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# Recovery mechanism of the reaction intermediate produced by photoinduced cleavage of the intramolecular hydrogen bond of dibenzoylmethane

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## Abstract

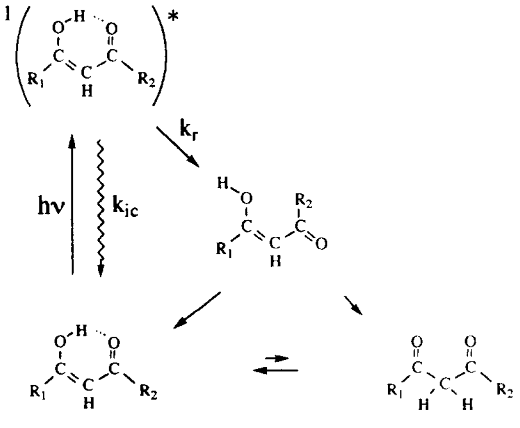
The recovery mechanism of the reaction intermediate (non- chelated enol form) produced by photoinduced cleavage of the intramolecular hydrogen bond of dibenzoylmethane was studied in various solvents by nanosecond laser flash photolysis. The recovery rate and mechanism depend strongly on the nature of the solvent. Unimolecular recovery of the intermediate to the chelated enol form takes place in acetonitrile, diethyl ether and dimethylsulphoxide with extremely small rate constants (1.1, 1.5 and 6.6 $s^{-1}$ respectively) despite the small activation energy (3.6 kcal $mol^{-1}$ in 3-methylpentane). The slow unimolecular recovery rate can be ascribed to the small frequency factor ($7.0 \times 10^5$ $s^{-1}$), i.e. the large negative entropy change for the formation of the chelated enol form. In non-polar aliphatic hydrocarbon solvents, a bimolecular recovery process via hydrogen-bond interactions between two intermediate molecules is included in addition to unimolecular recovery. In alcohols, a solvent-assisted recovery process by mutual hydrogen exchange between the intermediate and alcohol molecule(s) accelerates the recovery rate. Basic catalysts, e.g. KOH in ethanol and triethylamine in acetonitrile, increase the recovery rate considerably by an additional process through the enolate anion.

*Keywords:* Recovery mechanisms; Reaction intermediates; Photoinduced cleavage; Intramolecular hydrogen bond; Dibenzoylmethane

## 1. Introduction

1,3-Dicarbonyl compounds show keto–enol tautomerism. Considerable attention has been focused on the equilibrium populations of each tautomer in various solvents [1–6]. The keto/enol tautomer ratio depends on the nature of the α substituents, the nature of the solvents, the temperature and the presence of traces of proton acceptors and/or donors. In non-polar aliphatic hydrocarbon solvents, 1,3-dicarbonyl compounds exist mainly as the chelated enol form due to stabilization by an intramolecular hydrogen bond. The chelated enol form of 1,3-dicarbonyl compounds usually exhibits strong absorption bands in the UV region originating from π–π* transitions in the chelated quasi-aromatic π-electron system. Nevertheless, many 1,3-dicarbonyl compounds are almost non-fluorescent in solution, suggesting the presence of very efficient non-radiative processes from the lowest excited singlet state. Due to their large absorptivity and almost non-fluorescent nature, 1,3-dicarbonyl compounds can be used as photostabilization agents [7].

Veierov et al. [8–10] have reported the photoinduced hydrogen-bond cleavage and subsequent formation of a non-chelated enol form of 1,3-dicarbonyl compounds. Similar photochemical structural changes of 1,3-dicarbonyl compounds (malonaldehyde and acetylacetone) have also been studied by high-resolution Fourier transform IR (FTIR) spectrometry [11,12] and theoretical molecular orbital (MO) calculations [13]. Scheme 1 shows the photochemical



Scheme 1.

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formation of the non-chelated intermediate suggested by Veierov et al. [8–10], together with enol–diketo tautomerism. It has been suggested that this intermediate (non-chelated enol) reverts thermally to the original chelated enol form or tautomerizes to the corresponding diketones. It is expected that the chelated enol form will be relatively inert towards the surrounding solvent molecules, whereas the non-chelated intermediate will interact more strongly with solvents or additives such as proton acceptors and/or donors. Furthermore, participation of the intermediate in the enol–diketo tautomerism of 1,3-dicarbonyl compounds is also of interest. However, the details of the recovery mechanism and the transient interactions of the intermediate with the solvent molecules are not yet fully understood.

In this study, we chose dibenzoylmethane (DBM) as a typical 1,3-dicarbonyl compound. The recovery processes of the intermediate (DBM′), produced by laser photolysis at 355 nm, to the chelated enol form of DBM were studied in detail by measuring the transient absorption and bleaching spectra. From detailed analysis of the transient differential absorption spectra and their time profiles, various interactions of the intermediate with solvent molecules or additives (proton acceptors and donors) were revealed.

## 2. Experimental details

DBM (G.R. grade products, Tokyo Kasei) was purified by repeated recrystallization from *n*-hexane. Acetonitrile and chloroform were dried over molecular sieves 4A and distilled from $P_2O_5$. Traces of $P_2O_5$ were then removed by distillation from anhydrous $K_2CO_3$. Cyclohexane, *n*-hexane and 3-methylpentane were dried with sodium and fractionally distilled. Ethanol, methanol and 1-propanol were distilled from $CaH_2$. Diethyl ether (Infinity pure grade products, Wako) was used without further purification.

A nanosecond laser photolysis system, consisting of the third harmonic (355 nm; pulse width, 6 ns) of an $Nd^{3+}$:YAG laser (Spectra Physics GCR 130) and a 150 W Xe lamp, was used for measurement of the transient absorption spectra of DBM. The detection system has been described elsewhere [14]. Data analysis was performed on a personal computer (NEC PC9821Ap).

## 3. Results and discussion

### 3.1. Transient absorption spectra and recovery kinetics of the intermediate in non-polar aliphatic hydrocarbons

Table 1
Equilibrium constant $K$ for keto–enol tautomerism of DBM and recovery rate constants ($k_1$, $k_2^{ROH}$ and $k_2^{IM}$) of chelated DBM in various solvents at 293 K[a]

| Solvent | $K$[b] | $\epsilon$ | $k_1$ ($s^{-1}$) | $k_1^{ROH}$ ($s^{-1}$) | $k_2^{IM}$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| Acetonitrile | 12 | 35.94[c] | 1.1 | | |
| Diethyl ether | 30 | 4.335[d] | 1.5 | | |
| Dimethylsulphoxide | | 46.45[c] | 6.6 | | |
| Methanol | 24 | 32.66[c] | | $2.7 \times 10^3$ | |
| Methanol – $d_1$ | | | | $3.2 \times 10^3$ | |
| Ethanol | 26 | 24.55[c] | | $6.2 \times 10^2$ | |
| 1-Propanol | | 20.45[c] | | $7.6 \times 10^2$ | |
| Glycerol | | 42.5[c] | | $2.0 \times 10^2$ | |
| *n*-Hexane | 98 | 1.886[d] | 28 | | $3.6 \times 10^7$ |
| Cyclohexane | 89 | 2.023[d] | 12 | | $2.1 \times 10^6$ |
| Chloroform | 24 | 4.806[d] | 36 | | $2.0 \times 10^7$ |
| Paraffin | | | 76 | | $2.0 \times 10^7$ |

[a] For details, see text.
[b] Taken from Ref. [4].
[c] Dielectric constant at 298 K taken from Ref. [15].
[d] Dielectric constant at 293 K taken from Ref. [15].

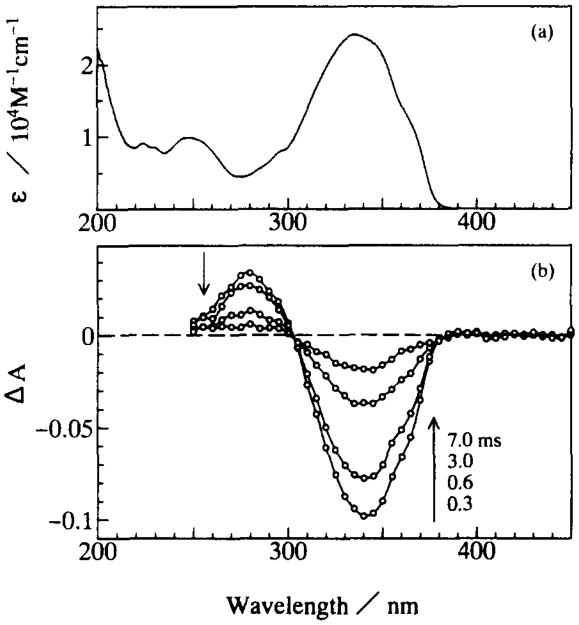


Fig. 1. (a) Absorption spectrum of DBM in *n*-hexane at 293 K. (b) Differential absorption spectra obtained by 355 nm laser flash photolysis of DBM in *n*-hexane at 293 K.

DBM exists as a keto/enol equilibrium mixture in solution. The keto/enol equilibrium content depends on the nature of the solvent. Moriyasu et al. [4] have recently reported the equilibrium constants ($K$ = [enol]/[keto]) for keto–enol tautomerism of DBM in various solvents at 25 °C using low-temperature high performance liquid chromatography (HPLC) (Table 1). The results show that DBM exists mainly in the chelated enol form in both non-polar and polar solvents, although the enol content is higher in non-polar solvents because of the strong intramolecular hydrogen bond. Fig. 1(a) shows the absorption spectrum of DBM in *n*-hexane at room temperature. The first absorption band at around 340 nm, which has a large molar extinction coefficient of $2.38 \times 10^4$ $M^{-1}$ $cm^{-1}$, can be assigned to a $\pi$–$\pi^*$ transition of the chelated enol form [16,17]. In spite of the large oscillator strength of the first absorption band, DBM is almost non-fluorescent in solution. This implies the presence of very rapid non-radiative processes in the excited singlet ($S_1$) state. Fig. 1(b) shows the transient differential absorption spectra obtained by 355 nm laser flash photolysis of DBM ($2 \times 10^{-5}$ M) in *n*-hexane at 293 K. The spectra consist of two bands: (1) ground state bleaching around 340 nm; (2) transient absorption band at 280 nm. The recovery rate to chelated DBM, monitored at 340 nm, and the decay rate of the transient absorption band at 280 nm are almost the same. Both rates are extremely slow as shown below. Furthermore, the dissolved oxygen in the sample solutions has no effect on the decay rates of bleaching or the absorption bands. These observations indicate that chelated DBM isomerizes rapidly to a short-lived intermediate from the $S_1$ state. The probable structure of the reaction intermediate is a geometrical isomer, i.e. a non-chelated enol form of DBM, as suggested by Veierov et al. [8–10].

In order to clarify the interactions of the transient intermediate with solvent molecules (or additives), the recovery time profiles at 340 nm were analysed in detail. Fig. 2 shows the recovery time profiles of DBM in *n*-hexane monitored at 340 nm at different laser intensities. The time profiles follow a mixed first- and second-order decay law. The contribution of the second-order component increases with increasing laser power as shown in Figs. 2(a)–2(c). The time-dependent absorbance change $\Delta A(t)$ can be fitted to Eq. (1)

$$\Delta A(t) = (k_1 \Delta A(0)\, e^{-k_1 t}) / [k_1 + 2k_2(\Delta A(0)/\epsilon_s)(e^{-k_1 t} - 1)] \qquad (1)$$

where $k_1$ and $k_2$ are the first- and second-order rate constants respectively, $\Delta A(0)$ is the initial absorbance at 340 nm just after the laser pulse and $\epsilon_s$ is the molar extinction coefficient at 340 nm ($2.38 \times 10^4$ $M^{-1}$ $cm^{-1}$) of the $S_1 \leftarrow S_0$ absorption band. By the least-squares fitting procedure, the best-fit rate constants, $k_1$ and $k_2$, were obtained as 28 $s^{-1}$ and $3.6 \times 10^7$ $M^{-1}$ $s^{-1}$ respectively. The time profiles calculated using these optimized $k$ values are in good agreement with the experimentally observed profiles as shown by the full lines in Fig. 2. These observations indicate that both unimolecular and bimolecular (including two intermediate molecules) recovery processes participate in the back reaction to the starting material in *n*-hexane. This intermolecular interaction between the non-chelated intermediates contrasts with the lack of a similar intermolecular hydrogen-bond interaction of the chelated enol DBM [18].

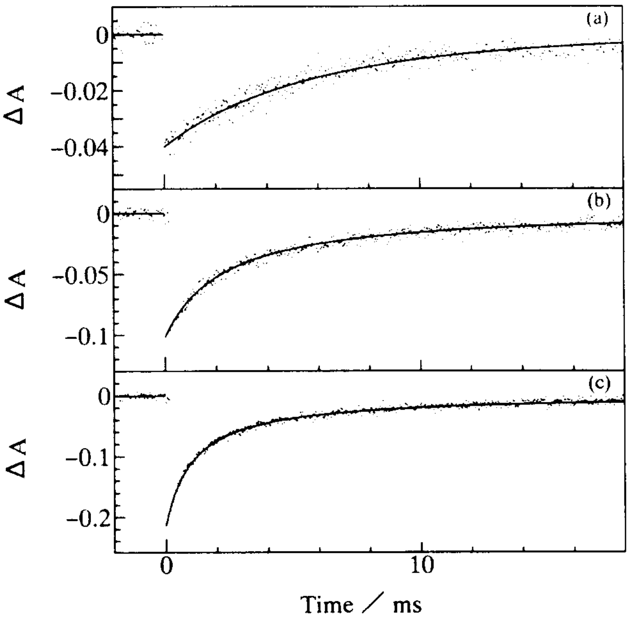


Fig. 2. Time traces of the differential absorption spectrum of DBM in *n*-hexane monitored at 340 nm at different laser intensities: (a) 6 mJ pulse$^{-1}$ cm$^{-2}$; (b) 15 mJ pulse$^{-1}$ cm$^{-2}$; (c) 23 mJ pulse$^{-1}$ cm$^{-2}$.

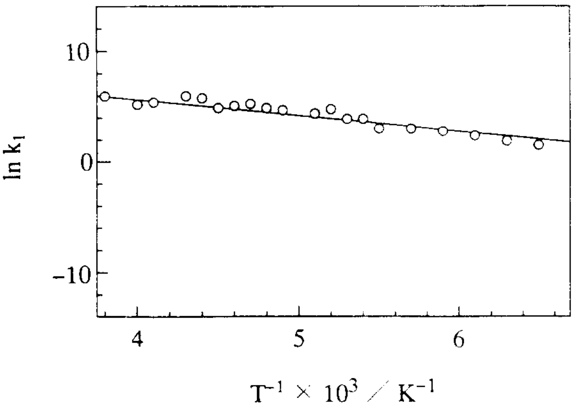


Fig. 3. Arrhenius plot of the unimolecular recovery rate constant of the intermediate to chelated DBM in 3-methylpentane.

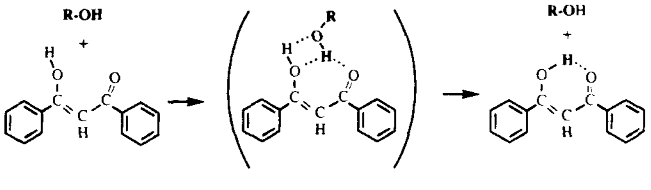
To reveal the thermodynamic properties of the unimolecular recovery process, the temperature dependence of the recovery rate of DBM was examined in 3-methylpentane. Fig. 3 shows an Arrhenius plot of the unimolecular recovery rate constant $k_1$ of DBM in 3-methylpentane. In the rate measurements, the laser intensities were lowered to eliminate the contribution of the bimolecular process. From the straight line in Fig. 3, the activation energy and frequency factor for the unimolecular recovery process were obtained as 3.6 kcal $mol^{-1}$ and $7.0 \times 10^5$ $s^{-1}$ respectively. The extremely small frequency factor is thought to be the main reason why the recovery process is very slow despite the relatively small activation energy (3.6 kcal $mol^{-1}$) of the isomerization. The small frequency factor for the unimolecular recovery process originates from the large negative entropy change for the formation of the chelated enol form.

### 3.2. *Solvent effects on the recovery rate of the intermediate*

The transient absorption spectra of DBM were measured in various solvents. The spectra in acetonitrile, diethyl ether, dimethylsulphoxide and alcohols are similar to those in aliphatic hydrocarbon solvents. However, the recovery rates and kinetics differ, depending on the nature of the solvents. In acetonitrile, diethyl ether and dimethylsulphoxide, the unimolecular process dominates the recovery to chelated DBM with extremely small rate constants of 1.1, 1.5 and 6.6 $s^{-1}$ respectively at 293 K. The small values are probably due to the relatively large dielectric constants of acetonitrile (35.94) and dimethylsulphoxide (46.45), resulting in destabilization of the product (chelated DBM), leading to a small enthalpy change. In the case of diethyl ether, the intermediate may be stabilized by hydrogen-bond formation with ether molecules, resulting in a suppression of the recovery rate. Of the solvents used in this study, the formation of the diketo tautomer by laser photolysis is found only in acetonitrile. The spectral change from the chelated enol form of DBM to the corresponding diketo form, with a characteristic absorption band at 243 nm, was also confirmed by steady state UV irradiation at 362 nm of chelated DBM in acetonitrile. The fact that photoinduced diketo formation is observed only in acetonitrile suggests that ketonization through the non-chelated enol form is more efficient than the direct process from the chelated enol form (Scheme 1).

In alcoholic solvents, the recovery process also follows first-order kinetics, and the rate constant increases strongly (about three orders of magnitude) compared with that in $CH_3CN$. The significant increase in the recovery rate constant in alcohols indicates that the interaction of the intermediate (non-chelated DBM) with alcohol molecule(s) assists the recovery process to chelated DBM. Therefore the re-formation of chelated DBM in alcohols is thought to follow pseudo-first-order kinetics with the rate constant represented by $k_1^{ROH} = k_1 + k_2[ROH]^n$. The values of $k_1^{ROH}$ in methanol and ethanol are $2.7 \times 10^3$ and $6.2 \times 10^2$ $s^{-1}$ respectively.

In order to determine the reason why alcohols facilitate the formation of the chelated enol form from the intermediate, the effects of methanol and deuterated methanol (methanol-$d_1$; $CH_3OD$) on the recovery rate were investigated by measuring the recovery profile at 340 nm of the transient differential absorption spectra of DBM. Fig. 4 shows the observed first-order recovery rate constant of chelated DBM ($2 \times 10^{-5}$ M) as a function of the methanol (or deuterated methanol) concentration in cyclohexane at 293 K. In both cases, with increasing $CH_3OH$ (or $CH_3OD$) concentration, the $k_1$ value begins to increase from a concentration of approximately $10^{-4}$ M and exhibits a maximum at around $10^{-2}$ M. In the concentration range higher than approximately $10^{-2}$ M, the rate constant declines because an increase in solvent polarity prevents hydrogen bonding between the intermediate and alcohol. Over the whole concentration range, a clear deuterium isotope effect on $k_1$ can be observed. These observations indicate that a mutual hydrogen exchange via intermolecular hydrogen bonding, as depicted in Scheme 2, accelerates the recovery rate. The recovery rate constants of chelated DBM obtained in various solvents are summarized in Table 1, where $k_1$ and $k_2^{IM}$ denote the first- and second-order recovery rate constants respectively and $k_1^{ROH}$ represents the pseudo-first-order recovery rate constant observed in alcohols.



Scheme 2.

### 3.3. Recovery processes in the presence of proton acceptors

The non-chelated enol form produced by excitation of chelated DBM possesses free hydroxyl and carbonyl groups which can interact with proton acceptors and/or donors added to the solution. The addition of a small amount of KOH in DBM–ethanol solution causes a spectral change from a KOH concentration of approximately $10^{-4}$ M. The first absorption band of chelated DBM, with a peak at 345 nm in ethanol, shifts to a longer wavelength with increasing KOH concentration due to the formation of the enolate anion ($DBM^-$). The absorption spectrum of $DBM^-$ at [KOH] = $1.0 \times 10^{-3}$ M is shown in Fig. 5, together with those of chelated DBM and the intermediate (DBM'). It should be noted that the extinction coefficient of the enolate anion (6300 $M^{-1}$ $cm^{-1}$) is larger than that of the chelated enol form (550 $M^{-1}$ $cm^{-1}$) at 385 nm. Fig. 6(a) shows the transient absorption spectra

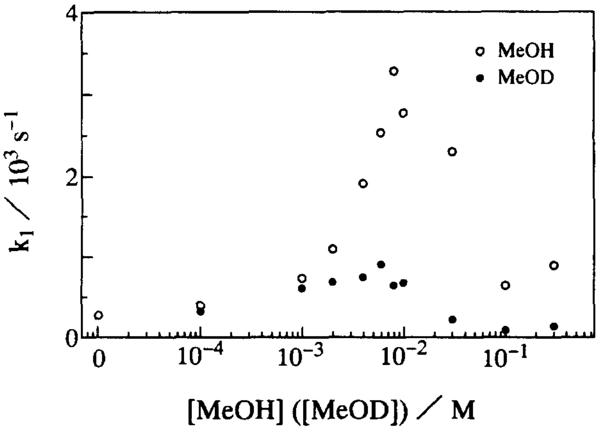


Fig. 4. Effect of $CH_3OH$ or $CH_3OD$ on the recovery rate of DBM ($2 \times 10^{-5}$ M) in cyclohexane at 293 K.

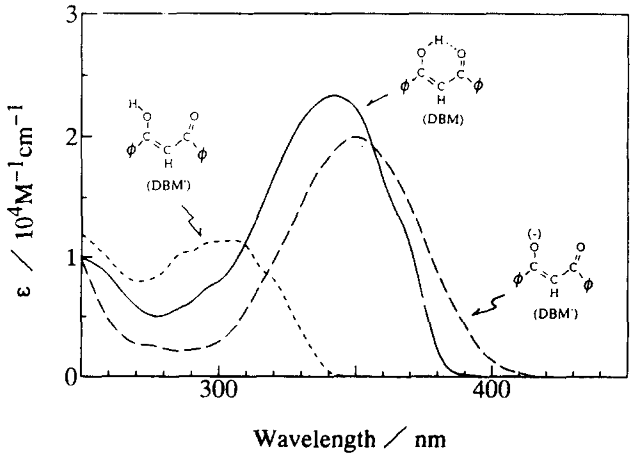


Fig. 5. Absorption spectra of chelated DBM, the enolate anion ($DBM^-$) at [KOH] = $10^{-3}$ M and non-chelated DBM (DBM').

of DBM in the presence of $7.5 \times 10^{-5}$ M KOH in ethanol. At $[\text{KOH}] = 7.5 \times 10^{-5}$ M, there is no significant change in the absorption spectrum of ground state DBM. With time, the band minimum is shifted to shorter wavelengths, and a new absorption band appears at 385 nm, showing the transient formation of the enolate anion during the recovery process in the presence of KOH in ethanol. The time profile monitored at 385 nm shows rise and decay components, and the recovery profile at 340 nm follows double-exponential kinetics.

The recovery mechanism of chelated DBM in the presence of KOH in ethanol is described in Scheme 3, where a consecutive recovery process through the enolate anion is taken into account. The rate constants for deprotonation from the intermediate and protonation to the enolate anion are given by Eqs. (2) and (3) respectively

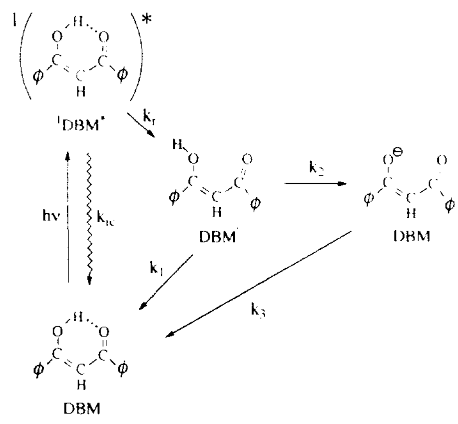
$$k_2 = k_2{}^0 + k_2{}^{\text{KOH}}[\text{KOH}] \tag{2}$$

$$k_3 = k_3{}^0 + k_3{}^{\text{KOH}}[\text{KOH}] \tag{3}$$

In Eqs. (2) and (3), $k_2{}^0$ and $k_3{}^0$ denote the deprotonation rate constant of DBM′ and the protonation rate constant of $\text{DBM}^-$ without KOH in ethanol, and $k_2{}^{\text{KOH}}$ and $k_3{}^{\text{KOH}}$ represent those induced by the presence of KOH. It is considered here that $k_3$ depends on the KOH concentration as a result of water molecules produced by the reaction of DBM′ with KOH. According to Scheme 3, the time-dependent absorbance change at wavelength $\lambda$, $\Delta A^\lambda(t)$, is given by using the concentrations of DBM, $\text{DBM}^-$ and DBM′ at the delay time $t$ as follows

$$\Delta A^\lambda(t) = -\epsilon_{\text{DBM}}{}^\lambda \Delta[\text{DBM}] + \epsilon_{\text{DBM}^-}{}^\lambda[\text{DBM}^-] + \epsilon_{\text{DBM}'}{}^\lambda[\text{DBM}'] \tag{4}$$

where $\epsilon_{\text{DBM}}{}^\lambda$, $\epsilon_{\text{DBM}^-}{}^\lambda$ and $\epsilon_{\text{DBM}'}{}^\lambda$ are the molar extinction coefficients of DBM, $\text{DBM}^-$ and DBM′ at wavelength $\lambda$, and $\Delta[\text{DBM}]$, $[\text{DBM}^-]$ and $[\text{DBM}']$ are the concentration change of chelated DBM and the concentrations of $\text{DBM}^-$ and DBM′ at the delay time $t$ respectively. The time dependence of $\Delta[\text{DBM}]$, $[\text{DBM}^-]$ and $[\text{DBM}']$ is given by



Scheme 3.

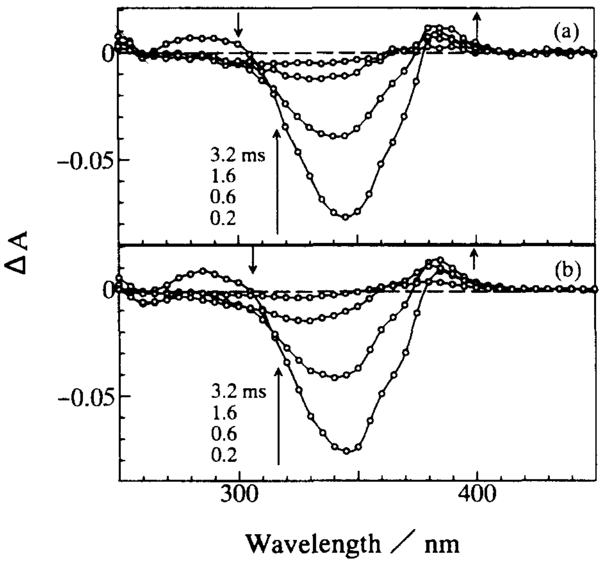


Fig. 6. (a) Differential absorption spectra obtained by 355 nm laser flash photolysis of DBM in the presence of $7.5 \times 10^{-5}$ M KOH in ethanol. (b) The simulated differential absorption spectra on the basis of Eqs. (4)–(7).

$$\Delta[\text{DBM}] = \frac{[\text{DMB}']_0}{k_1 + k_2 - k_3}[k_2\,\mathrm{e}^{-k_3 t} - (k_3 - k_1)\,\mathrm{e}^{-(k_1+k_2)t}] \tag{5}$$

$$[\text{DBM}^-] = \frac{k_2[\text{DBM}']_0}{k_1 + k_2 - k_3}[\mathrm{e}^{-k_3 t} - \mathrm{e}^{-(k_1+k_2)t}] \tag{6}$$

$$[\text{DBM}'] = [\text{DBM}']_0\,\mathrm{e}^{-(k_1+k_2)t} \tag{7}$$

where $[\text{DBM}']_0$ is the initial concentration of DBM′. Hence the time-dependent absorbance changes at 340 and 385 nm can be expressed by the following equations

$$\Delta A^{340}(t) = \frac{[\text{DBM}']_0}{k_1 + k_2 - k_3}\{(\epsilon_{\text{DBM}^-}{}^{340} - \epsilon_{\text{DBM}}{}^{340})k_2\,\mathrm{e}^{-k_3 t} + [\epsilon_{\text{DBM}}{}^{340}(k_3 - k_1) - \epsilon_{\text{DBM}^-}{}^{340}k_2]\,\mathrm{e}^{-(k_1+k_2)t}\} \tag{8}$$

$$\Delta A^{385}(t) = \frac{\epsilon_{\text{DBM}^-}{}^{385}k_2[\text{DBM}']_0}{k_1 + k_2 - k_3}[\mathrm{e}^{-k_3 t} - \mathrm{e}^{-(k_1+k_2)t}] \tag{9}$$

It can be expected from Eqs. (8) and (9) that the time trace at 340 nm will follow double-exponential kinetics with rate constants $(k_1 + k_2)$ and $k_3$, and that at 385 nm rise and decay components will be observed. Indeed, the time traces monitored at 340 and 385 nm are consistent with Eqs. (8) and (9). By carrying out numerical fitting procedures for the recovery time trace, monitored at 340 nm, of chelated DBM with $[\text{KOH}] = 7.5 \times 10^{-5}$ M, the rate constants $k_2$ and $k_3$ were determined to be $2 \times 10^3$ and $5 \times 10^2\ \text{s}^{-1}$ respectively. Fig. 6(b) shows the calculated time-resolved absorption spectra of DBM using these $k_2$ and $k_3$ values. The calculated transient absorption spectra agree well with the observed spectra in Fig. 6(a), indicating that the recovery mechanism described in Scheme 3 is reasonable in the present system. This provides corroborative evidence for enolate ion formation during the course of the recovery process to chelated DBM in the presence of KOH in ethanol. The effect of KOH was examined at various concentrations. Fig. 7 shows plots

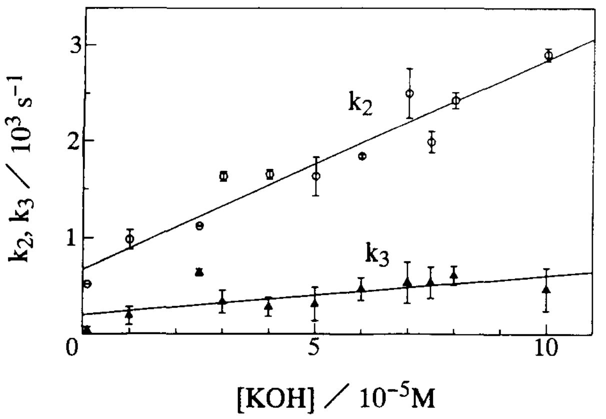


Fig. 7. Effect of KOH concentration on the values of $k_2$ and $k_3$ of DBM in ethanol at 293 K.

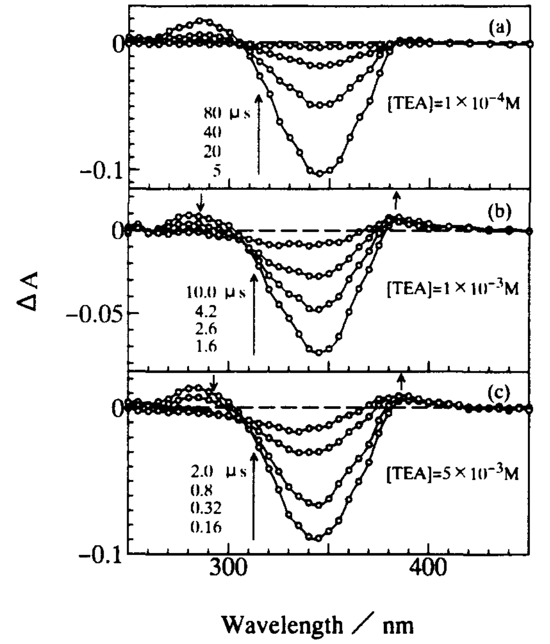


Fig. 8. Transient differential absorption spectra obtained by 355 nm laser flash photolysis of DBM in the presence of triethylamine in acetonitrile at 293 K: (a) [TEA] = $1\times10^{-4}$ M; (b) [TEA] = $1\times10^{-3}$ M; (c) [TEA] = $5\times10^{-3}$ M.

Table 2
Rate constants of base-assisted recovery processes of DBM at 293 K

| Additive (X) | Solvent | $k_2^{X}$ [a] ($10^7$ M$^{-1}$ s$^{-1}$) | $k_3^{X}$ [a] ($10^6$ M$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| KOH | Ethanol | 2.2 | 3.9 |
| TEA | Acetonitrile | 34 | 6.2 |

[a] $k_2^X$ and $k_3^X$ denote $k_2^{KOH}$ (or $k_2^{TEA}$) and $k_3^{KOH}$ (or $k_3^{TEA}$) respectively.

of the observed $k_2$ and $k_3$ values as a function of [KOH]. The linear dependence on the KOH concentration can be confirmed for both $k_2$ and $k_3$, and the values of $k_2^{KOH}$ and $k_3^{KOH}$ were obtained as $2.2\times10^7$ and $3.9\times10^6$ M$^{-1}$ s$^{-1}$ respectively.

A similar effect of additives was observed by adding a small amount of triethylamine (TEA) to the system in acetonitrile. Fig. 8 shows the transient absorption spectra of DBM in the presence of $(0.1–5)\times10^{-3}$ M TEA in acetonitrile. With an increase in [TEA], the recovery rate increases significantly, and the absorption band due to the formation of DBM$^-$ appears at around 385 nm. The rate constants $k_2$ and $k_3$ are given by

$$k_2 = k_2^0 + k_2^{TEA}[TEA] \tag{10}$$

$$k_3 = k_3^0 + k_3^{TEA}[TEA] \tag{11}$$

in a similar manner as for KOH in ethanol. Here the protonation rate ($k_3$) to DBM$^-$ is considered to be affected by [TEA], because the magnitude of $k_3$ depends on the concentration of protonated TEA produced by the deprotonation process of DBM′. The values of $k_2^{TEA}$ and $k_3^{TEA}$ were obtained as $3.4\times10^8$ and $6.2\times10^6$ M$^{-1}$ s$^{-1}$ respectively. The rate constants of the base-assisted recovery processes are listed in Table 2. Although the magnitude of $k_3^{TEA}$ in acetonitrile is almost comparable with that of $k_3^{KOH}$ in ethanol, the value of $k_2^{TEA}$ is much larger than that of $k_2^{KOH}$, indicating that TEA acts as a stronger catalyst in the recovery process through the enolate anion DBM$^-$.

The effect of proton donors on the recovery rate was also examined using acetic acid in ethanol. However, the addition of acetic acid in the concentration range $10^{-5}$–$10^{-2}$ M in ethanol scarcely increased the recovery rate of DBM. Therefore basic catalysts were found to be more effective in accelerating the re-formation of chelated DBM.

## 4. Concluding remarks

(1) On excitation of the chelated enol DBM in solution, the non-chelated intermediate (DBM′) is produced rapidly from the $S_1$ state. The intermediate reverts thermally to the original chelated form with solvent-dependent rate constants.

(2) In acetonitrile, diethyl ether and dimethylsulphoxide, the re-formation of chelated DBM from the intermediate follows unimolecular kinetics with extremely small rate constants (1.1, 1.5 and 6.6 s$^{-1}$ respectively at 293 K). Of the solvents used in this study, the photochemical formation of the diketo form is observed only in acetonitrile to a small extent.

(3) The activation energy and frequency factor for the recovery process of chelated DBM in 3-methylpentane are 3.6 kcal mol$^{-1}$ and $7.0\times10^5$ s$^{-1}$ respectively. The extremely small recovery rate can be attributed to the small frequency factor, i.e. the large negative entropy change for the formation of chelated DBM from DBM′.

(4) In non-polar aliphatic hydrocarbons, the bimolecular recovery process due to hydrogen-bond interactions between two intermediate molecules is involved in addition to the unimolecular process.

(5) In alcohols, the solvent-assisted recovery process by mutual hydrogen exchange increases the re-formation rate of chelated DBM.

(6) Basic catalysts, such as KOH in ethanol and triethylamine in acetonitrile, accelerate the recovery rate significantly. An additional recovery process through the enolate anion ($DBM^-$) of DBM is confirmed by kinetic analysis based on the transient absorption spectra.

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