Effect of concentrations of radical-ion intermediates in the photochemical redox reaction of the diphenylmethyl radical

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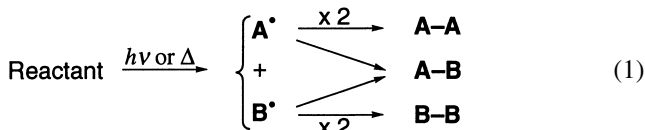
Abstract

Effect of concentrations of radical ion intermediates in photoinduced electron transfer (PET) reactions was examined for the redox reaction of diphenylmethyl radical. The irradiation of *sym*-tetraphenylacetone in the presence of aromatic donor and acceptor in MeOH–MeCN (1:9) leads to (i) the simultaneous generation of diphenylmethyl radical and a pair of radical ions, (ii) the electron transfers between them affording diphenylmethyl cation and anion, and (iii) the formation of Ph_2CHOMe and Ph_2CH_2 by the trapping reactions with methanol. The product ratios of Ph_2CH_2/Ph_2CHOMe are shown to be dominated by the steady-state concentrations of radical ions. Thus, pulsed irradiations resulted in quite different product ratios depending on the pulse intervals. The relative rates extrapolated to infinite, which are directly related to the intrinsic electron transfer rates with radical ions, are shown to follow the Rehm–Weller-type relationship. The importance of the persistent radical ion effect for PET reactions, just as the Ingold–Fischer persistent radical one, is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Persistent radical effect; Electron transfer; Diphenylmethyl radical; Radical ion; The Rehm–Weller relationship; Pulsed irradiation
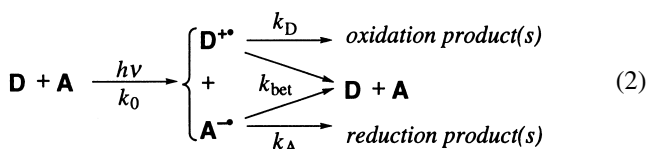
1. Introduction

When a thermal or photochemical reaction produces two free radicals, $A^\bullet$ and $B^\bullet$, in equal rates, the expected products are homo-couples, A–A and B–B, as well as cross-product (A–B) (Eq. (1)). If all the coupling reactions are diffusion-controlled,[1] two radicals exist in

$$\text{Reactant} \xrightarrow{h\nu \text{ or } \Delta} \begin{cases} A^\bullet \xrightarrow{\times 2} A\text{–}A \\ + \qquad\quad A\text{–}B \\ B^\bullet \xrightarrow{\times 2} B\text{–}B \end{cases} \quad (1)$$

identical steady-state concentrations, three products being formed in statistical yields of A–A:A–B:B–B=1:2:1. However, when homo-coupling of one radical is much slower than that of another, the steady-state concentration of more stable radical becomes quite high, and as a consequence the cross-coupling between $A^\bullet$ and $B^\bullet$ proceeds predominantly. Such conditions have been discussed by Fischer and co-

workers [2–5] and are now known as "the Ingold–Fischer persistent radical effect". A few examples have been presented in specific cases of radical reactions, e.g., thermal rearrangement of a coenzyme B_{12} model complex [6], cross-coupling of photochemically generated benzyl and ketyl radicals [7], and mixed peroxide formations from *tert*-butyl hydroperoxide with various substrates [8,9]. Despite its importance, this effect seems not to be well recognized since most of free radical reactions do not involve such highly persistent species. In photochemical reactions, intermediates usually exist in very low steady-state concentrations and therefore the effect of their concentrations has been virtually ignored [10].
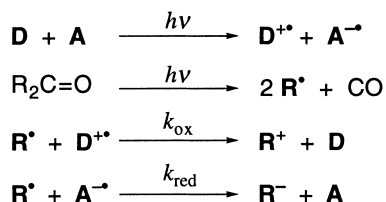
The persistent radical effect is a purely kinetic one, and hence the same treatment would be valid for other chemical systems as well. Typically, some photoinduced electron transfer (PET) reactions [11,12] (Eq. (2)) will satisfy the Ingold–Fischer condition, since (i) equal amounts

$$D + A \xrightarrow[k_0]{h\nu} \begin{cases} D^{+\bullet} \xrightarrow{k_D} \textit{oxidation product(s)} \\ + \quad \xrightarrow{k_{bet}} D + A \\ A^{-\bullet} \xrightarrow{k_A} \textit{reduction product(s)} \end{cases} \quad (2)$$

of radical cation and anion are generated simultaneously, and (ii) the relative lifetime of $D^{+\bullet}$ and $A^{-\bullet}$ may differ each

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[1] Because of the spin statistical effect [1], the maximum rate constants for radical dimerization or back electron transfer between radical ions are 1/4 of the actual diffusion controlled rates. For the simplicity, we use "diffusion controlled rate" for both meanings throughout this manuscript.

$$D + A \xrightarrow{\;h\nu\;} D^{+\bullet} + A^{-\bullet}$$

$$R_2C=O \xrightarrow{\;h\nu\;} 2\,R^{\bullet} + CO$$

$$R^{\bullet} + D^{+\bullet} \xrightarrow{\;k_{ox}\;} R^{+} + D$$

$$R^{\bullet} + A^{-\bullet} \xrightarrow{\;k_{red}\;} R^{-} + A$$

Scheme 1.

other depending on their stabilities. However, the direct determination of their steady-state concentrations, $[D^{+\bullet}]_{ss}$ and $[A^{-\bullet}]_{ss}$, is not possible because of too low concentrations.

Redox reactions of radical ions with easily oxidizable or reducible species may be an indicator of their intervention. Recently, we reported that the simultaneous generation of radical ions ($D^{+\bullet}$ and $A^{-\bullet}$) and benzyl-type radical ($R^{\bullet}$) by irradiating acetonitrile solutions involving donor (D), acceptor (A), and radical precursor lead to the efficient redox reactions [13]. Radicals were generated by photocleavage of appropriate ketones and could be oxidized or reduced by radical ions (Scheme 1) affording the corresponding carbocation R^{+} or carbanion R^{-}, respectively. In the presence of MeOH, the ions were trapped affording ROMe and RH, and from the resulting product ratios the relative efficiencies for the oxidation vs. reduction were examined. However, the efficiency in continuous photolysis may reflects not only the electron transfer rates but also the steady-state concentrations of the radical ions.

We wish to report here the results of further investigations on the redox of benzyl radicals, focusing on concentrations of radical ion intermediates. The results with continuous and pulsed irradiations have demonstrated the difference in the steady-state concentrations of radical ions under irradiations, and that the rates of the redox reactions follow the Rehm–Weller relationship.

2. Experimental

^{1}H NMR spectra were recorded with Varian GEMINI-200 (200 MHz) NMR spectrometers. GLC analyses were performed with a Shimadzu GC-14A gas chromatograph, using 2.5 mm×1 m column of Carbowax 300 M (2%) on Chromosorb WAW. Shimadzu Chromatopac C-R3A integrator was used for quantitative analyses. GC–MS analyses were carried out with a Shimadzu QP-5000 mass spectrometer using a 0.2 mm×25 m capillary column of CBP1-M50-025. Absorption spectra were recorded on a Shimadzu UV-265 ultraviolet spectrometer.

2.1. Materials

Acetonitrile was distilled from phosphorus pentoxide. Methyl alcohol (Dotite Spectrozol) and 4,4′-dimethyldiphenyl (DMD; Aldrich) were used as received. Naphthalene (Np), 2-methoxynaphthalene (MeONp), and 1-cyanonaphthalene (CN) were purified by recrystallizations. 2-Methylnaphthalene (MN) was received from Tokyo Kasei and distilled. sym-tetraphenylacetone (1) [14], dicyanodurene (TMDCB) [15], and 1,4-dicyanonaphthalene (DCN) [16] were prepared as reported.

2.2. Typical procedure of photolyses

Continuous irradiations were done with a 300 W medium pressure mercury lamp for sample solutions in 25 cm^3 Pyrex test tube, i.e., >300 nm, after purging with argon through rubber cap as described before [13]. A typical sample solution was 10 mM Np, 10 mM DCB, and 2 mM 1 in MeOH–MeCN (1:9) under argon. Products were identified by GC–MS, and yields were determined by GLC.

Pulsed irradiations were done with a Lambda Physik MINex excimer laser (XeCl, 308 nm, 10 ns, 15 mJ/pulse) as the excitation source and carried out by continuous flowing (4 cm^3/min) of sample solution through a $3\times1\times0.1$ cm^3 quartz cell. Typically, 200 cm^3 MeOH–MeCN (1:9) solution of 2.0 mM ketone 1, 10 mM Np, and 10 mM DCB was purged with argon for 30 min in a reservoir and was transferred into the flow cell, where repetitive pulsed irradiations (1–50 Hz) were carried out at $20\pm3°$C. The solutions (ca. 10 cm^3) photolyzed at several repetitive rates were collected from output of the cell for analyses.

2.3. Time-resolved absorption spectroscopy

Laser flash photolysis experiments were carried out using a nanosecond laser system similar to those previously described [17]. The excitation source was a Lambda Physik MINex XeCl excimer laser (308 mM, 10 ns, 15 mJ/pulse). An argon-saturated solution of ketone 1 including sensitizers was irradiated in $4\times1\times1$ cm^3 cell made of quartz and analyzed spectroscopically.
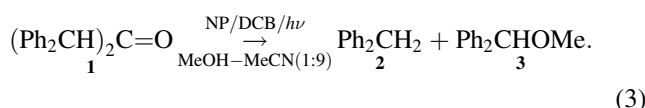
3. Results

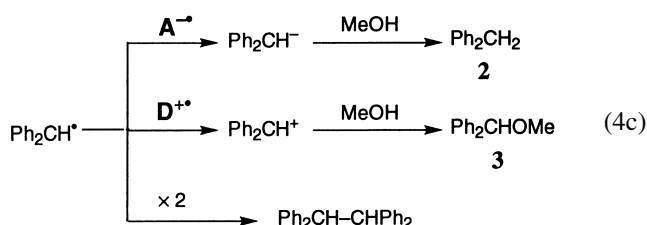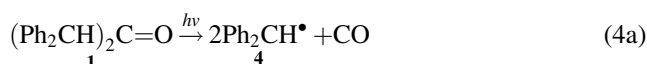### 3.1. Redox reaction of diphenylmethyl radical during continuous irradiations

As reported previously [13], radicals ($R^{\bullet}$) produced by photolysis of $R_2C=O$ can be subject to redox reactions with radical ions ($A^{-\bullet}$ and $D^{+\bullet}$). The reaction in MeOH–MeCN (1:9) affords ROMe and RH via (i) simultaneous generation of the radical and a pair of radical ions, (ii) electron transfer affording carbon-centered cation and anion, as shown in Scheme 1, and (iii) the trapping reactions with methanol. Most intriguing was that the oxidation by radical cation was less effective than the reduction as the exothermicity of the former electron transfer was greater than that of the latter. Thus, the redox reaction was suggested as a novel example

of the Marcus inverted region [18,19]. Most important here, however, may be the actual concentrations of $A^{-\bullet}$ and $D^{+\bullet}$ during the irradiations. The effects of radical ion concentrations and of electron transfer rates on the redox reactions are analyzed from the product ratios of ROMe and RH as stated below.

Diphenylmethyl radical ($Ph_2CH^\bullet$) was selected as the indicator radical from the following reasons; (i) the radical can be generated rapidly (<10 ns) by the photolysis of *sym*-tetraphenylacetone (**1**) [20], (ii) the radical is proved to be stable to yield its dimer quantitatively even in MeOH–MeCN (1:9), and (iii) its redox potentials are known ($E_{1/2}^{ox} = +0.35$ V and $E_{1/2}^{red} = -1.14$ V vs. SCE) [21–23]. Under appropriate conditions (i.e., choice of A and D and their concentrations) of continuous irradiation, the production of diphenylmethane (**2**) and diphenylmethyl methyl ether (**3**) is the major reaction compared to the formation of dimer ($Ph_2CH–CHPh_2$) as shown in Eq. (3).

$$(Ph_2CH)_2C{=}O \underset{MeOH-MeCN(1:9)}{\overset{NP/DCB/h\nu}{\longrightarrow}} Ph_2CH_2 + Ph_2CHOMe.$$
$$\underset{\textbf{1}}{\phantom{(Ph_2CH)_2C{=}O}} \qquad \underset{\textbf{2}}{} \quad \underset{\textbf{3}}{}$$
(3)

Major processes involved here are as shown Eqs. (4a), (4b) and (4c).

$$(Ph_2CH)_2C{=}O \overset{h\nu}{\rightarrow} 2Ph_2CH^\bullet + CO$$
$$\underset{\textbf{1}}{\phantom{(Ph_2CH)_2C{=}O}} \quad \underset{\textbf{4}}{} \qquad (4a)$$

$$D + A \overset{h\nu}{\rightarrow} D^{+\bullet}A^{-\bullet} \qquad (4b)$$

Resulting ratios of **2/3** reflect the relative efficiencies for the reduction and oxidation of diphenylmethyl radical (**4**). Under the continuous irradiations it was known that the recoveries of radical **4** were mostly in the range of 70–80% and the consumption of sensitizers was small (i.e., <5%) [13].

Naphthalene (Np) and dicyanobenzene (DCB) were employed as the typical redox couple. The electron transfer quenching of excited singlet Np ($E_{1/2}^{ox} = +1.80$ vs. SCE) [24] by electron acceptor DCB ($E_{1/2}^{red} = -1.60$ V vs. SCE) [10] is known to produce free radical ions, $Np^{+\bullet}$ and $DCB^{-\bullet}$ [25–27]. The continuous irradiation of **1**, Np and DCB with a Hg lamp, where **1** and Np absorb light, resulted in the formation of **2** and **3** in about 10:1 ratio in MeOH–MeCN (1:9). This result is striking because the oxidation of $Ph_2CH^\bullet$ with $Np^{+\bullet}$ is much more exothermic (i.e., $\Delta G_{ox}{=}-1.45$ eV) than the reduction with $DCB^{-\bullet}$ ($\Delta G_{red}{=}-0.46$ eV). Here, the free energy changes of redox reactions of radical ($R^\bullet$) are calculated according to Eqs. (5) and (6).

$$\Delta G_{ox} = E_{1/2}^{ox}(R^\bullet) - E_{1/2}^{ox}(D) \qquad (5)$$

$$\Delta G_{red} = E_{1/2}^{red}(A) - E_{1/2}^{red}(R^\bullet). \qquad (6)$$

Redox reactions with various kind of donors and acceptors with continuous irradiations were examined and the resulting ratios of **2/3** are in the range 3–10 as listed in Table 1.

Previously, it was assumed that two radical ions are formed and exist in 1:1 ratio since the irradiation of 10 mM (10^{-2} mol dm^{-3}) each of Np and DCB in MeOH–MeCN (1:9) for 2 h resulted in no apparent chemical reaction. This result, however, does not always prove that the both radical ions are completely stable and exist in a 1:1 ratio. It is known that radical cations of aromatics are reactive toward nucleophiles [28,29] and that $Np^{+\bullet}$ generated by radiolysis [30] or photolysis [31] in water has a short lifetime of ca. 10^{-4} s affording OH-adducts. Similar reaction may be expected for the present case of MeOH and in

Table 1
Product ratios on the co-irradiation of **1** and donor–acceptor systems[a]

D[b]	$-\Delta G_{ox}$ (eV)[c]	A[d]	$-\Delta G_{red}$ (eV)[e]	2/3[f]	
				Continuous[g]	Pulsed[h]
Np	1.45	DCB	0.46	9.9	0.95±0.16
MNp	1.33	DCB	0.46	7.9	0.59±0.08
MeONp	1.17	DCB	0.46	3.8	0.85±0.02
Np	1.45	TMDCB	0.76	–[i]	0.89±0.03
DMD	1.32	CN	0.84	2.9	0.72±0.05
DMD	1.32	DCN	0.14	2.9	<0.1

[a] A solution of 2.0 mM **1**, donor, and acceptor in MeOH–MeCN (1:9) was irradiated under argon at 20±3°C.
[b] Donor, 10 mM: Naphthalene (Np), 2-methylnaphthalene (MNp), 1-methoxynaphthalene (MeONp), and 4,4′-dimethyldiphenyl (DMD).
[c] The free energy change on the electron-transfer from $Ph_2CH^\bullet$ to $D^{+\bullet}$ as calculated by Eq. (5).
[d] Acceptor: 10 mM 1,4-dicyanobenzene (DCB), 6.5 mM 2,3,5,6-tetramethyl-1,4-dicyanobenzene (TMDCB), 5 mM 1-cyanonaphthalene (CN), and 5 mM 1,4-dicyanonaphthalene (DCN).
[e] The free energy change on the electron-transfer to $Ph_2CH^\bullet$ from $A^{-\bullet}$ as calculated by Eq. (5).
[f] Extrapolated product ratios of Ph_2CH_2/Ph_2CHOMe determined by GLC.
[g] Irradiated with a Hg lamp (>300 nm) for 30–120 min.
[h] Irradiated with a XeCl excimer laser (308 nm, 10 ns).
[i] The product ratio could not be determined because of too low yields due to the significant absorption of light by TMDCB.

fact a small amount of methoxynaphthalene's were detected [13]. On the other hand, radical anions of aromatic nitriles have been known to be relatively stable [24]. The lifetime of $DCB^{-\bullet}$ is longer than 1 s as indicated by the observation of a reversible reduction peak upon cyclic voltammetric analysis (in 0.1 M n-Bu$_4$NBF$_4$/MeOH–MeCN (1:9), 100 mV/s). These facts led us to examine the relative concentrations of $A^{-\bullet}$ and $D^{+\bullet}$ during irradiations. This was clarified by comparing with results from pulsed conditions as described in the following.

3.2. Redox reaction in pulsed irradiations

The uncertainty of the photostationary state under continuous irradiations (Fig. 1(a)) could be eliminated by employing a pulsed light, which produces intermediates only at the pulse duration (Fig. 1(b)). When a pulse laser is employed, the pulse width is much shorter than the period to achieve the photostationary states. Since the quantity of products formed by single pulse of a milli-Joule scale laser is only sub-milligram at most, the irradiations should be iterated until products are accumulated to allow their quantitative analyses. Such repetitive conditions might result in a quasi-steady state (see Fig. 1(c)) if the pulse interval is not sufficiently long.

We tried to monitor the redox reaction of $DCB^{-\bullet}$ and $Np^{+\bullet}$ with $Ph_2CH^{\bullet}$ by nanosecond laser flash spectroscopy. The pulsed irradiation (XeCl excimer laser, 308 nm, 10 ns) of 10 mM each of Np and DCB in MeCN showed the efficient formation of monomer and dimer radical cations of naphthalene ($Np^{+\bullet}$, λ_{max}=625 and 685 nm; $(Np)_2^{+\bullet}$, λ_{max}=570 nm), dicyanobenzene radical anion ($DCB^{-\bullet}$, λ_{max}=340 and 430 nm) as well as the triplet excited state of Np (λ_{max}=410 nm) [26]. The disappearance of $Np^{+\bullet}$ and $DCB^{-\bullet}$ followed the same second order rate law, in the

absence or presence of 10% methanol, indicating that these radical ions decayed by diffusion-controlled back electron transfer [32]. After the completion of back electron transfer (ca. 20 μs after the laser pulse), no residual absorption could be detected. By the addition of **1** which also absorbs the 308 nm light, an absorption of $Ph_2CH^{\bullet}$ (λ_{max}=325 nm) [33] appeared, and decayed by diffusion-controlled dimerization. The kinetic behavior of these intermediates was examined at various concentrations of Np, DCB, **1** and MeOH. No apparent difference could be observed in decay curves between $DCB^{-\bullet}$ and $Np^{+\bullet}$ in the presence of small amount of radical **4**. But, it was not possible to obtain their decay curves accurately in the presence of comparable amount of radical **4**, since the absorbence of **4** was too large at 340 nm (i.e., the absorption maximum of $DCB^{-\bullet}$) and that of $Np^{+\bullet}$ was too small to follow.

The reaction of $Np^{+\bullet}$ with 5–10% MeOH was assumed to be relatively slow, probably of ms order in analogy with the addition of water, and could not be traced by the transient absorption spectroscopy with μs order time window. This implies that the products on the laser photolysis is not affected by the slow reaction of $Np^{+\bullet}$ and reflect the relative ET rates between the two radical ions. Thus, we tried to determine the product ratios from the laser photolysis.

The pulsed irradiations were carried out in a 1 mm thick quartz cell under the continuous flow of solutions in order to utilize all the laser light and to minimize the secondary photolysis of products. Typically, 10 mM each of Np and DCB and 2 mM **1** in MeOH–MeCN (1:9) were irradiated by a XeCl excimer laser (308 nm, 10 ns, 4 mJ). Because of known multiple-photon chemistry of diphenylmethyl radical [34–37] the intensity of laser must be kept low and the laser beam was only slightly focused on the cell. When the irradiation was carried out by repetitive pulses with the frequencies of 1–50 Hz (pulse intervals of 1–0.02 s), a part of **1** was consumed and the products (majorly **2** and **3**) were obtained. Under these conditions, the conversions of substances (i.e., <2%) were too low to be measured correctly. However, the yields of products were determined by GLC analysis by collecting the irradiated solutions. The formation of radical dimer was negligible, indicating that the amounts of radical ions were much greater than that of diphenylmethyl radical **4**. Other by-products were not detected by GC–MS analysis, suggesting the redox reactions (4c) being the major reactions.

Fig. 2(a) shows the plots of the resulting product ratios of **2/3** were determined vs. pulse intervals. The values of 1–2.4 are significantly lower than the previous one of **10** under continuous irradiation. The product ratios decrease with the increasing pulse intervals, approaching to a constant value of ca. **1**. Since one pulse produces radical cation and anion in the 1:1 ratio, the oxidation of $Ph_2CH^{\bullet}$ by $Np^{+\bullet}$ and the reduction by $DCB^{-\bullet}$ seem to proceed in the same rate.

Notably, the ratio of **2/3** increased with increasing frequency of pulse. This indicates that, while most of $Np^{+\bullet}$ disappears by back electron transfer within 20 μs as
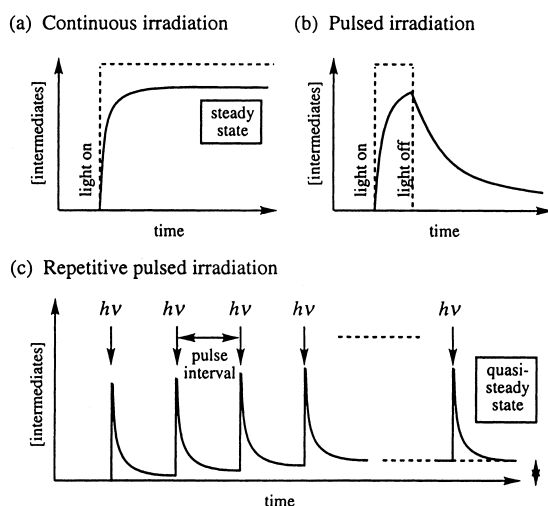

Fig. 1. Schematic drawings of kinetic behaviors of photogenerated intermediates under (a) continuous irradiation, (b) pulsed irradiation, and (c) repetitive pulsed irradiation.
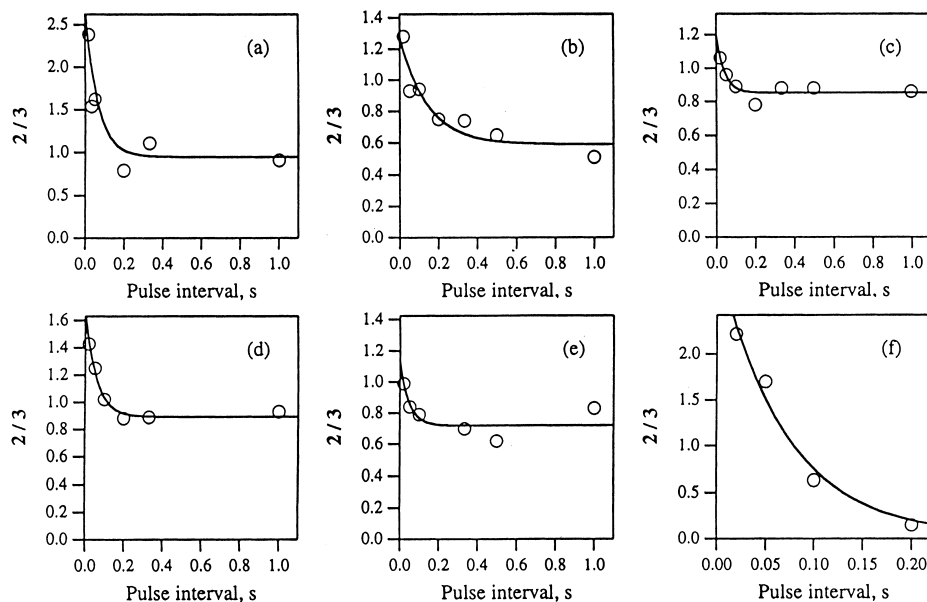
Fig. 2. Plots of product ratios of Ph$_2$CH$_2$/Ph$_2$CHOMe vs. pulse intervals on the repetitive pulsed irradiations of 2.0 mM **1** with (a) 10 mM Np and 10 mM DCB, (b) 10 mM MNp and 10 mM DCB, (c) 10 mM MeONp and 10 mM DCB, (d) 10 mM Np and 6.5 mM TMDCB, (e) 10 mM DMD and 5 mM CN, and (f) 10 mM DMD and 5 mM DCN in MeOH–MeCN (1:9).

observed by transient absorption spectroscopy, competitive slow reaction of Np$^{+\bullet}$ leave a small amount of DCB$^{-\bullet}$ in the solution. When the pulse interval is not sufficiently long, next pulse comes before the complete disappearance of DCB$^{-\bullet}$, resulting in the quasi-steady state (Fig. 1(c)) with higher [DCB$^{-\bullet}$] than [Np$^{+\bullet}$]. Thus, the formation of **2** becomes favorable at shorter pulse intervals as observed in Fig. 2(a). The interval dependence may imply the approximate lifetime of DCB$^{-\bullet}$ of ∼0.1 s under the condition, which is shorter than that estimated from cyclic voltammetric analysis (>1 s). The discrepancy seems not to be unreasonable since H$^+$ is formed by the reaction of Np$^{+\bullet}$ with MeOH which makes the solution slightly acidic.

3.3. Dependence on free energy changes

Product ratios of **2/3** with a variety of donor–acceptor pairs were determined in order to examine the free energy change dependence on the redox reaction. Donors employed were 2-methylnaphthalene (MNp, $E_{1/2}^{ox} = +1.68$ V) [38], 1-methoxynaphthalene (MeONp, $+1.59$ V) [24], 4,4′-dimethyldiphenyl (DMD,$+1.67$ V vs. SCE) [31], and acceptors were 2,3,5,6-tetramethyl-1,4-dicyanobenzene (TMDCB, $E_{1/2}^{red} = -1.90$ V) [13], 1-cyanonaphthalene (CN, -1.90 V) [31], and 1,4-dicyanonaphthalene (DCN, -1.28 V vs. SCE) [31]. The pulsed irradiations were carried out for MeOH–MeCN (1:9) solutions of **1**, donor, and acceptor.

The resulting product ratios of **2/3** at various pulse intervals are shown in Fig. 2(b)–(e), indicating the similar interval dependence approaching to constant ratios of 0.6–1.0. An exceptional case is DMD–DCN pair of Fig. 2(f) in which

the ratio falls down to <0.1 because of too slow reduction by DCN$^{-\bullet}$ (see the discussion below). From the extrapolated product ratios as summarized in Table 1, the relative ET rates could be obtained for the oxidation of Ph$_2$CH$^\bullet$ with radical cations of Np, MNp and MeONp, and for the reduction with radical anions of DCB and TMDCB. Relative rates for the reduction with radical anions of CN and DCN may be estimated by assuming that their ET rates are close to those of radical cations of MNp and DMD since they are two-ring donor with almost same oxidation potentials [38–41]. Resulting relative rates for Np$^{+\bullet}$, MNp$^{+\bullet}$ (≡DMD$^{+\bullet}$), MeONp$^{+\bullet}$, DCB$^{-\bullet}$, TMDCB$^{-\bullet}$, CN$^{-\bullet}$ and DCN$^{-\bullet}$ are 0.62, 1.0, 0.69, 0.59, 0.55, 0.72 and <0.1, respectively.

The plots of relative ET rates for radical ions vs. ΔG are shown in Fig. 3. Apparently, the relative rates are constant in the range of $\Delta G < -0.5$ eV, where the ET is diffusion-controlled. The lower value for the reduction with DCN$^{-\bullet}$ is explicable on the basis of too small exothermicity ($\Delta G = -0.14$ eV). The solid curve in Fig. 3 is reproduced by the Rehm–Weller equation (Eqs. (7) and (8)) with the standard value of $\Delta G^{\neq}(0)$ of 0.14 eV together with k_{diff}(relative)=1.19.

$$k_{\text{et}} = \frac{k_{\text{diff}}}{1 + 0.25\left[\exp(\Delta G^{\neq}/RT) + \exp(\Delta G/RT)\right]} \quad (7)$$

$$\Delta G^{\neq} = \sqrt{(\Delta G/2)^2 + (\Delta G^{\neq}(0))^2} + \Delta G/2. \quad (8)$$

It is shown that the redox reaction between Ph$_2$CH$^\bullet$ and radical ions does not show, as proposed previously [13], the Marcus inverted region. The apparent inverted region is now found to be due to higher [A$^{-\bullet}$]$_{ss}$ in comparison to [D$^{+\bullet}$]$_{ss}$ under continuous irradiations.
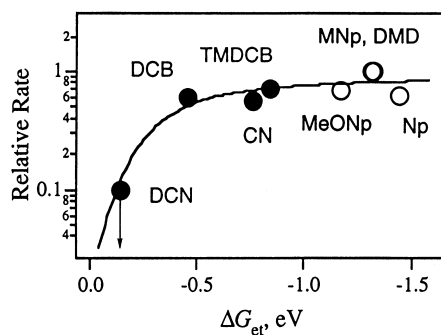
Fig. 3. Plots of relative ET rates vs. free energy change (ΔG) between $Ph_2CH^\bullet$ and aromatic radical cation (open circle) or radical anion of cyanoaromatics (filled circle). The curve is calculated by the Rehm–Weller equation (Eq. (7)) with $\Delta G^{\neq}(0)=0.14$ eV and $k_{diff}=1.19$.

4. Discussion

4.1. Steady-state concentrations of radical ion intermediates

Behaviors of free radical ions in PET reactions can be described by kinetics with the steady-state approximation, as done by Fischer and co-workers [2–5] for radical coupling reactions. The system considered here is the simplest PET reaction of Eq. (2). Radical cation of donor D and radical anion of acceptor A are generated with the same rate constant (k_0) and disappear by bimolecular back electron transfer (k_{bet}) and by first-order (or pseudo-first-order) reactions (k_D and k_A) leading to products. The rate expressions for $D^{+\bullet}$ and $A^{-\bullet}$ are given as follows:

$$\frac{d[D^{+\bullet}]}{dt} = k_0 - k_{bet}[D^{+\bullet}][A^{-\bullet}] - k_D[D^{+\bullet}] \tag{9}$$

$$\frac{d[A^{-\bullet}]}{dt} = k_0 - k_{bet}[D^{+\bullet}][A^{-\bullet}] - k_A[A^{-\bullet}]. \tag{10}$$

By the assumption of steady-state conditions (i.e., $d[D^{+\bullet}]/dt=d[A^{-\bullet}]/dt=0$), the first and second terms of right side in Eqs. (9) and (10) are cancelled, and hence the ratio of steady-state concentrations depends on neither k_{bet} nor k_0 (i.e., intensity of light) and is equal to the inverse ratio of each first-order rate constants.

$$\frac{[D^{+\bullet}]_{ss}}{[A^{-\bullet}]_{ss}} = \frac{k_A}{k_D}. \tag{11}$$

The steady-state concentrations of radical ions can be calculated from Eqs. (9) and (10) and classified as follows: (i) When both radical ions are completely persistent (i.e., $k_D=k_A=0$), their steady-state concentrations are given by Eq. (12) and are assumed to be quite low, e.g., 10^{-8} M with typical values of $k_0=10^{-6}$/s and $k_{bet}=10^{10}$/M s.

$$[D^{+\bullet}]_{ss} = [A^{-\bullet}]_{ss} = \sqrt{\frac{k_0}{k_{bet}}}. \tag{12}$$

(ii) When either radical ion is completely persistent (i.e.,

$k_D=0$ or $k_A=0$), no stationary state exist, and the concentration of the persistent radical ion increases to infinite. (iii) When $D^{+\bullet}$ and $A^{-\bullet}$ have a finite lifetime (i.e., $k_D\neq0$ and $k_A\neq0$), concentrations of radical ions are given as follows:

$$[D^{+\bullet}]_{ss} = \frac{k_A}{2k_{bet}}\left(-1 + \sqrt{1 + \frac{4k_0k_{bet}}{k_Dk_A}}\right), \tag{13}$$

$$[A^{-\bullet}]_{ss} = \frac{k_D}{2k_{bet}}\left(-1 + \sqrt{1 + \frac{4k_0k_{bet}}{k_Dk_A}}\right). \tag{14}$$

If the condition satisfies $k_Dk_A \ll k_0k_{bet}$ and $k_D>k_A$, the back electron transfer dominates, and the radical ion concentrations are approximated as follows:

$$[D^{+\bullet}]_{ss} \approx \sqrt{\frac{k_Ak_0}{k_Dk_{bet}}} < \sqrt{\frac{k_0}{k_{bet}}} \tag{15}$$

$$[A^{-\bullet}]_{ss} \approx \sqrt{\frac{k_Dk_0}{k_Ak_{bet}}} > \sqrt{\frac{k_0}{k_{bet}}}. \tag{16}$$

Now it is apparent that the steady-state concentrations of $[D^{+\bullet}]_{ss}$ and $[A^{-\bullet}]_{ss}$ depend on the rate ratios of k_D/k_A; for example, $[A^{-\bullet}]/[D^{+\bullet}]$ is 100 if $k_D/k_A=100$, and $[A^{-\bullet}]_{ss}$ can be greater than the steady-state concentration given in Eq. (12).

4.2. Persistent radical ion effect in PET reactions

Recent advances in PET have uncovered a large number of synthetically useful reactions, mostly involving the intermediacy of free radical ions in polar solvents. Quantum yields of such PET reactions are usually determined by efficiencies of three fundamental steps; (i) the intermolecular electron transfer quenching of excited state molecules, (ii) the dissociation of geminate radical ion pairs in competition with the in-cage back electron transfer, and (iii) dark processes of freely diffusing intermediates. The first step depend on the excited state lifetimes, the concentration of quenchers, and the quenching rates predictable from the Rehm–Weller relationship. As for step (ii), the events happening in geminate radical ion pairs had long been a "black box", but could be well characterized by recent high speed spectroscopic studies [42,43]. It has been established that the efficiency of the free ion yields can be improved (a) by selecting sensitizer and co-sensitizers [38] so that the back electron transfer in the Marcus inverted region becomes highly exothermic [39–41], (b) by using triplet sensitizers where the back electron transfer is spin-forbidden [44], or (c) by the addition of salts to assist ionic dissociations [45–47].

As for step (iii), laser kinetic spectroscopy is applicable for fast reactions of μs order, but not for much slower processes. Thus, the steady-state continuous irradiation is another "black box" since there is no way to survey what is happening between undetectable intermediates. Some description concerning the concentration effect of radical ions is found in a recent paper by Dinnocenzo et al. [48], in

which the importance of removal of air by degassing was stressed to avoid the consumption of sensitizer radical anions. The importance of persistency of radical anions in PET reactions under the photostationary states is apparent, but only a little informations are available on the slow reactions of cyanoaromatic radical anions [49,50]. In some PET reactions, 9,10-dicyanoanthracene radical anion has been observed by ESR [51,52] and absorption spectroscopy [49,50,53]. The actual difference in concentrations between transient and persistent radical ions may be utilized in selective coupling reactions between them. For instance, an irreversible one-electron oxidation or reduction may be carried out via PET processes. If $D^{+\bullet}$ is so unstable and disappears instantaneously, $A^{-\bullet}$ of a quite high steady-state concentration may act as an effective reducing agent.

In spite of the wide application of pulse lasers in spectroscopy and analytical chemistry, only a few works have been done in the field of synthetic organic photochemistry. Most of studies are carried out by utilizing the high intensity of lasers [54–56], allowing the photochemical activation of short-lived intermediates and the generation in much higher concentrations. Another prominent feature of pulse laser is its short pulse width, which leads to different kinetics when intermediates are generated only at instant. Thus, the present result demonstrates a novel application of pulse lasers for kinetic control of photochemical reactions.

The present redox reaction of diphenylmethyl radical takes place between intermediates generated by two independent photoreactions Scheme 1. In such a system, the steady-state concentrations of intermediates may play a crucial role in determining product selectivities. By analogy with the Ingold–Fischer persistent radical effect [2–5] the reaction of $Np^{+\bullet}$ will be significantly reduced if the counterpart radical anion is persistent. That is, when a small part of $Np^{+\bullet}$ is consumed, an equal amount of $DCB^{-\bullet}$ will be accumulated in the irradiating solution. After the achievement of the steady-state, the solution is to involve a substantial amount of $DCB^{-\bullet}$, which will efficiently quench the freshly formed $Np^{+\bullet}$ by back electron transfer. Thus, the net reaction of $Np^{+\bullet}$ does not proceed further after the consumption of trace amount of $Np^{+\bullet}$, and at the stationary state the ratio of $[DCB^{-\bullet}]_{ss}:[Np^{+\bullet}]_{ss}$ will be significantly deviated from the initial ratio of 1:1. This clarification was supported by the comparison with those of pulsed irradiations.

Previously, we proposed the Marcus inverted region to explain the resulting relative product yields [13]. As described above, the Rehm–Weller relationship holds in the present ET reaction of diphenylmethyl radical. The lack of the Marcus inverted region is not surprising as discussed below. Many electron transfers via diffusional collision are known to show no inverted region because of (a) masking by diffusion limit [57], (b) the participation of low-lying excited states [58–60], and (c) the distance dependence of solvent reorganization energies [61–63]. The previous correlation as a Marcus inverted region from product yields [13]

is now explicable by the change of steady-state concentrations of intermediary radical ions.

5. Conclusions

The persistent radical effect suggests a novel insight on efficiencies and selectivities of PET reactions. The present redox reaction of diphenylmethyl radical by continuous irradiations is shown to be controlled by the steady-state concentrations of radical ion intermediates. Thus, pulsed irradiation produces the radical cation and anion in 1:1 ratio which lead to the relative redox rates showing the Rehm–Weller relationship. It is concluded that under the photostationary states the reaction of persistent radical ion is so important and controls the overall selectivities, while the kinetics are basically different when intermediates are generated by pulsed irradiations. These findings lead to better understandings of reactions involving reactive intermediates such as unobservable dark processes in PET reactions.

Acknowledgements

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