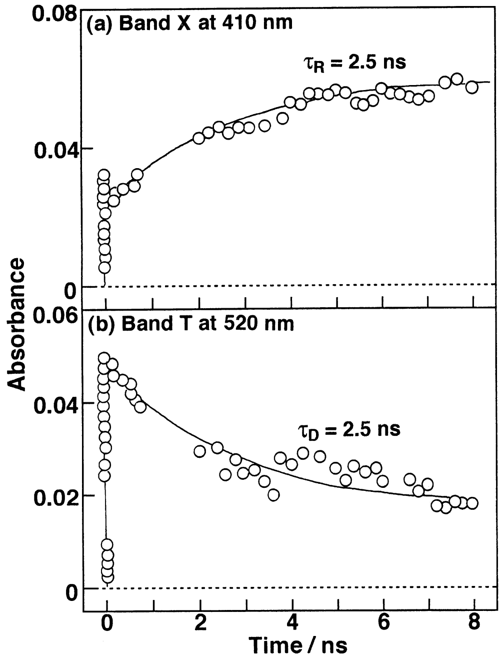


Fig. 6. Absorbance changes of bands (a) X and (b) T with time (○) monitored at 410 and 520 nm, respectively. The solid curves are the single-exponential functions with a rise (τ_R) or decay (τ_D) time of 2.5 ns.

In order to find out the detailed reaction kinetics originating from $^3MBP^*$, therefore, nanosecond laser photolysis of MBP at room temperature in ethanol is also performed and the results obtained are as follows: (i) The time-dependent A → B → C spectral changes can be seen as shown in Fig. 7 and, as shown in Fig. 5(d), normalization of spectrum A (the

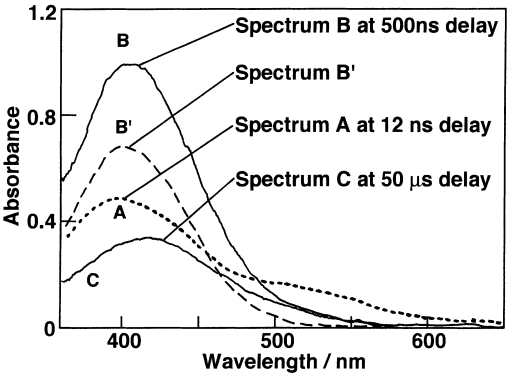


Fig. 7. Transient absorption spectra (A, B and C) obtained by nanosecond laser photolysis of MBP at room temperature in ethanol, where spectrum B′ is the difference spectrum between spectra B and C.

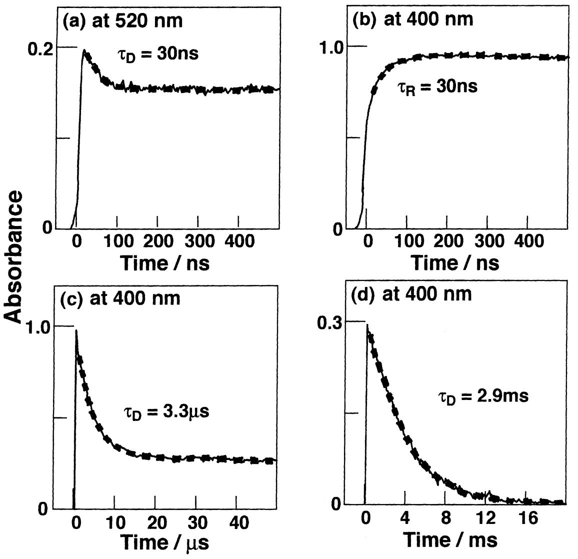
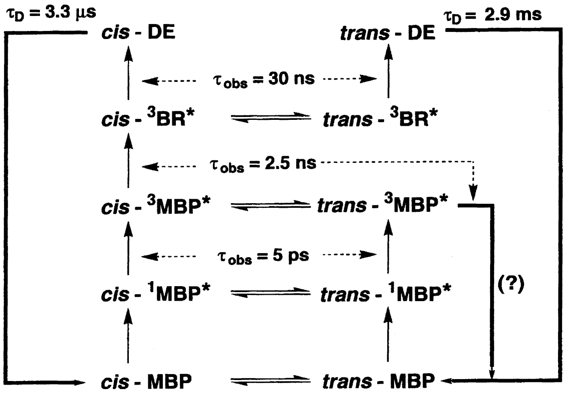


Fig. 8. Absorbance changes of spectra A, B and C with time (—) monitored at (a) 520 and (b–d) 400 nm. The dashed curves are the single-exponential functions with the decay (τ_D) or rise (τ_R) times indicated.

dotted line) to the solid spectrum (with band X) obtained by sub-picosecond laser photolysis at 8 ns delay reveals no spectral difference; spectrum C is very similar to the product absorption spectrum (with band P) obtained by steady-state photolysis of MBP at 77 K in EPA (cf. Fig. 1). (ii) The transient absorption monitored at 520 nm appears within a duration of nanosecond pulse excitation and then decreases to a constant absorbance following a single-exponential function with a lifetime ($\tau_D = 30$ ns) equal to the single-exponential rise time ($\tau_R = 30$ ns) of transient absorption monitored at 400 nm (cf. Fig. 8(a) and (b)), i.e. the time constant for the A → B spectral change is 30 ns. (iii) At much longer delay times, the transient absorption monitored at 400 nm decreases to a constant absorbance and then disappears following two single-exponential functions with lifetimes (τ_D) of 3.3 μs and 2.9 ms, respectively (cf. Fig. 8(c) and (d)); in Fig. 7, the difference spectrum (B′) between spectra B and C can thus be ascribed to the absorption due to a transient species with a lifetime of 3.3 μs.

Grimaud et al. [20] reported that over 70% of MBP had the *cis* form and Wagner [21] suggested the existence of kinetically independent *cis* and *trans* forms of ^{3}MBP*. In spite of these circumstances, the existence of rapid interconversion between the *cis* and *trans* forms of MBP, ^{1}MBP*, ^{3}MBP* or the lowest excited triplet 1,4-biradical (^{3}BR*) is reasonable, because no time-dependent spectral changes can be seen for bands S, T and X shown in Fig. 3 and Fig. 5; even if only the *cis* form of MBP is excited, one cannot neglect the possibility of rapid interconversion between the *cis* and *trans* forms of ^{1}MBP*. Hence, the time constant obtained for the single-exponential absorbance decrease or increase of band S, T or X (or spectrum A) can be expressed by $\tau_{obs} = (1 + K)/(k_c + Kk_t)$, where the decay rate constants of the *cis* and *trans* forms of a given transient species (^{1}MBP*, ^{3}MBP* or ^{3}BR*) are denoted by k_c and k_t, respectively, and $K = k'/k$ is the ratio of the rate constants for *cis* $k \rightleftharpoons k'$ transinterconversion [22]. Since all the results obtained so far by nanosecond laser photolysis in ethanol are consistent with our previous results using a photographic method [9] as well as those obtained by Suzuki et al. [23] using a time-resolved thermal lensing technique, the photophysics and photochemistry of MBP at room temperature in ethanol can be interpreted as follows (cf. Scheme 1):



Scheme 1.

(1) The decay or rise time ($\tau_D = \tau_R = 5$ ps) obtained for band S or T shown in Fig. 3 is the experimental time constant (τ_{obs}) defined previously as a function of the rate constants for *cis*-^{1}MBP* $\rightleftharpoons$ *trans*-^{1}MBP* interconversion as well as those for intersystem crossing from the *cis*(*cis*-^{1}MBP*) and *trans*(*trans*-^{1}MBP*) forms of ^{1}MBP* to the corresponding *cis*(*cis*-^{3}MBP*) and *trans*-^{3}MBP* forms of ^{3}MBP*. (2) In spite of the existence of rapid *cis*-^{3}MBP* $\rightleftharpoons$ *trans*-^{3}MBP* interconversion, only *cis*-^{3}MBP* may undergo intramolecular hydrogen-atom transfer (from the methyl group to the carbonyl oxygen) generating the *cis*(*cis*-^{3}BR*) and then *trans*(*trans*-^{3}BR*) forms of ^{3}BR*; band X (with a rise time of $\tau_{obs} = \tau_R = 2.5$ ns) shown in Fig. 5 and spectrum A (with a rise or decay time of $\tau_{obs} = \tau_R = \tau_D = 30$ ns) shown in Fig. 7 can thus be ascribed to the superposition of absorptions due to *cis*-^{3}BR* and *trans*-^{3}BR* existing in rapid interconversion[2]. (3) *cis*-^{3}BR* and *trans*-^{3}BR* convert to the *cis*(*cis*-DE) and *trans*(*trans*-DE) dienols followed by reversion to the original *cis*(*cis*-MBP) and *trans*(*trans*-MBP) ketones, respectively, i.e. in Fig. 7, spectra B′ and C are due to the absorptions of *cis*-DE (with a lifetime of $\tau_D = 3.3$ μs) and *trans*-DE (with a lifetime of $\tau_D = 2.9$ ms), respectively, and thus spectrum B is the superposition of spectra B′ and C.

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[2] Das and Scaiano [8] also proposed generation of *cis*-^{3}BR* and trans-^{3}BR* only from *cis*-^{3}MBP* but the existence of rapid *cis*-^{3}MBP* $\rightleftharpoons$ *trans*-^{3}MBP* interconversion was ruled out; however, the existence of rapid *cis*-^{3}BR* $\rightleftharpoons$ *trans*-^{3}BR* interconversion was proposed.

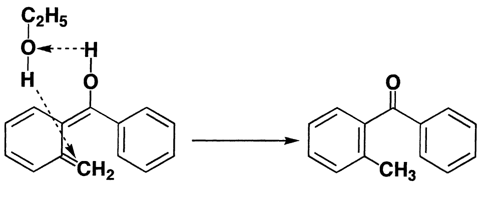
Table 1
Lifetimes (τ_{obs}) of *cis*- and *trans*-^{3}BR*, and those (τ_D) of *cis*- and *trans*-DE at room temperature in several solvents

Solvent	τ_{obc} (ns^{-1})	τ_D (μs^{-1})	τ_D (ms^{-1})
	cis- and *trans*-^{3}BR*	*cis*-DE	*trans*-DE
Ethanol ($\varepsilon = 24.6$)[a]	30	3.3	2.9
Acetonitrile ($\varepsilon = 37.5$)[a]	<20	1.3	990
Benzene ($\varepsilon = 2.275$)[a]	<20 (14)[b]	0.087 (0.077)[b]	840

[a] [24].
[b] [25].

At room temperature in acetonitrile and benzene, nanosecond laser photolysis of MBP reveals that not spectrum A but spectrum B appears even immediately after pulse excitation; naturally, both the B → C spectral change and the corresponding absorbance decreases of transient absorptions with time are found to be similar to those observed in ethanol. By comparison of the lifetimes of transient species obtained in ethanol with those obtained in acetonitrile and benzene (cf. Table 1), we suppose that the major solvent effect on the stability (or the reactivity) of a given transient species may be due to not the dielectric constant (ε [24]) but the hydrogen bonding; in Table 1, the lifetimes shown in parantheses were obtained by Ishida et al. [25] using a nanosecond pulse radiolysis technique. Extremely rapid *trans*-DE → *trans*-MBP reversion in ethanol compared with that in the other two solvents, however, can tentatively be ascribed to double-proton transfer through ethanol-bridged two hydrogen bonds (cf. Scheme 2).

By nanosecond laser photolysis of 2,4-dimethylbenzophenone, Haag et al. [26] observed that the decay time (30 ns) of the 535 nm absorption was equal to the rise time of the 420 nm absorption and concluded that the former absorption as due to the excited triplet states of the dienols. In many papers [7,9,23,25,27,28], one can also find a statement that the lowest excited triplet states of *o*-alkylbenzophenones undergo intramolecular hydrogen-atom transfer generating the lowest excited triplet states of either the 1,4 biradicals or the dienols. As stated previously, *trans*-DE is formed as the stable product by steady-state photolysis of MBP at 77 K in EPA, methylcyclohexane and 2-methyltetrahydrofuran, but neither emission not transient absorption responsible for the lowest excited singlet or triplet state of *trans*-DE can be detectable. In contrast, 355 nm nanosecond laser photolysis (performed after steady-state photolysis of MBP at 77 K in the solvents stated above) gives rise to the appearance of only the $T_n \leftarrow T_1$ absorption due to ^{3}MBP*, but the corresponding phosphorescence spectrum recorded by excitation at wavelengths between 320 and 370 nm is somewhat different from that of ^{3}MBP* in regard to the intensity ratios of emission peaks; of course, no phosphorescence can be seen by excitation at wavelengths between 410 and 470 nm. A typical phosphorescence spectrum (the solid line) obtained after 4 min steady-state photolysis of MBP at 77 K in EPA is shown in Fig. 9(a), where the corresponding phosphorescence lifetime (3.0 ms) is found to be equal to that of ^{3}MBP* which gives the dotted phosphorescence spectrum . As shown in Fig. 9(b), furthermore, the phosphorescence excitation spectrum (the solid line obtained after 4 min steady-state photolysis of MBP) is almost identical with the dotted one (which is the phosphorescence excitation spectrum of ^{3}MBP*) but clearly different from the absorption spectrum (the dashed line) of *trans*-DE. These results may suggest that solid spectrum shown in Fig. 9(a) can be ascribed to the phosphorescence originating from ^{3}MBP* superposed by the weak one orignating from the lowest excited triplet state of another product (P–X) formed upon excitation of *trans*-DE.



Scheme 2.

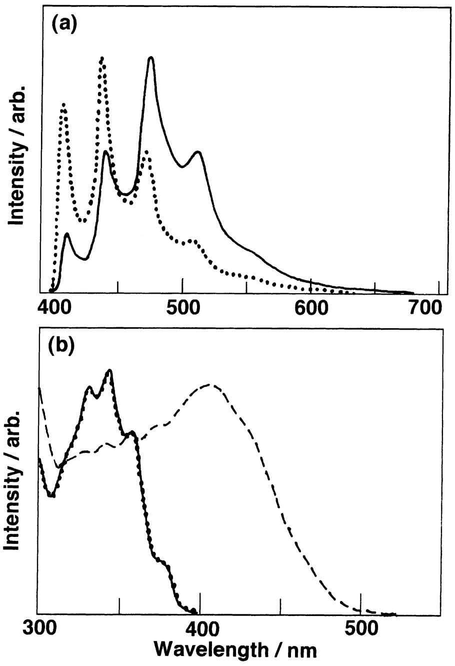


Fig. 9. (a) Phosphorescence and (b) its excitation spectra (—) recorded after 4 min steady-state photolysis of MBP at 77 K in EPA. The dotted spectrum in (a) is the phosphorescence spectrum of ^{3}MBP*, while the dashed and dotted spectra in (b) are the absorption and phosphorescence excitation spectra obtained for *trans*-DE and MBP, respectively.

Fig. 10 demonstrates that steady-state photolysis of *trans*-DE at 77 K in EPA causes the disappearance of band P. After then, elevation of temperature up to room temperature followed by re-cooling down to 77 K reveals that the resulting absorption, phosphorescence and its excitation spectra are identical with those obtained for MBP in regards

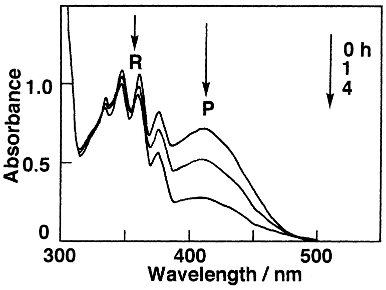


Fig. 10. Absorption spectral change upon 405 nm steady-state photolysis of *trans*-DE at 77 K in EPA.

to the spectral profile and intensity. This indicates that excitation of *trans*-DE at 77 K gives rise to formation of P–X which also reverts to MBP at a higher temperature than 77 K; similar results are also obtained in methylcyclohexane and 2-methyltetrahydrofuran. In connection with these results, for 2-methylbenzophenone and 2,4-dimethylbenzophenone, Ullman and Huffman [3], Heindal et al. [5] and Porter et al. [27,28] proposed that excitation of *trans*-DE gave rise to formation of dihydroanthrone (DHA) reverting thermally to *trans*-DE (cf. Scheme 3). In the presence of oxygen, furthermore, Ullman and Huffman [3] reported conversion of DHA to anthrone. In the absence of oxygen, we have observed no phosphorescence responsible for anthrone (and thus no fluorescence responsible for 9-anthrol [29]). Since no fluorescence responsible for DHA can also be seen, we propose that the non-emissive lowest excited singlet or triplet state of *trans*-DE yields P–X which is the keto form (K-1 or K-2) of DHA (cf. Scheme 3). P–X → MBP reversion occurring at a higher temperature than 77 K can thus be ascribed to thermal reversion of K-1 (or K-2) to *trans*-MBP via DHA and then *trans*-DE, and oxidation of DHA and/or K-1 (or K-2) by oxygen may yield anthrone and 9-anthrol in equilibrium.

In conclusion, we believe that *trans*-^{3}BR* (generated by intramolecular hydrogen-atom transfer of *cis*-^{3}MBP* followed by *cis* → *trans* conversion of *cis*-^{3}BR*) is different from the excited triplet state of *trans*-DE (formed by intersystem crossing from the lowest excited singlet state of *trans*-DE). Owing to no existence of *cis*-DE as a stable product even at 77 K, no experimental confirmation has been performed but *cis*-^{3}BR* may also be different from the excited triplet state of *cis*-DE.

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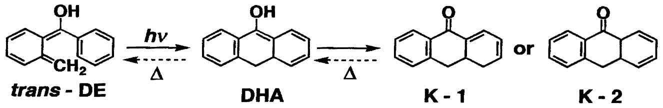

Scheme 3.

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