ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 143 (2001) 153–159

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photoinduced hydride transfer reaction between methylene blue and leuco crystal violet

Yingjin Liu, Shunzo Yamamoto*, Yoshimi Sueishi

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

Received 27 April 2001; received in revised form 19 June 2001; accepted 10 July 2001

Abstract

The photoinduced hydride transfer reaction between methylene blue (MB^+) and leuco crystal violet (CVH) was investigated spectrophotometrically under conditions of direct excitation of MB^+ with steady-illumination of visible light and of photosensitization by benzophenone (BP) and α-nitronaphthalene (NNP) with UV light. It was found that upon the irradiation of the solution of MB^+ and CVH with visible light, MB^+ disappeared and crystal violet (CV^+) formed simultaneously. The ratio of the CV^+ concentration formed to that of MB^+ consumed was unity. The photosensitized reactions by NNP gave similar results. From the findings that the fluorescence of MB^+ was not quenched by CVH and the triplet photosensitizations were observed, it was concluded that the hydride transfer reaction in acetonitrile occurs in the triplet state of MB^+. The quantum yield for the disappearance of MB^+ in acetonitrile was estimated to be 1.1×10^{-4} and it was independent of CVH concentration. The electron transfer from CVH to triplet methylene blue ($^3MB^{+*}$) and the back electron transfer within the geminate radical pair must occur effectively. A spin adduct of a radical formed during the reaction was detected by the ESR method with 2-methyl-2-nitrosopropane (MNP) as a radical trap. This radical was attributed to $CV^\bullet$. The results can be explained by a mechanism with stepwise electron–proton–electron transfers. In *tert*-butyl alcohol, however, it was observed that the fluorescence of MB^+ was quenched by CVH and the quantum yield of the disappearance of MB^+ depended on CVH concentration. Different mechanism from that in acetonitrile was proposed for the reaction in *tert*-butyl alcohol.

Keywords: Photoinduced hydride transfer; Methylene blue; Leuco crystal violet; Steady-illumination photolysis; Stepwise transfer mechanism

1. Introduction

Although some hydride transfer reactions have been believed to proceed through stepwise electron–proton–electron transfer pathway [1–7], for hydride transfer reactions between NAD^+ analogues in which the reactants and products have the same charge type and are structurally similar, one-step mechanism of the type shown in Eq. (1) is proposed [8–12]

$$A_i^+ + A_jH \rightarrow A_iH + A_j^+ \qquad (1)$$

Recently, we have studied the kinetics of the reactions of leuco methylene blue (MBH) and leuco thionine (TH) with some *p*-benzoquinones [13] and ferric ion (Fe^{3+}) [14] and reported that these reactions proceed through stepwise hydride transfer pathways. However, the reaction between MBH and thionine (T^+) was found to be a reversible one-step hydride transfer [15].

Many studies have been reported on the photoreduction of methylene blue (MB^+) with various organic reducing agents by steady-irradiation photolysis or by flash photolysis. Nemoto et al. [16] used direct and sensitized photoreduction of MB^+ to determine intersystem crossing probability for MB^+. In the case of aromatic compounds for which the standard free energy change (ΔG°_{et}) of electron transfer from these compounds to triplet MB^+ is negative, the electron transfer was found to occur and produce semireduced MB^+ ($MB^\bullet$). Vogelmann et al. [17] and Kikuchi et al. [18] found that the rate constant for the electron transfer in the triplet state can be correlated to ΔG°_{et}. Neumann et al. [19] studied the photoreduction of MB^+ in the presence of arylaminomethanesulfonates ($RC_6H_5NH_2CH_2SO_3^-$) and found a relationship between the rate constants for the quenching of MB^+ triplet and ΔG°_{et}. They also pointed out that a second order decay rate constant for the $MB^\bullet$ is attributed to a proton transfer from the radical zwitterion ($RC_6H_5N^+H_2CH_2SO_3^-$) to $MB^\bullet$. Timpe and Neuenfeld [20] and Manring et al. [21] studied photochemistry of MB^+ with styrene and *trans*-stilbene, respectively. Since for styrene and stilbene the ΔG°_{et} values are positive for triplet

---

* Corresponding author. Tel.: +81-86-251-7835; fax: +81-86-251-7853.
E-mail address: yamashun@cc.okayama-u.ac.jp (S. Yamamoto).

1010-6030/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(01)00530-5

MB^+, photoreduction of MB^+ was not observed with these compounds of concentration at 10^{-4} M level. With higher concentration (0.1–5 M), however, the photoreduction was observed. They showed that the electron transfer occurs between singlet MB^+ and these compounds.

In these studies for photoreduction of MB^+ with organic reductants, the changes of species from MB^+ to MBH were mainly followed, but little was known for changes of reductants except for the formation of radical cation of aromatic compounds.

Seava and Olin [22] studied the pyrylium salt sensitized photooxidation of leuco crystal violet (CVH). They followed both changes in pyrylium salt and CVH and proposed the mechanistic scheme that shows a sequential electron–proton–electron transfer process.

Since it is well known that MB^+ acts as a hydride (or electron–proton–electron) acceptor and CVH as a hydride (or electron–proton–electron) donor, photochemistry of a mixture of MB^+ and CVH is expected to give information for the detailed reaction mechanism. The electrochemical properties of MB^+ and CVH indicate that an electron transfer from CVH to MB^+ is a thermochemically unfavorable process in the ground state, i.e. $\Delta G^{\circ}_{\mathrm{et}} = +1.09\,\mathrm{eV}$ ($+105\,\mathrm{kJ\,mol^{-1}}$). Solutions of MB^+ and CVH in some solvents are stable in the absence of light, i.e. the decrease in the concentration of MB^+ and formation of CV^+ could not be detected spectrophotometrically even after several days. Upon the irradiation of the solutions of MB^+ and CVH with visible light, the disappearance of MB^+ and the simultaneous formation of CV^+ were observed.

We report on the results of the photoinduced hydride transfer reaction from CVH to MB^+ studied in acetonitrile and *tert*-butyl alcohol with steady-illumination method.

2. Experimental

2.1. Materials

$MB^+ Cl^-$ and crystal violet ($CV^+ Cl^-$) were purchased from Wako Pure Chemical Industries and used as received. CVH, benzophenone (BP) and chloranil (CA) were purchased from Wako Pure Chemical Industries and used after recrystallization. α-Nitronaphthalene (NNP), allylthiourea (ATU) and 2-methyl-2-nitrosopropane (MNP) were purchased from Wako Pure Chemical Industries and used as received. Acetonitrile and *tert*-butyl alcohol were dried over a molecular sieve 3A-1/16 and distilled.

2.2. Kinetic measurements

For measurements of the rate of photoinduced hydride transfer reaction between MB^+ and CVH, solutions of MB^+ and CVH were deaerated by bubbling with nitrogen gas or degassed by four freeze–pump–thaw cycles. The solutions in a 10 mm quartz cell were irradiated with a 650 W projector lamp filtered through a Toshiba interference filter, KL-65, with maximum emission at 650 nm (band width at half-height, 20 nm), a wavelength at which radiation is absorbed only by MB^+. For the photosensitized hydride transfer reactions, solutions of MB^+, CVH and a sensitizer (BP or NNP) were deaerated by bubbling with nitrogen gas. They were irradiated with a 650 W projector lamp filtered through two filters (Toshiba glass filter, UV-35 and UVD36C); maximum emission at 365 nm (band width at half-height, 50 nm), a wavelength at which radiation is absorbed by BP or NNP.

Absorption spectra were measured at several reaction times under steady-illumination conditions at room temperature with a Hitachi 2001 spectrophotometer. Fluorescence spectra were measured at room temperature with a Shimadzu spectrofluorophotometer, model RF-1500. Excitation was effected at 650 nm in each case in order to prevent the interference of the products.

2.3. ESR measurement

Reaction solutions of MB^+ and CVH were introduced separately into an H-shaped tube with a side tube (i.d. 1 mm) for ESR measurements (when spin trapping was used, solutions of MB^+, CVH and MNP were introduced separately into three tubes). After the solutions were degassed by freezing and thawing under vacuum, the solutions were mixed and transferred into the side tube. After the mixed solution in the side tube was irradiated with visible light, ESR spectrum was measured with a JEOL JES-FE3XG spectrometer equipped with a 100 kHz field modulator and a TE 011 cavity.

3. Results

We have checked briefly whether thermal hydride transfer occurs between MB^+ and CVH. Spectra of solutions of MB^+ and CVH in dry acetonitrile did not change even after several days in the absence of light.

As mentioned above, upon the irradiation of the solutions of MB^+ and CVH with visible light, MB^+ disappeared and CV^+ formed. Fig. 1 shows the change in absorption spectrum for the reaction between MB^+ and CVH. A clean isosbestic point indicates the absence of significant concentration of any intermediate species. After 520 min of irradiation, it was found that MB^+ disappeared completely and the spectrum obtained at that time is consistent with that of CV^+. The straight line, which passes through the origin and has the slope of unity, was obtained between the CV^+ concentration formed (estimated using $\varepsilon = 10{,}400\,\mathrm{m^2\,mol^{-1}}$ at 589 nm for CV^+ and corrected for the small absorption by MB^+ at 589 nm) and the MB^+ concentration consumed (estimated using $\varepsilon = 8600\,\mathrm{m^2\,mol^{-1}}$ at 655 nm). Furthermore, the ratio of the CV^+ concentration formed at the time when MB^+ completely disappeared to the initial MB^+ concentration ($[CV^+]_\infty/[MB^+]_0$) is unity when CVH is in excess.

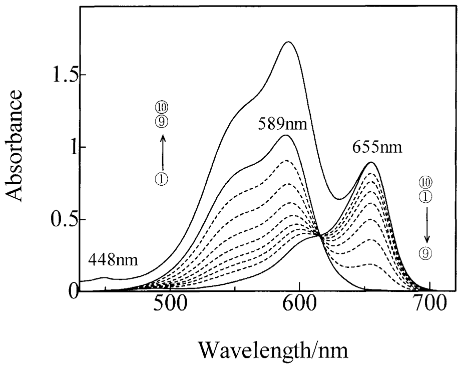


Fig. 1. Time dependence of the spectrum in the photoreaction between MB^+ and CVH in acetonitrile at room temperature ($[MB^+]_0 = 1.0 \times 10^{-5}$ M, $[CVH]_0 = 5.5 \times 10^{-4}$ M, $\lambda_{ex} = 650$ nm). Irradiation times are ① 0; ② 120; ③ 300; ④ 600; ⑤ 1200; ⑥ 2400; ⑦ 4800; ⑧ 9600; ⑨ 31,200 s; ⑩ after adding CA.

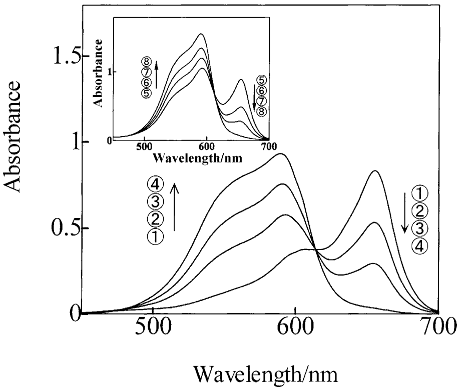
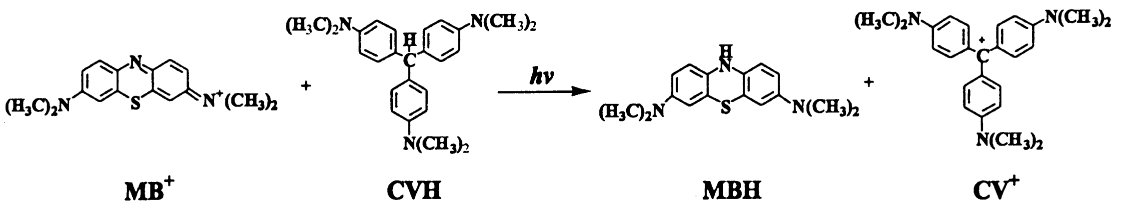


Fig. 2. Time dependence of the spectrum in the photoreaction between MB^+ and CVH in *tert*-butyl alcohol at room temperature ($[MB^+]_0 = 9.7 \times 10^{-6}$ M, $[CVH]_0 = 8.7 \times 10^{-4}$ M, $\lambda_{ex} = 650$ nm). Irradiation times are ① 0; ② 20; ③ 60; ④ 360 s. Inset: spectral change in the second cycle for the hydride transfer reaction starting from residual CVH and MB^+ recovered by oxidation of MBH with oxygen. Irradiation times are ① 0; ② 30; ③ 90; ④ 540 s.

Fig. 1 also shows that the MB^+ concentration was recovered almost quantitatively to the initial value by adding CA to the reaction mixture in which MB^+ disappeared completely (CV^+ also formed with oxidation of CVH by CA). Fig. 2 shows the change in absorption spectrum for the reaction between MB^+ and CVH in *tert*-butyl alcohol at several reaction times under excitation at 650 nm of a solution of MB^+ and CVH. The reaction is faster in *tert*-butyl alcohol than in acetonitrile. As the spectrum ⑤ in the inset of Fig. 2 shows, MB^+ fully recovered on aeration (CV^+ was not formed with oxidation by O_2). These findings show that the disappearance of MB^+ is due to its reduction to MBH. The cycle of photoreduction and recovery of MB^+ could be repeated several times with little loss of MB^+. The photoreduction in every cycle accompanied the nearly quantitative formation of CV^+. The spectral changes in the second cycle are shown in the inset of Fig. 2. Thus, the stoichiometry for the reaction can be given by the following equation.



(2)

In order to know that the hydride transfer from CVH to MB^+ occurs in the singlet or the triplet state, we carried out some measurements for fluorescence quenching of MB^+ by CVH and photosensitized reduction of MB^+ with CVH using BP and NNP.

Turro and coworkers [23] studied photoinduced energy and electron transfers between ketone triplet and some organic dyes. They pointed out that for the reaction of MB^+ with $^3BP^*$ in acetonitrile solution, triplet energy transfer effectively occurs. Jockusch and Timpe also obtained the same conclusion [24].

When BP was added to a MB^+/CVH solution and was excited at 365 nm, the photosensitized reduction of MB^+ was observed, but the formation of CV^+ was not clear (Fig. 3(a)). As is shown by the spectra of dashed lines in Fig. 3(a) which show the separation of the spectrum into two components, CV^+ exists in the reaction mixture, but its amount is smaller than expected. This may be due to the further reaction of CV^+ with $^3BP^*$ during the irradiation as discussed in detail by Jockusch and Timpe [24]. We also ascertained the disappearance of CV^+ by irradiation at 365 nm to the solutions of CV^+ and BP. Fig. 3(b) shows the spectral change of the photosensitized hydride transfer using NNP as another sensitizer. The decrease in MB^+ concentration and simultaneous formation of CV^+ are clear in Fig. 3(b). In the absence of sensitizers, no photoreduction of MB^+ was observed by the irradiation at this wavelength. The fluorescence of MB^+ was quenched by CVH in *tert*-butyl alcohol (Fig. 4(a)), but was little affected in acetonitrile.

The quantum yield (ϕ) of the photoreduction of MB^+ with CVH was estimated using the value of 1.2×10^{-2} for photoreduction of MB^+ by ATU in ethanol according to the method of Koizumi and coworkers [16,25]. The value of $\phi = 5.3 \times 10^{-4}$ was obtained in ethanol and this value was independent of the concentration of CVH in the range

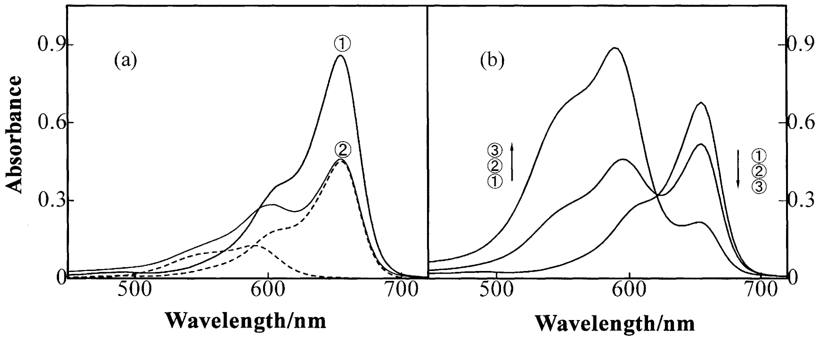


Fig. 3. (a) Change in spectrum for the reaction between MB^+ and CVH photosensitized by BP ($[MB^+]_0 = 1.0 \times 10^{-5}$ M, $[CVH]_0 = 3.4 \times 10^{-4}$ M, $[BP]_0 = 1.9 \times 10^{-3}$ M, $\lambda_{ex} = 365$ nm). Irradiation times are ① 0; ② 180 s. Dashed lines show the separation of the spectrum into two components. (b) Change in spectrum for the reaction between MB^+ and CVH photosensitized by NNP ($[MB^+]_0 = 7.9 \times 10^{-6}$ M, $[CVH]_0 = 5.5 \times 10^{-4}$ M, $[NNP]_0 = 7.3 \times 10^{-4}$ M, $\lambda_{ex} = 365$ nm). Irradiation times are ① 0; ② 300; ③ 900 s.

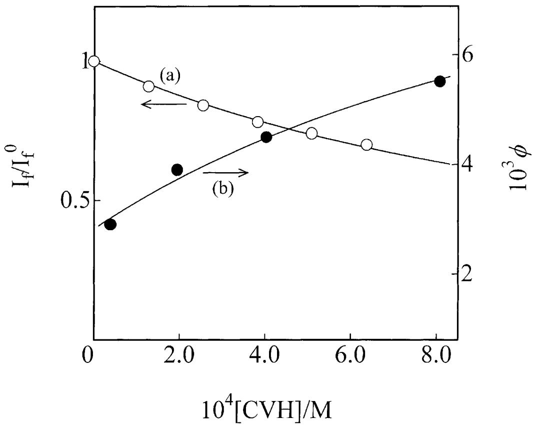


Fig. 4. Dependencies of (a) the fluorescence intensity of MB^+ ($\lambda_{ex} = 650$ nm) and (b) the quantum yield of the disappearance of MB^+ on the concentration of CVH. Solid lines show calculated values (see text).

of (1–10) $\times 10^{-4}$ M. The quantum yields in acetonitrile and *tert*-butyl alcohol were estimated by comparing the rates of disappearance of MB^+ in these solvents with that in ethanol. The quantum yield obtained in acetonitrile was $\phi = 1.1 \times 10^{-4}$ and was independent of the concentration of CVH in the rage of $(1\text{–}10) \times 10^{-4}$ M. However, ϕ in *tert*-butyl alcohol was found to be considerably larger than that in acetonitrile and ethanol, and to depend on the concentration of CVH in the range of (0.5–8.0) $\times 10^{-4}$ M (Fig. 4(b)).

4. Discussion

As mentioned above, the fluorescence of MB^+ was not quenched by CVH in acetonitrile and BP and NNP photosensitized the hydride transfer reaction from CVH to MB^+. These findings indicate that the hydride transfer reaction between MB^+ and CVH occurs in the triplet state of MB^+ (possibility of reaction in the singlet state cannot be excluded in *tert*-butyl alcohol). It was reported that many photoreductions of MB^+ with various reductants such as EDTA, ATU and so on proceed in the triplet state of MB^+ [16,19,25,26]. The photoreduction of MB^+ by styrene [20] however, is reported to proceed in the singlet state of MB^+, because the standard free energy change for electron transfer from styrene to triplet methylene blue ($^3MB^{+*}$) is positive and this process is thermodynamically unfavorable.

The standard free energy change of the electron transfer from CVH to $^3MB^{+*}$ can be estimated with the Rehm and Weller equation [27,28].

$$\Delta G^\circ_{et} = E(CVH^{\bullet+}/CVH)^\circ - E(MB^+/MB^\bullet)^\circ - E_{0,0} - E_{Coul} \qquad (3)$$

Here $E(CVH^{\bullet+}/CVH)^\circ$ is the oxidation potential of CVH (0.70 V versus SCE [29]), $E(MB^+/MB^\bullet)^\circ$ the reduction potential of MB^+ (−0.39 V versus SCE [18]), $E_{0,0}$ the excitation energy for the triplet state of MB^+ (1.44 eV [18]) and E_{Coul} is the Coulombic energy of solvation of the solvent-separated ions (which can be neglected in the present case, because products of electron transfer between MB^+ and CVH are $MB^\bullet$ and $CVH^{\bullet+}$). The value of ΔG°_{et} calculated is −0.35 eV (−33.7 kJ mol^{-1}). This supports the conclusion that the photoreduction of MB^+ occurs in the triplet state.

Kikuchi et al. [18] studied the electron transfer reaction between $^3MB^{+*}$ and aromatic compounds, and obtained the relationship between the rate constant and the standard free energy change of the electron transfer reaction in the triplet state. When ΔG°_{et} is less than −41.8 kJ mol^{-1}, the rate constant is the order of the diffusion-controlled rate. From the ΔG°_{et} value for MB^++CVH, the rate constant of the electron transfer reaction is estimated to be about 6×10^9 M^{-1} s^{-1} using the curve which shows the relationship between the rate constant and ΔG°_{et} given by Kikuchi et al. Since the lifetime of the triplet state of MB^+ is rather long (45 μs in water [30]), the electron transfer may occur almost exclusively from CVH to $^3MB^{+*}$ in the case of [CVH] $> 1 \times 10^{-4}$ M (conditions used in the present study).

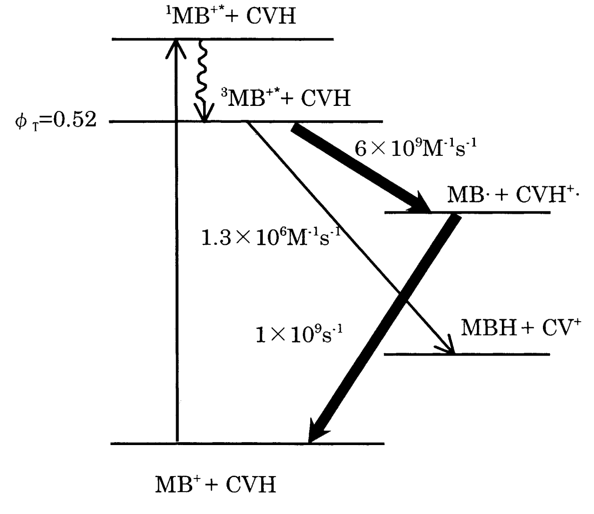
Grampp and Hetz [31] studied back electron transfers within geminate radical pairs formed by photoinduced electron transfer from several aromatic donors (D) to triplet thionine ($^3T^{+*}$), and gave the plot of the rate constant of back electron transfer versus the standard free energy change $\Delta G^\circ_{-\mathrm{et}}$ which was calculated from

$$\Delta G^\circ_{-\mathrm{et}} = E(\mathrm{T}^+/\mathrm{T}^\bullet)^\circ - E(\mathrm{D}^+/\mathrm{D})^\circ \tag{4}$$

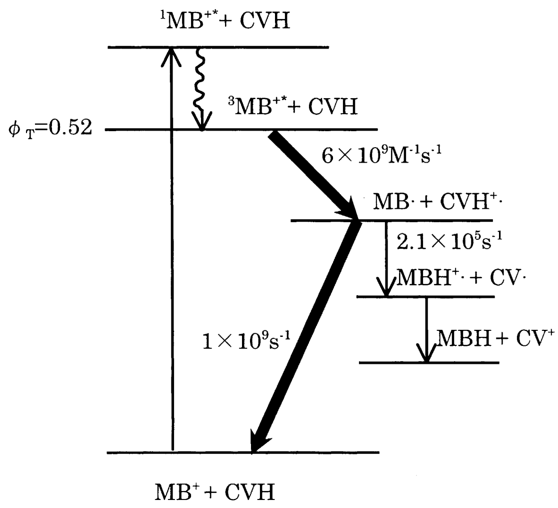
where $E(\mathrm{T}^+/\mathrm{T}^\bullet)^\circ$ is the reduction potential of T^+ and $E(\mathrm{D}^+/\mathrm{D})^\circ$ the oxidation potential of D. From the resemblance in the electronic and geometric structure between MB^+ and T^+, we can estimate the rough rate constant of back electron transfer for MB^+ from the value of $\Delta G^\circ_{-\mathrm{et}}$ using the plot which shows the relationship between the rate constant of back electron transfer and $\Delta G^\circ_{-\mathrm{et}}$ for T^+. We could obtain the value of about $1 \times 10^9\,\mathrm{s}^{-1}$ for $k_{-\mathrm{et}}$ using the value of -1.09 eV ($-105\,\mathrm{kJ\,mol}^{-1}$) for $\Delta G^\circ_{-\mathrm{et}}$.

As mentioned above, the electron transfer between $^3MB^{+*}$ and CVH and the back electron transfer within the geminate radical pair are fast and these processes must be the main processes. However, these reactions do not result in the hydride transfer from CVH to MB^+. The hydride transfer reaction may be rather a minor reaction in the present system; this is clear from the small quantum yield for the disappearance of MB^+ mentioned above.

Two mechanistic pathways must be considered as possibilities for the hydride transfer process. They are a direct hydride transfer and a stepwise electron–proton–electron transfer, as in the thermal hydride transfer reactions. These mechanisms are shown in Schemes 1 and 2.



Scheme 1.



Scheme 2.

In the former single-step mechanism, the hydride transfer process competes with the electron transfer process from CVH to $^3MB^{+*}$, and the quantum yield (ϕ) for the disappearance of MB^+ is given as follows:

$$\phi = \phi_{\mathrm{isc}} \frac{k_{\mathrm{H}}[\mathrm{CVH}]}{(1/\tau_{\mathrm{T}}) + k_{\mathrm{et}}[\mathrm{CVH}] + k_{\mathrm{H}}[\mathrm{CVH}]} \tag{5}$$

Here ϕ_{isc} is the quantum yield of intersystem crossing of $^1MB^{+*}$, τ_{T} the lifetime of triplet MB^+, and k_{et} and k_{H} are rate constants for electron and hydride transfer reactions. The rate constant for this hydride transfer process can be calculated to be $1.3 \times 10^6\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ using $\phi_{\mathrm{isc}} = 0.52$ [16], $\tau_{\mathrm{T}} = 45\,\mu\mathrm{s}$ [30], $k_{\mathrm{et}} = 6 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $\phi = 1.1 \times 10^{-4}$ (this corresponds to the observed one). In the previous study, we have estimated the rate constant for the thermal hydride transfer from TH to MB^+ and obtained the value of $8.3\times10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ [15]. Since the reactivity of CVH is lower than that of TH, but the reactivity of $^3MB^{+*}$ is much higher than that of MB^+, the value of $1.3 \times 10^6\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the reaction of $^3MB^{+*}$ with CVH seems to be possible.

In the latter multi-step mechanism, the proton transfer process in the geminate radical pair formed by the electron transfer step may compete with the back electron transfer process. If the quantum yield for the photoreduction of MB^+ is determined by the efficiencies of the intersystem crossing and the proton transfer step, it is expressed as follows:

$$\phi = \phi_{\mathrm{isc}} \frac{k_{\mathrm{p}}}{k_{-\mathrm{et}} + k_{\mathrm{p}}} \tag{6}$$

where $k_{-\mathrm{et}}$ and k_{p} are rate constants for back electron transfer and proton transfer within geminate radical pair. The value of $2.1 \times 10^5\,\mathrm{s}^{-1}$ for k_{p} was obtained by using values for ϕ_{isc} and $k_{-\mathrm{et}}$ mentioned above. In Schemes 1 and 2, the rate constants estimated are shown. The rate constants for steps included in the mechanism shown in Schemes 1 and 2 are all possible, and it is difficult to say which mechanism is more plausible from this point of view.

In the previous studies on flash photolysis of MB^+ in acetonitrile, transient absorption spectra of $^3MB^{+*}$ and the semireduced dye (MB$^\bullet$) were observed. In the present system, the formations of these species are major processes. However, the detection of these species are not conclusive factors to determine which scheme is more plausible, because these species are main intermediates in both reaction schemes. If MBH$^{\bullet +}$ (or CV$^\bullet$) can be detected, it can be said that Scheme 2 is better. As is shown in Scheme 2, however, MBH$^{\bullet +}$ is only minor species in the events from ^{3}MB^{+*} (if exists, the expected concentration of MBH$^{\bullet +}$ is 10^{-3} times less than those of ^{3}MB^{+*} and MB$^\bullet$), and it may be difficult to detect it even by flash photolysis.

In the reaction system of photoinduced hydride transfer from CVH to MB$^+$, no ESR signal was observed. This shows that stable radicals are not present in this system. Spin trapping is known to be a powerful method for detecting unstable neutral radicals. MNP is known as a spin trap. In order to obtain further information for radicals occurring in the present system, we added MNP to the MB$^+$/CVH system. Although the quantum yield of the photoreduction of MB$^+$ is very small, it seems to be possible to observe CV$^\bullet$ by spin trapping method, because main pathway is that goes back to the reactants (any side-reactions is neglected) and the spin adduct can be accumulated. A triplet with a hyper fine coupling constant (hfcc) of 1.60 mT and $g = 2.0058$ was observed and can be ascribed to a spin adduct. It was reported that ^{3}BP* reacts very effectively with CV$^+$ and produces CV$^\bullet$ radical by the electron transfer from ^{3}BP* to CV$^+$ [24]. Therefore, the triplet with a hfcc of 1.61 mT and $g = 2.0058$ obtained from photoreaction of BP/CV$^+$ system with MNP as a spin trap can be ascribed to the spin adduct of MNP with CV$^\bullet$. The ESR spectra observed in these systems are very similar. If the ESR signal shown obtained in MB$^+$/CVH system is identical to that obtained in BP/CV$^+$ system, it can be said that CV$^\bullet$ radical is present in MB$^+$/CVH system.

Saeva and Olin [22] reported that the photoexcited cation (2,4,6-tri-*p*-tolylpyrylium tetrafluoroborate) sensitized oxidation of CVH occurs by a sequential electron–proton–electron transfer process. The mechanism associated with the sequential electron–proton–electron transfer within the geminate pair as shown in Scheme 2 is probable also for the photoinduced hydride transfer between MB$^+$ and CVH in acetonitrile.

The photoreduction of MB$^+$ with CVH in *tert*-butyl alcohol shows several different aspects from that in acetonitrile. It was found that (1) the disappearance of MB$^+$ in *tert*-butyl alcohol is much faster than that in acetonitrile; (2) CVH quenches MB$^+$ fluorescence in *tert*-butyl alcohol (the possibility that the decrease in the intensity of MB$^+$ fluorescence found upon the addition of CVH in *tert*-butyl alcohol comes from the absorption of the exciting light by CV$^+$ formed in the fast reaction is excluded by the following fact that the absorption spectrum of the solution was little changed after the measurement of the fluorescence and the absorption coefficient of CV$^+$ at 650 nm is very small ($\varepsilon_{650}(\mathrm{CV}^+)/\varepsilon_{650}(\mathrm{MB}^+) \approx 0.05$); and (3) the quantum yield of disappearance of MB$^+$ depends on the concentration of CVH in the range of $(0.50–8.0) \times 10^{-4}$ M. These findings seem to show that the photoinduced hydride transfer from CVH to MB$^+$ in *tert*-butyl alcohol occurs in the singlet state of MB$^+$. Judging from the short lifetime of ^{1}MB^{+*} (345 ps in water [30]), however, it seems to be improbable that CVH in the concentration of 10^{-5} to 10^{-4} M order interacts with ^{1}MB^{+*} in the normal manner. Indeed, Timpe and Neuenfeld [20] used styrene of 5 M in the photoreduction of MB$^+$ by styrene which is reported to occur in the singlet state of MB$^+$. Therefore, static quenching through the formation of a complex between MB$^+$ and CVH in the ground state may be proposed to explain the observation in *tert*-butyl alcohol.

Hamai and Satou [32] observed that the fluorescence intensity of MB$^+$ reduced when Acid orange 7 (AO7) is added to an MB$^+$ aqueous solution in the low concentration of AO7 ([AO7] $= (0.1–1.0) \times 10^{-4}$ M). They proposed the formation of non-fluorescent 1:1 complex between MB$^+$ and AO7 in the ground state. In this system, the absorption spectrum of MB$^+$ also changes upon the addition of AO7. Neumann et al. [19] proposed the mechanism which includes the formation of a ground state ion pair for the photoreduction of MB$^+$ in the presence of arylaminomethanesulfonates. They reported that the absorption spectrum of the ion pair is similar to that of free MB$^+$.

Although the indication of interaction between MB$^+$ and CVH in the ground state was not obtained by the differential absorption spectra of a 9.0×10^{-6} M solution of MB$^+$ in *tert*-butyl alcohol with and without CVH in concentration of $(0.1–8.0) \times 10^{-4}$ M, the mechanism for the photoreduction of MB$^+$ in *tert*-butyl alcohol with the formation of non-fluorescent 1:1 complex between MB$^+$ and CVH (based on Scheme 2) was tentatively proposed to explain the fluorescence quenching and the concentration dependence of photoreduction rate.

$$\mathrm{MB}^+ + \mathrm{CVH} \xrightarrow{K} (\mathrm{MB}^+\mathrm{CVH})$$

$$\mathrm{MB}^+ + h\nu \xrightarrow{I_1} {}^1\mathrm{MB}^{+*}$$

$$(\mathrm{MB}^+\mathrm{CVH}) + h\nu \xrightarrow{I_2} ({}^1\mathrm{MB}^{+*}\mathrm{CVH})$$

$${}^1\mathrm{MB}^{+*} \xrightarrow{k_0} \mathrm{MB}^+ + h\nu_\mathrm{f}$$

$${}^1\mathrm{MB}^{+*} \xrightarrow{k_1} \mathrm{MB}^+$$

$${}^1\mathrm{MB}^{+*} \xrightarrow{k_2} {}^3\mathrm{MB}^{+*}$$

$$({}^1\mathrm{MB}^{+*}\mathrm{CVH}) \xrightarrow{k_\mathrm{et}^1} \mathrm{MB}^\bullet + \mathrm{CVH}^{\bullet +}$$

$$({}^1\mathrm{MB}^{+*} + \mathrm{CVH}) \xrightarrow{k_\mathrm{H}^1} \mathrm{MBH} + \mathrm{CV}^+$$

$${}^3\mathrm{MB}^{+*} + \mathrm{CVH} \xrightarrow{k_\mathrm{et}} \mathrm{MB}^\bullet + \mathrm{CVH}^{\bullet +}$$

$$\mathrm{MB}^\bullet + \mathrm{CVH}^{\bullet +} \xrightarrow{k_{-\mathrm{et}}} \mathrm{MB}^+ + \mathrm{CVH}$$

$$\mathrm{MB}^\bullet + \mathrm{CVH}^{\bullet +} \xrightarrow{k_\mathrm{p}} \mathrm{MBH}^{\bullet +} + \mathrm{CV}^\bullet$$

$$\mathrm{MBH^{\bullet +}CV^{\bullet}} \xrightarrow{k_4} \mathrm{MBH} + \mathrm{CV^{+}}$$

Here K is the equilibrium constant for the formation of the complex, I_1 and I_2 are the fractions of light intensities absorbed by free $\mathrm{MB^+}$ and the complex, respectively.

According to the above mechanism, the fluorescence intensity of $\mathrm{MB^+}$ is given as

$$I_\mathrm{f} = I_1 \frac{k_0}{k_0 + k_1 + k_2} \quad (7)$$

Since the molar absorption coefficient of the complex can be assumed to be the same as that of free $\mathrm{MB^+}$ from the comparison of absorption spectra of $\mathrm{MB^+}$ with and without CVH, I_1 and I_2 are expressed as follows:

$$I_1 \propto \varepsilon[\mathrm{MB^+}] \quad (8)$$

$$I_2 \propto \varepsilon[\mathrm{MB^+CVH}] \quad (9)$$

where ε denotes the molar absorption coefficient of $\mathrm{MB^+}$. Since $[\mathrm{MB^+}]$ and $[\mathrm{MB^+CVH}]$ in the equilibrium mixtures between $\mathrm{MB^+}$ and CVH are given as

$$[\mathrm{MB^+}] = \frac{1}{1 + K[\mathrm{CVH}]}[\mathrm{MB^+}]_\mathrm{t} \quad (10)$$

$$[\mathrm{MB^+CVH}] = \frac{K[\mathrm{CVH}]}{1 + K[\mathrm{CVH}]}[\mathrm{MB^+}]_\mathrm{t} \quad (11)$$

where $[\mathrm{MB^+}]_\mathrm{t}$ is the sum of $[\mathrm{MB^+}]$ and $[\mathrm{MB^+CVH}]$, the following equation is obtained

$$\frac{I_\mathrm{f}}{I_\mathrm{f}^0} = \frac{1}{1 + K[\mathrm{CVH}]} \quad (12)$$

where I_f^0 denotes the fluorescence intensity in the absence of CVH.

According to the above mechanism, the quantum yield of the disappearance of $\mathrm{MB^+}$ is expressed by the following equation.

$$\phi = \left(\frac{1}{1 + K[\mathrm{CVH}]}\phi_\mathrm{isc} + \frac{(1+\alpha)K[\mathrm{CVH}]}{1 + K[\mathrm{CVH}]}\right)\beta + \frac{K[\mathrm{CVH}]}{1 + K[\mathrm{CVH}]}\alpha \quad (13)$$

where $\alpha = k_\mathrm{H}^1/(k_\mathrm{et}^1 + k_\mathrm{H}^1)$ and $\beta = k_\mathrm{p}/(k_{-\mathrm{et}} + k_\mathrm{p})$.

In Fig. 4, the relative fluorescence intensity $(I_\mathrm{f}/I_\mathrm{f}^0)$ and the quantum yield (ϕ) of the disappearance on $\mathrm{MB^+}$ are shown as functions of [CVH]. The solid lines show the calculated values of $I_\mathrm{f}/I_\mathrm{f}^0$ and ϕ obtained using $K = 7.0 \times 10^2\,\mathrm{M^{-1}}$, $\alpha = 4.9 \times 10^{-3}$ and $\beta = 5.4 \times 10^{-3}$ with $\phi_\mathrm{isc} = 0.52$. These values are all probable. The above mechanism can explain the findings in *tert*-butyl alcohol. Although there is no direct evidence for the formation of the complex and the nature of the interaction between $\mathrm{MB^+}$ and CVH is not clear (London dispersion force and "hydrophobic bonding" may work as in the dimer formation of $\mathrm{MB^+}$ in aqueous solution [33]), in the complex assumed in the above mechanism, CVH may be loosely connected to the $\mathrm{MB^+}$ molecule by assistance of *tert*-butyl alcohol and can transfer an electron or a hydride ion to $^1\mathrm{MB^{+*}}$ during the short lifetime of $^1\mathrm{MB^{+*}}$.

References

[1] T. Okamoto, A. Ohno, S. Oka, Bull. Chem. Soc. Jpn. 53 (1980) 330.

[2] A. Ohno, H. Yamamoto, S. Oka, J. Am. Chem. Soc. 103 (1981) 2041.

[3] A. Ohno, T. Shio, H. Yamamoto, S. Oka, J. Am. Chem. Soc. 103 (1981) 2045.

[4] S. Fukuzumi, K. Hironaka, T. Tanaka, J. Am. Chem. Soc. 105 (1983) 4722.

[5] S. Fukuzumi, N. Nishizawa, T. Tanaka, J. Org. Chem. 49 (1984) 3571.

[6] M.F. Powell, J.C. Wu, T.C. Bruice, J. Am. Chem. Soc. 106 (1984) 3850.

[7] L.L. Miller, J.R. Valentine, J. Am. Chem. Soc. 110 (1988) 3982.

[8] R.M.G. Roberts, D. Ostovic, M.M. Kreevoy, Faraday Discuss. Chem. Soc. 74 (1982) 257.

[9] D. Ostivic, R.M.G. Roverts, M.M. Kreevoy, J. Am. Chem. Soc. 105 (1983) 7629.

[10] M.M. Kreevoy, A.T. Kotcherar, J. Am. Chem. Soc. 112 (1990) 3579.

[11] Y. Kim, D.G. Truhlar, M.M. Kreevoy, J. Am. Chem. Soc. 1138 (1991) 7837.

[12] I.H. Lee, E.H. Jeovrg, M.M. Kreevoy, J. Am. Chem. Soc. 119 (1997) 2722.

[13] S. Yamamoto, Y. Fujiyama, M. Shiozaki, Y. Sueishi, N. Nishimura, J. Phys. Org. Chem. 8 (1995) 805.

[14] Y.J. Liu, S. Yamamoto, Y. Sueishi, J. Phys. Org. Chem. 12 (1999) 194.

[15] Y.J. Liu, S. Yamamoto, Y. Fujiyama, Y. Sueishi, Phys. Chem. Chem. Phys. 2 (2000) 2367.

[16] M. Nemoto, H. Kokubun, M. Koizumi, Bull. Chem. Soc. Jpn. 42 (1969) 1223.

[17] E. Vogelmann, S. Schreiner, W. Rauscher, H.E.A. Kramer, Z. Physik. Chem. N.F. 101 (1976) 321.

[18] K. Kikuchi, S. Tamaru, C. Iwanaga, H. Kokubun, Y. Usui, Z. Phys. Chem. N.F. 106 (1977) 17.

[19] M.G. Neumann, J.I. Matthews, K.S. Braslavsky, Photochem. Photobiol. 39 (1984) 31.

[20] H.-J. Timpe, S. Neuenfeld, J. Chem. Soc., Faraday Trans. 88 (1992) 2329S.

[21] L.E. Manring, J. Eriksen, C.S. Foote, J. Am. Chem. Soc. 101 (1980) 4275.

[22] F.D. Saeva, G.R. Olin, J. Chem. Soc., Chem. Commun. (1976) 943.

[23] S. Jockusch, H.-J. Timpe, W. Schnabel, N.J. Turro, J. Phys. Chem. A 101 (1997) 440.

[24] S. Jockusch, H.-J. Timpe, J. Photochem. Photobiol. A: Chem. 63 (1992) 217.

[25] N. Kosui, K. Uchida, M. Koizumi, Bull. Chem. Soc. Jpn. 38 (1965) 1958.

[26] N.A. Evans, I.H. Leaver, Aust. J. Chem. 27 (1974) 1797.

[27] D. Rehm, A. Weller, Ber. Bunsenges. Physik. Chem. 73 (1969) 834.

[28] D. Rehm, A. Weller, Israel J. Chem. 8 (1970) 259.

[29] S. Yamamoto, T. Sakurai, Y.J. Liu, Y. Sueishi, Phys. Chem. Chem. Phys. 1 (1999) 833.

[30] S.J. Atherton, A. Harriman, J. Am. Chem. Soc. 115 (1993) 1816.

[31] G. Grampp, G. Hetz, Ber. Bunsenges. Phys. Chem. 96 (1992) 198.

[32] S. Hamai, H. Satou, Bull. Chem. Soc. Jpn. 73 (2000) 2207.

[33] K. Bergmann, C.T. O'Konski, J. Phys. Chem. 67 (1963) 2169.