J. Phys. Chem. A **2007,** *111,* 223−229

Intermolecular Electron Transfer from Excited Benzophenone Ketyl Radical

Masanori Sakamoto, Xichen Cai, Sung Sik Kim, Mamoru Fujitsuka, and Tetsuro Majima*

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Received: July 24, 2006; In Final Form: October 10, 2006

The electron transfer from the benzophenone ketyl radical in the excited state ($BPH^•(D_1)$) to several quenchers (Qs) was investigated using nanosecond/picosecond two-color two-laser flash photolysis and nanosecond/nanosecond two-color two-laser flash photolysis. The electron transfer from $BPH^•(D_1)$ to Qs was confirmed by the transient absorption and fluorescence quenching measurements. The intermolecular electron-transfer rate constants were determined using the Stern−Volmer analysis. The driving force dependence of the electron-transfer rate was revealed.

Introduction

Radicals are one of the most important intermediates in the field of chemistry, biology, and physics. The properties and reactivity of radicals have attracted the attention of numerous scientists. Radicals have been applied to various photochemical reactions. It is known that ketyl radicals of benzophenone (BP) and acetophenone have high reducing power. Because of the fact that these ketyl radicals can be conveniently generated using the photochemical method, they recently have been used as reducing agents of metal ions to fabricate metal nanoparticles.[1−3]

The excited radicals are also a promising candidate for the reducing agent, because the excited radicals, which can be obtained via photoexcitation of the radicals in the ground state, have high reactivity, compared to radicals in the ground state.[4] Some excited radicals, such as the diphenyl methyl radical, naphthylmethyl the radical, and the benzophenone ketyl radical ($BPH^•$), have been indicated to show high reducing power.[5−9] We have reported efficient photochemical fabrication of gold nanoparticles in a poly(vinyl alcohol) (PVA) film using the benzophenone ketyl radical in the excited state ($BPH^•(D_1)$).[5]

Although electron transfer from excited radicals has been reported, the number is quite small, compared to that from molecules in the singlet or triplet excited state.[5−7] Furthermore, the systematic research of the electron transfer from excited radicals is also limited, even for the electron transfer from $BPH^•(D_1)$. Turro et al. investigated electron transfer from $BPH^•(D_1)$ using a laser.[6] They used metal salt and amines as quenchers of $BPH^•(D_1)$. However, the transient absorption measurement of the electron-transfer process was not performed. In addition, time-resolved investigation was impossible, because of the poor time resolution of their instruments when taking the short lifetime of $BPH^•(D_1)$ into account.

Recently, the development of short-pulse lasers and detection systems made the detailed investigation of short-lived species, such as $BPH^•(D_1)$, possible.[8−10] In our previous papers, we reported the electron transfer from ketyl radicals of benzophenone derivatives in the excited state ($BPDH^•(D_1)$) to the ground-state parent molecules using nanosecond/picosecond two-color two-laser flash photolysis.[8,9] However, quantitative information about the electron transfer from $BPDH^•(D_1)$ was rather limited. Because the quenchers also work as precursors of the radicals in the experiment, the systematic research, such as the driving force ($-\Delta G$) dependence of the electron-transfer rate, could not be performed.

The difficulty of the investigation of the electron transfer from $BPDH^•(D_1)$ can be attributed to the serious requirement for the electron acceptor in the experiment. The electron acceptor should meet the following requirements. First, the triplet energy of the electron acceptor should be similar to or higher than that of BP. If the acceptor of triplet energy is lower than that of BP, efficient triplet energy transfer from BP in the triplet state ($BP(T_1)$) to the acceptor inhibits the formation of $BPH^•$.[11] Second, the acceptor should be inert toward the reactive $BPH^•$.

In the present paper, we used benzonitrile, 4-methoxybenzonitrile, 4-chlorobenzonitrile, pyrazine, benzoic acid, 1,4-dicyanobenzene, 1,3-dicyanobenzene, BP, phthalimide, *N*-methylphthalimide, and phthalic anhydride, which satisfy the aforementioned requirements, as the electron acceptor. The electron transfer from $BPH^•(D_1)$ was investigated using nanosecond/picosecond two-color two-laser flash photolysis and nanosecond/nanosecond two-color two-laser flash photolysis. The electron transfers from $BPH^•(D_1)$ to quenchers (Qs) were confirmed by the transient absorption and fluorescence quenching measurements. The intermolecular electron-transfer rate constants were determined by the Stern−Volmer analysis. The $-\Delta G$ dependence of the electron-transfer rate was investigated.

Experimental Section

The nanosecond/picosecond two-color two-laser flash photolysis experiment was performed using the third harmonic oscillation (355 nm) of a nanosecond Nd^{3+}:YAG laser (Quantel, Brilliant; 5 ns full width at half maximum (fwhm)) as the first laser and the second harmonic oscillation (532 nm) of a picosecond Nd^{3+}:YAG laser (Continuum, RGA69-10; 30 ps fwhm) as the second laser. The delay time of the two laser flashes was adjusted to 1 μs by four-channel digital delay/pulse generators (Stanford Research Systems, Model DG 535). The breakdown of xenon gas generated by the fundamental pulse of the picosecond Nd^{3+}:YAG laser was used as a probe light. Transient absorption spectra and kinetic traces were measured using a streak camera (Hamamatsu Photonics, Model C7700)

---

* Author to whom correspondence should be addressed. E-mail: majima@sanken.osaka-u.ac.jp.

10.1021/jp064718y CCC: $37.00

that was equipped with a charge-coupled device (CCD) camera (Hamamatsu Photonics, Model C4742-98), and were stored on a personal computer (PC). To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were used. The samples were allowed to flow in a transparent rectangular quartz cell (1.0 cm × 0.5 cm × 2.0 cm). For the measurements of both fluorescence spectra and decay profiles, the streak camera was used as the detector.

The nanosecond/nanosecond two-color two-laser flash photolysis experiment was performed using the third harmonic oscillation (355 nm) of an Nd^{3+}:YAG laser (Quantel, Brilliant; 5 ns fwhm) as the first laser and the second harmonic oscillation (532 nm) Nd^{3+}:YAG laser (Continuum, Surelite II-10; 5 ns fwhm) as the second laser. The delay time of two laser flashes was adjusted to 1 μs by three four-channel digital delay/pulse generators. Two laser beams were adjusted to overlap at the sample. The monitor light source was a 450 W xenon lamp (Osram, Model XBO-450) that was synchronized with the laser flash. The monitor light perpendicular to the laser beams was focused on a monochromator (Nikon, Model G250). The output of the monochromator was monitored using a photomultiplier tube (PMT) (Hamamatsu Photonics, Model R928). The signal from the PMT was recorded on a transient digitizer (Tektronix, Model TDS 580D four-channel digital phosphor oscilloscope). To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were used. The samples were contained in a transparent rectangular quartz cell (1.0 cm × 1.0 cm × 4.0 cm) at room temperature.

BP, 1,3-dicyanobenzene, and 1,4-dicyanobenzene were purchased from Tokyo Kasei and recrystallized three times from ethanol before use. Phthalimide, *N*-methylphthalimide, phthalic anhydride, and benzonitrile were purchased from Tokyo Kasei and used as received. 4-Methoxybenzonitrile, 4-chlorobenzonitrile, pyrazine, and benzoic acid were purchased from Aldrich and used as received. 1,4-Cyclohexadiene was purchased from Aldrich and distilled before use. Sample solutions were prepared in acetonitrile and deoxygenated by bubbling with argon gas for 30 min before irradiation. All experiments were conducted in an ambient atmosphere.

Results and Discussion

Generation of Ketyl Radical. $BPH^{\bullet}$ was generated by the hydrogen abstraction of BP in the triplet excited state ($BP(T_1)$) from 1,4-cyclohexadiene. When BP was excited by the 355-nm first laser, $BP(T_1)$ was formed via the fast intersystem crossing (ISC) from BP in the singlet excited state ($BP(S_1)$):

$$\mathrm{BP} \xrightarrow{h\nu} \mathrm{BP(S_1)} \xrightarrow[\mathrm{ISC}]{} \mathrm{BP(T_1)} \tag{1}$$

The rate constant of the ISC was reported to be ~1 × 10^{11} s^{-1}.[12] The formed $BP(T_1)$ abstracts the hydrogen from 1,4-cyclohexadiene to form $BPH^{\bullet}$:

$$\mathrm{BP(T_1)} \xrightarrow{\text{1,4-cyclohexadiene}} \mathrm{BPH^{\bullet}} \tag{2}$$

The rate constant of hydrogen abstraction was reported to be 2.9 × 10^8 M^{-1} s^{-1}.[13] The absorption spectrum of the generated $BPH^{\bullet}$ with two peaks in the ultraviolet (UV) and visible regions agrees with the reported spectrum (Figure 1).[14] The decay curve of $BPH^{\bullet}$ was not changed, even in the presence of Qs, indicating that the electron transfer from $BPH^{\bullet}$ to Qs was negligible.

Fluorescence Spectrum and Lifetime of $BPH^{\bullet}(D_1)$. The generated $BPH^{\bullet}$ was excited at the visible absorption band, using the second laser (532 nm, 10 mJ/pulse, 30 ps fwhm) with a delay time of 1 μs after the first laser (355 nm, 20 mJ/pulse, 5 ns fwhm).

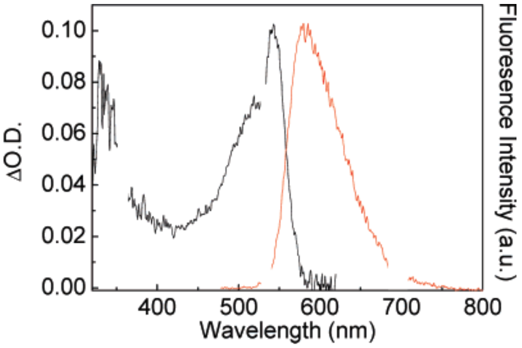


Figure 1. Absorption (black line) and fluorescence (red line) spectra of the benzophenone ketyl radical ($BPH^{\bullet}$) in argon-saturated acetonitrile containing 1,4-cyclohexadiene (30 mM) and BP (5 mM). The absorption spectrum was obtained during the 355-nm laser flash photolysis, and the fluorescence spectrum was obtained during the 355- and 532-nm two-color two-laser flash photolysis. Blanks around 355, 532, and 710 nm in the spectrum are due to the residual third harmonic generation (THG) and second harmonic generation (SHG) of the Nd^{3+}:YAG laser.

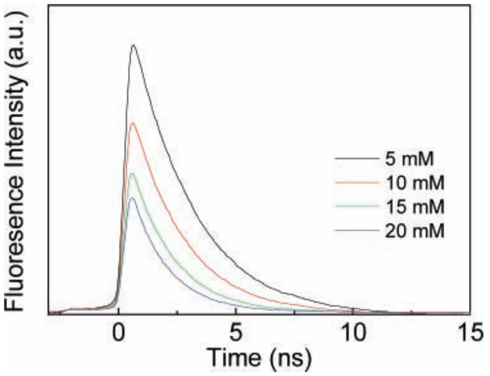


Figure 2. Kinetic trace of fluorescence intensity in the presence of several concentrations of *N*-methylphthalimide.

$$\mathrm{BPH^{\bullet}} \xrightarrow{h\nu} \mathrm{BPH^{\bullet}(D_1)} \tag{3}$$

Upon excitation, the fluorescence of $BPH^{\bullet}(D_1)$ with a peak at 582 nm, which is almost a mirror image of the absorption spectrum of $BPH^{\bullet}$, was observed (see Figure 1). From the peak of fluorescence, the energy of $BPH^{\bullet}(D_1)$ ($\Delta E(D_1 - D_0)$) was estimated to be 2.1 eV. The lifetime of fluorescence (τ_f) is dependent on the concentration of BP.[8,9] When the concentration of BP was 1 mM, τ_f was estimated to be 4.7 ± 0.2 ns. The affect of 1,4-cyclohexadiene on the τ_f was negligible. In the presence of Qs, the value of τ_f decreased as the concentration of Qs increased (see Figure 2). This observation indicates that the intermolecular reaction between $BPH^{\bullet}(D_1)$ and Qs occurred.

Transient Absorption Measurement. *In the Absence of Qs.* The transient absorption spectra in the absence of Qs during the nanosecond/picosecond two-color two-laser flash photolysis are shown in Figure 3. Immediately after the second laser irradiation, the bleaching of $BPH^{\bullet}(D_0)$ is observed, together with the appearance of an absorption band, with peaks at 350 and 430 nm, and a broad absorption band, at 600−800 nm.

Because the lifetime of the absorption band with peaks at 350 and 430 nm was similar to τ_f, the absorption band was attributed to $BPH^{\bullet}(D_1)$.[8−10] In the case of nanosecond/picosecond two-color two-laser laser flash photolysis, the bleaching amount appears rather low, because of overlap of the absorption band of $BPH^{\bullet}(D_1)$ and artifacts such as the power

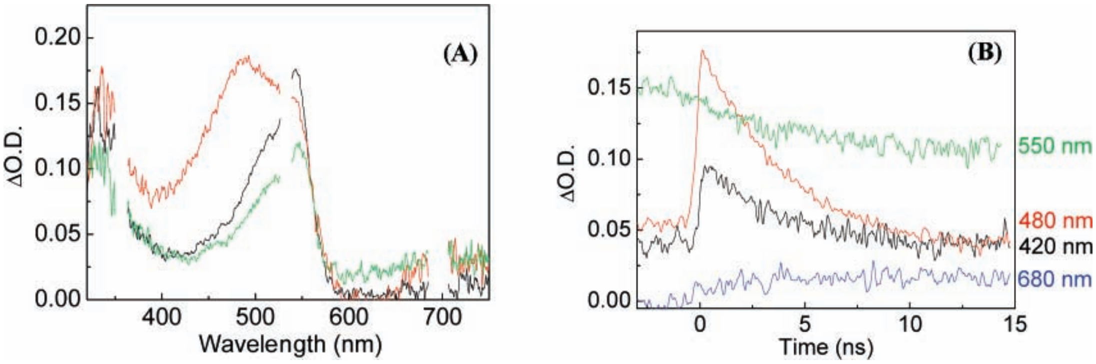


Figure 3. (A) Transient absorption spectra observed before laser irradiation (black line) and 0.5 ns (red line) and 15 ns (green line) after the second laser irradiation during the nanosecond/picosecond two-color two-laser photolysis (355 and 532 nm) of BP (5 mM) in argon-saturated acetonitrile containing 1,4-cyclohexadiene (30 mM). (B) The second laser was irradiated at 1 μs after the first laser pulse. Blanks around 355 and 532 nm in the spectrum are due to the residual THG and SHG of the Nd^{3+}:YAG laser. Kinetic traces of ΔO.D. at 420, 480, 550, and 680 nm (black, red, green, and blue lines, respectively) during the nanosecond/picosecond two-color two-laser photolysis.

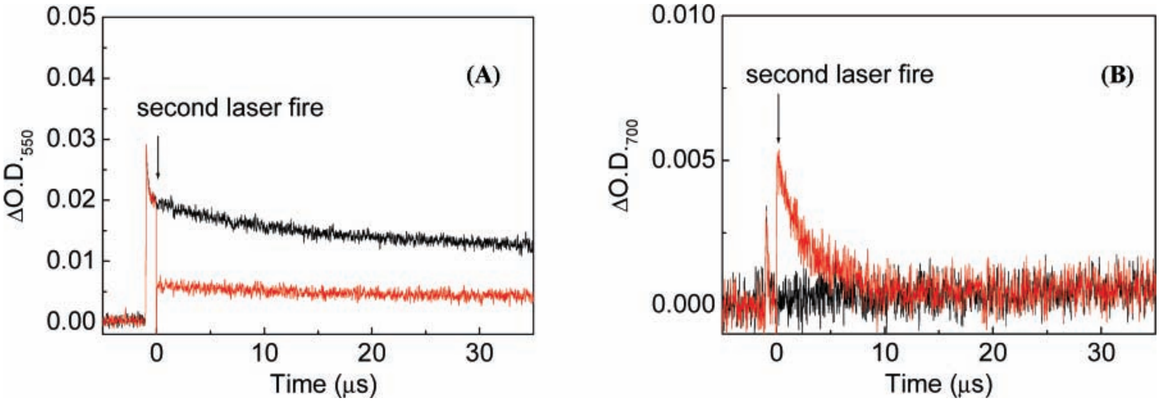
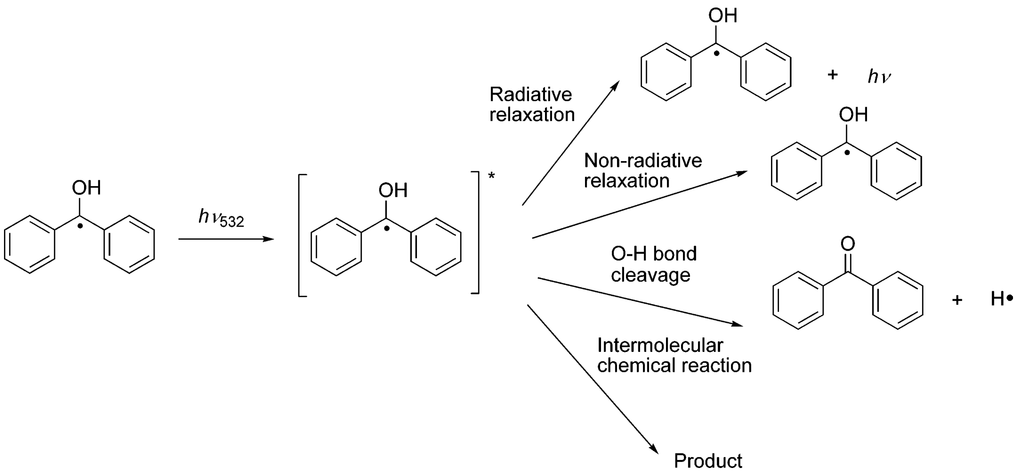


Figure 4. Kinetic traces of ΔO.D. at (A) 550 nm and (B) 700 nm during the nanosecond one-laser irradiation (black line) and nanosecond/nanosecond two-color two-laser irradiation (red line) of BP (5 mM) in argon-saturated acetonitrile containing 1,4-cyclohexadiene (30 mM). The second laser was irradiated at 1 μs after the first laser pulse.

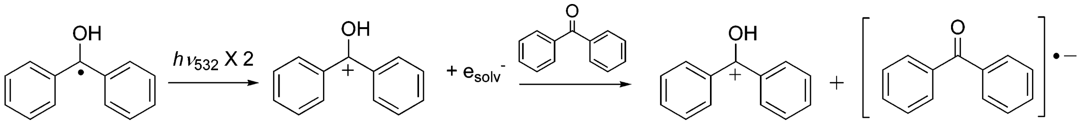
and photon density of second laser, and overlap of two lasers. The bleaching was clearer during the nanosecond/nanosecond two-color two-laser laser flash photolysis, which covers a longer time region (see Figure 4A). The bleaching of $BPH^{\bullet}(D_0)$ was not recovered completely. The lifetime of the transient species, which has a broad absorption band at 600−800 nm, was much longer than that of $BPH^{\bullet}(D_1)$ (3 μs) (see Figure 4B). The transient species was assigned to the BP radical anion ($BP^{\bullet-}$).[14]

The $BPH^{\bullet}(D_1)$ decayed via radiative and nonradiative relaxations, and unimolecular and intermolecular chemical reaction processes (see Scheme 1).[8,9,15,16] Chemical reaction processes were reported to be the O−H bond cleavage of $BPH^{\bullet}(D_1)$ and electron transfer from $BPH^{\bullet}(D_1)$ to BP. In addition, the ionization of $BPH^{\bullet}(D_0)$ by the second laser irradiation occurred in polar solvents (see Scheme 2).[16] $BPH^{\bullet}(D_0)$ was ionized via stepwise two-photon absorption to form a diphenylmethanol cation and a solvated electron (e_{solv}^-). The e_{solv}^- was quickly trapped by BP to generate $BP^{\bullet-}$ (see Scheme 2). The incomplete recovery of the $BPH^{\bullet}(D_0)$ was caused by the chemical reaction processes and ionization, because those processes do not regenerate the $BPH^{\bullet}(D_0)$. For the generation of $BP^{\bullet-}$, there are two pathways. One is the electron transfer from $BPH^{\bullet}(D_1)$ to

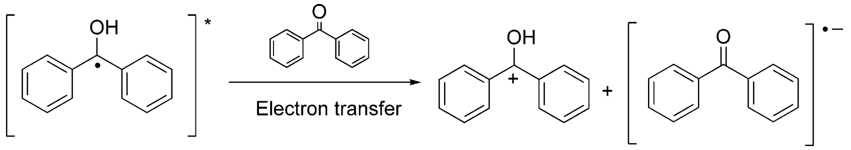
SCHEME 1



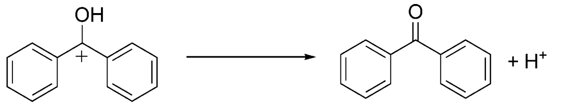
SCHEME 2



SCHEME 3



SCHEME 4



BP (see Scheme 3),[8,9] and the other is the ionization of BPH$^\bullet$, following the trapping of e_{solv}^{-} to BP (see Scheme 2).[16]

The decay of generated BP$^{\bullet-}$ did not follow the second-order kinetics. Because the diphenylmethanol cation, which was formed by the ionization of BPH$^\bullet$ and electron transfer from BPH$^\bullet$(D$_1$), was quickly deprotonated to regenerate BP, the charge recombination process between the diphenylmethanol cation and BP$^{\bullet-}$ was suppressed (see Scheme 4).[17] It is suggested that BP$^{\bullet-}$ decayed via several complicated reactions, such as reaction with a proton and/or BPH$^\bullet$.

The percentage of formed BP$^{\bullet-}$ in the bleached component of BPH$^\bullet$ ($f_{BP^{\bullet-}}$) when subjected to the second laser excitation was calculated from eq 4:

$$f_{BP^{\bullet-}} = \frac{\Delta O.D._{700}\epsilon_{BP^{\bullet-}}}{|\Delta\Delta O.D._{550}\epsilon_{BPH^{\bullet}} - \Delta O.D._{550}\epsilon_{BP^{\bullet-}}|} \times 100 \qquad (4)$$

where $\epsilon_{BP^{\bullet-}}$ and $\epsilon_{BPH^{\bullet}}$ are the respective extinction coefficients of BP$^{\bullet-}$ and BPH$^\bullet$ at each wavelength ($\epsilon_{BPH^{\bullet}} = 3500$ M^{-1} cm^{-1} at 550 nm, and $\epsilon_{BP^{\bullet-}} = 1800$ and 7000 M^{-1} cm^{-1} at 550 and 700 nm, respectively).[15] The values of ΔΔO.D.$_{550}$ and ΔΔO.D.$_{700}$ were estimated from the result of nanosecond/nanosecond two-color two-laser flash photolysis. From eq 3, it was revealed that BP$^{\bullet-}$ is formed in 14% yield among the bleached component of BPH$^\bullet$. The percentage of formed BP$^{\bullet-}$ in the present experiment was smaller than that obtained in the previous work,[16] because the ionization of BPH$^\bullet$ is dependent on several artifacts, such as the second laser power and the overlap of two lasers.

Intrinsic Fluorescence Lifetime of BPH$^\bullet$(D$_1$). Because electron transfer from BPH$^\bullet$(D$_1$) to BP in the ground state occurs, the intrinsic fluorescence lifetime of BPH$^\bullet$(D$_1$) (τ_{f0}) was calculated from eq 5:

$$\frac{1}{\tau_f} = \frac{1}{\tau_{f0}} + k'_{ELT}[BP] \qquad (5)$$

where k'_{ELT} is the electron-transfer rate constant between BPH$^\bullet$(D$_1$) and BP (2.1×10^{10} M^{-1} s^{-1}).[9] From eq 4, the value of τ_{f0} was calculated to be 5.2 ± 0.4 ns.

In the Presence of Qs. The transient absorption spectra in the presence of *N*-methylphthalimide (10 mM) during the nanosecond/picosecond two-color two-laser flash photolysis are shown in Figure 5. In the presence of *N*-methylphthalimide, the absorption band of the *N*-methylphthalimide radical anion, at ~420 nm, was observed after the second laser excitation.[18] As in the case of BP$^{\bullet-}$, two formation pathways of the *N*-methylphthalimide radical anion were expected. One possible process is the trap of e_{solv}^{-}, which is generated from the ionization of BPH$^\bullet$, by *N*-methylphthalimide. Because *N*-methylphthalimide is a better electron acceptor than BP, e_{solv}^{-} would attach to *N*-methylphthalimide favorably. The other process is the intermolecular electron transfer from BPH$^\bullet$(D$_1$) to *N*-methylphthalimide.

The percentage of generated *N*-methylphthalimide radical anions in the bleached component ($f_{Qs^{\bullet-}}$) was calculated from eq 6:

$$f_{Qs^{\bullet-}} = \frac{\Delta O.D._{420}\epsilon_{Qs^{\bullet-}}}{|\Delta\Delta O.D._{550}\epsilon_{BPH^{\bullet}}|} \times 100 \qquad (6)$$

where $\epsilon_{Qs^{\bullet-}}$ is the extinction coefficient of the *N*-methylphthalimide radical anion ($\epsilon_{PI^{\bullet-}} = 3500$ M^{-1} cm^{-1} at 420 nm).[18] The values of ΔΔO.D.$_{550}$ and ΔΔO.D.$_{420}$ were estimated from the result of nanosecond/nanosecond two-color two-laser flash photolysis. The percentage of generated *N*-methylphthalimide radical anions in the bleached component was 25%. Because *N*-methylphthalimide is a favorable electron acceptor and its concentration was larger than that of BP, the percentage of generated *N*-methylphthalimide radical anions increased. The decrease of BP$^{\bullet-}$ by the addition of *N*-methylphthalimide can also be explained by competitive trapping of e_{solv}^{-} by *N*-methylphthalimide and BP.

Figure 6 shows the kinetic traces of BPH$^\bullet$(D$_0$) and *N*-methylphthalimide radical anions during the nanosecond/nanosecond two-color two-laser flash photolysis. The lifetime of the formed *N*-methylphthalimide radical anion was estimated to be 6 μs (see Figure 6B). The decay of the generated *N*-methylphthalimide radical anion followed the second-order kinetics (see Figure 6C). As mentioned previously, the diphenylmethanol cation was quickly deprotonated to form a proton and BP. Because the *N*-methylphthalimide radical anion would decay predominantly via the reaction with a proton, the decay follows the second-order kinetics (4×10^{11} M^{-1} s^{-1}).

In the case of Qs except for *N*-methylphthalimide and phthalimide, the formation of radical anions was not observed, although the τ_f of BPH$^\bullet$(D$_1$) was decreased by the addition of Qs. Because the radical anions of those Qs show only weak absorption in the region of <350 nm, the radical anions cannot be observed, because of the overlap with the absorption of BPH$^\bullet$.[14]

Diffusion of BPH$^\bullet$ in Acetonitrile. It is known that the diffusion of radicals is anomalously slow, because of the strong interaction between the radical and the surrounding molecule.[19−21]

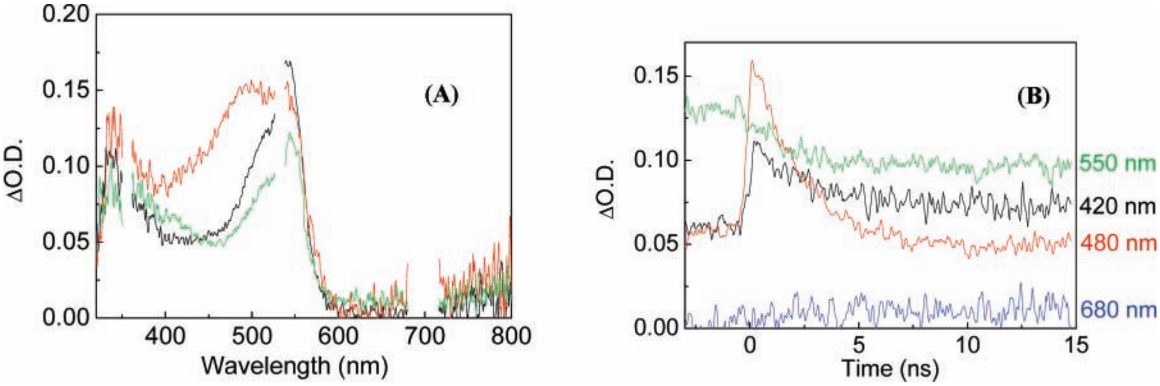


Figure 5. (A) Transient absorption spectra observed before irradiation (black line) and 0.5 ns (red line) and 15 ns (green line) after the second laser irradiation during the nanosecond/picosecond two-color two-laser photolysis (355 and 532 nm) of BP (5 mM) in the presence of *N*-methylphthalimide (10 mM) in argon-saturated acetonitrile containing 1,4-cyclohexadiene (30 mM). (Blanks around 355 and 532 nm in the spectra are due to the residual THG and SHG of Nd^{3+}:YAG laser.) (B) Kinetic traces of ΔO.D. at 420, 480, 550, and 680 nm (black, red, green, and blue line, respectively) during the nanosecond/picosecond two-color two-laser photolysis.

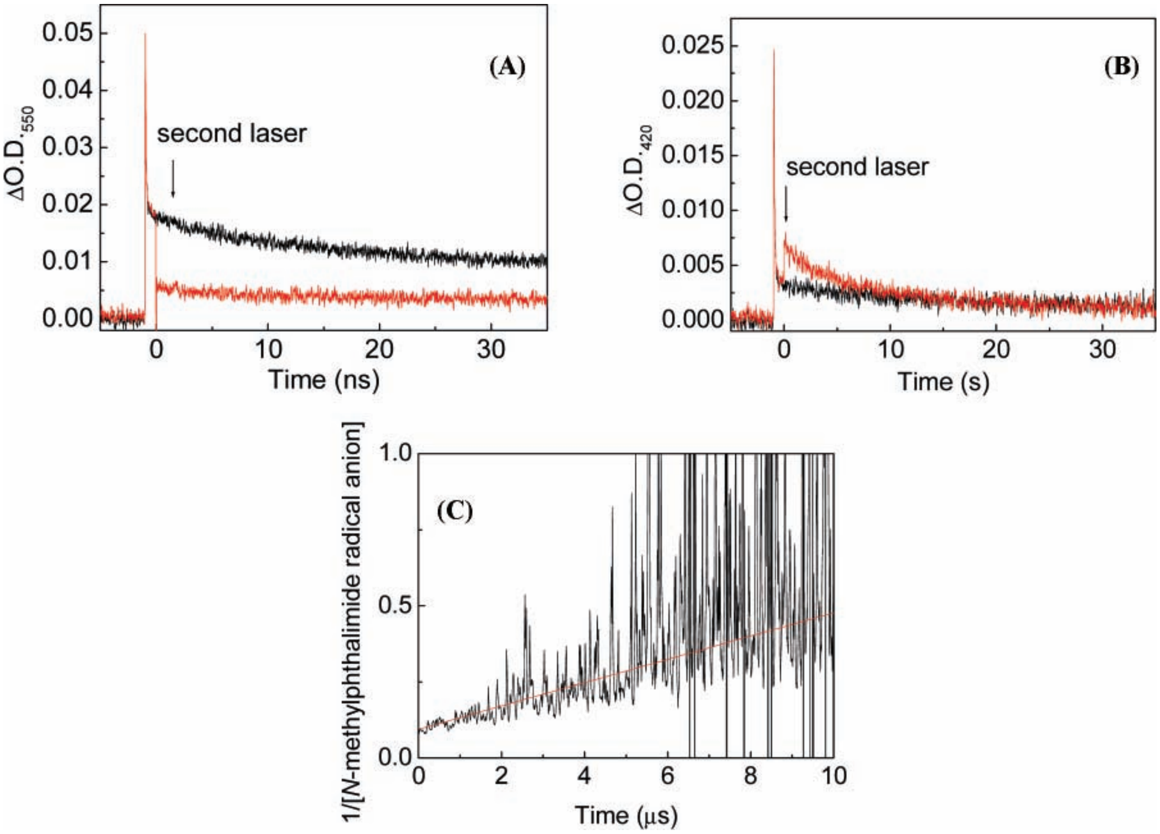


Figure 6. Kinetic traces of ΔO.D. at (A) 550 and (B) 420 nm during the nanosecond one-laser irradiation (black line) and nanosecond/nanosecond two-color two-laser irradiation (red line) of BP (5 mM) in the presence of *N*-methylphthalimide (10 mM) in argon-saturated acetonitrile containing 1,4-cyclohexadiene (30 mM). Panel C shows the second-order plot of the *N*-methylphthalimide radical anion.

According to the Smoluchowski equation, the diffusion-controlled rate constant (k_{diff}) was expressed as[11,22]

$$k_{\mathrm{diff}} = 4\pi D_{\mathrm{DA}} d_{\mathrm{cc}} \tag{7}$$

where D_{DA} denotes the sum of diffusion constants of $\mathrm{BPH}^\bullet$(D_1) ($D_{\mathrm{BPH}\bullet}$) and quenchers (D_{Qs}) and d_{cc} is the reaction distance (d_{cc} = 6 Å). D_{Qs} was calculated from the Stokes−Einstein relation:[11,22]

$$D_{\mathrm{Qs}} = \frac{k_{\mathrm{B}}T}{6\pi r_{\mathrm{A}}\eta} \tag{8}$$

where k_{B} is the Boltzmann constant, r_{A} the radius of the solute, η the viscosity of the solvent, and T the temperature.[22] Terazima et al. reported that the D value of $\mathrm{BPH}^\bullet$ that was generated exhibited D values that were 2−3 times smaller than that of the parent molecule, even though $\mathrm{BPH}^\bullet$ and BP have almost the same size and shape. Thus, we used the D value of $\mathrm{BPH}^\bullet$ in acetonitrile for $D_{\mathrm{BPH}^\bullet}$, which was measured by the time-resolved transient grating method.[20] From eq 7, the k_{diff} value of $\mathrm{BPH}^\bullet$ and Qs in the acetonitrile was calculated to be 1.6×10^{10} M^{-1} s^{-1}.

Rate Constant of Electron Transfer from $\mathrm{BPH}^\bullet$(D_1) to Qs. To determine the intermolecular electron-transfer rate constant, the τ_{f} value was measured as a function of the concentration of Qs ([Qs]). The electron transfer from $\mathrm{BPH}^\bullet$(D_1) to Qs leads to a decrease of τ_{f} with increasing [Qs]. From the plots of the

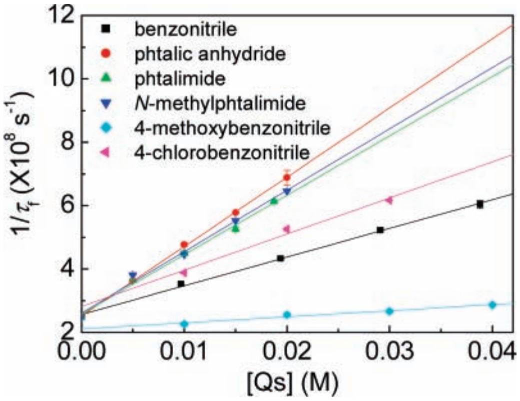


Figure 7. Plots of k_{ELT} vs [Qs].

reciprocal τ_f against [Qs] (Figure 7), the electron-transfer rate constant (k_{ELT}) was determined from eq 9:

$$\frac{1}{\tau_f} = \frac{1}{\tau_{f0}} + k_{ELT}[(Qs)] + k'_{ELT}[BP] \qquad (9)$$

The k_{ELT} value from BPH$^•$(D$_1$) to *N*-methylphthalimide was calculated to be 2.0 × 10^{10} M^{-1} s^{-1}, which is similar to the diffusion-controlled rate constant previously discussed. The k_{ELT} values from BPH$^•$(D$_1$) to several Qs were also calculated and listed in Table 1. The calculated k_{ELT} values of the electron transfer from BPH$^•$(D$_1$) to Qs were similar to the diffusion-controlled rate constant, except for the electron transfer from BPH$^•$(D$_1$) to benzonitrile, 4-methoxybenzonitrile, 4-chlorobenzonitrile, and benzoic acid, which were relatively slow, compared with those of other compounds.

For electron transfer from organic molecules in the excited singlet and triplet states, k_{ELT} usually is dependent on $-\Delta G$.[25] The $-\Delta G$ dependence of k_{ELT} of BPH$^•$(D$_1$) was examined. The $-\Delta G$ of the electron transfer from BPH$^•$(D$_1$) to Qs is represented by eq 10:

$$\Delta G = E_{OX} - E_{RED} + w_p - \Delta E(D_1 - D_0) \qquad (10)$$

where E_{OX} is the oxidation potential of BPH$^•$(E_{OX} = −0.25 V vs SCE in acetonitrile),[26] E_{RED} is the reduction potential of Qs, and w_p represents the Coulombic energy (−0.06 eV). The $-\Delta G$ values have been calculated and listed in Table 1. The plots of log(k_{ELT}) vs $-\Delta G$ were shown in Figure 8. As shown in Figure 8, k_{ELT} increased as the $-\Delta G$ value increased and saturated at a value approximately equal to the diffusion-controlled rate constant. Thus, the slow electron transfer from BPH$^•$(D$_1$) to benzonitrile, 4-methoxybenzonitrile, 4-chlorobenzonitrile, and benzoic acid can be attributed to the small $-\Delta G$. It was indicated that the electron transfer from the excited radical is dependent on $-\Delta G$.

TABLE 1: Triplet Energy (E_T) and Reduction Potential (E_{RED}) of Qs, and Driving Force ($-\Delta G$) and Rate Constant (k_{ELT}) of the Intermolecular Electron Transfer from BPH$^•$(D$_1$) to Qs

Qs	E_T (eV)	E_{RED} (V vs SCE)	-ΔG (eV)	k_{ELT} (× 10^{10} s^{-1})
benzonitrile	3.3[a]	−2.49[a]	−0.08	0.901 ± 0.022
1,3-dicyanobenzene	3.3[a]	−1.72[a]	0.69	1.86 ± 0.05
1,4-dicyanobenzene	3.0[a]	−1.92[a]	0.49	1.93 ± 0.03
phthalimide	3[b]	−1.47[a]	0.94	1.89 ± 0.02
N-methyphthalimide	3[b]	−1.37[c]	1.04	2.0
phthalic anhydride	3.2[a]	−1.27[a]	1.14	2.15 ± 0.04
benzophenone	2.97[a]	−1.87[a]	0.54	2.1[d]
4-methoxybenzonitrile	3.3[a]	−2.71[a]	−0.30	0.15 ± 0.02
4-chlorobenzonitrile	3.2[a]	−2.11[a]	0.30	1.4
benzoic acid	3.4[a]	−2.24[a]	0.17	0.81 ± 0.10
pyrazine	3.3[a]	−2.08[a]	0.33	1.1

[a] Data taken from ref 22. [b] Data taken from ref 23. [c] Data taken from ref 24. [d] Data taken from ref 9.

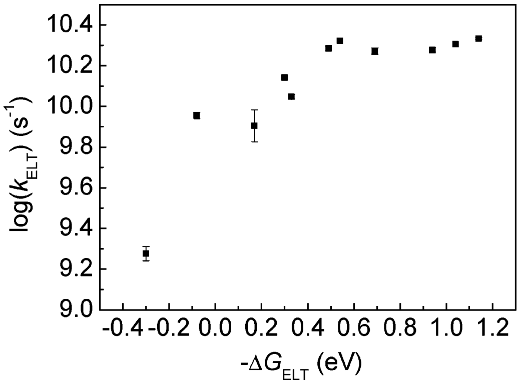


Figure 8. Plots of log(k_{ELT}) vs $-\Delta G$.

Conclusions

The electron transfer from the benzophenone ketyl radical (BPH$^•$(D$_1$)) to a series of quenchers (Qs) was investigated using nanosecond/picosecond two-color two-laser flash photolysis. The electron transfer from BPH$^•$(D$_1$) to Qs was confirmed by the transient absorption measurement and fluorescence quenching experiments. The intermolecular electron transfer rate (k_{ELT}) was determined using the Stern−Volmer analysis. The electron transfer from the excited radical is dependent on $-\Delta G$. It was confirmed that BPH$^•$(D$_1$) was a favorable reducing reagent.

Acknowledgment. This work has been partly supported by a Grant-in-Aid for Scientific Research (Project 17105005, Priority Area (417), 21st Century COE Research, and others) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

References and Notes

(1) (a) Korchev, A. S.; Bozack, M. J.; Slaten, B. L.; Mills, G. *J. Am. Chem. Soc.* **2004**, *126*, 10. (b) Korchev, A. S.; Shulyak, T. S.; Salten, B. L.; Gale, W. F.; Mills, G. *J. Phys. Chem. B* **2005**, *109*, 7733. (c) Sakamoto, M.; Tachikawa, T.; Fujitsuka, M.; Majima, T. *Langmuir* **2006**, *22*, 6361.

(2) (a) El-Sayed, M.; Schill, A. W.; Smirnova, N.; Eremenko, A.; Krylova, G.; Eustis, S. *Photochem. Photobiol. Sci.* **2005**, *4*, 154. (b) Kometani, N.; Doi, H.; Asami, K.; Yonezawa, Y. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5142.

(3) Sato, T.; Onaka, H.; Yonezawa, Y. *J. Photochem. Photobiol. A* **1999**, *127*, 83.

(4) (a) Ramamurthy, V.; Schanze, K. S. *Molecular and Supramolecular Photochemistry, Vol. 2*; Marcel Dekker: New York, 1994. (b) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22. (c) Melnikov, M. Y.; Smirnov, V. A. *Handbook of Photochemistry of Organic Radicals*; Begell House: New York, 1996.

(5) Sakamoto, M.; Tachikawa, T.; Fujitsuka, M.; Majima, T. *Chem. Phys. Lett.* **2006**, *420*, 90.

(6) Baumann, H.; Merckel, C.; Timpe, H.-J.; Graness, A.; Kleinschmidt, J.; Gould, I. R.; Turro, N. J. *Chem. Phys. Lett.* **1984**, *103*, 497.

(7) (a) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978. (b) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396. (c) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368. (d) Weir, D. *J. Phys. Chem.* **1990**, *94*, 5870. (e) Weir, D.; Johnston, L. J.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1742. (f) Fox, M. A.; Gaillard, E.; Chen, C.-C. *J. Am. Chem. Soc.* **1987**, *108*, 7088. (g) Netto-Ferreira, J. C.; Scaiano, J. C. *J. Chem. Soc. Chem. Commun.* **1989**, 435. (h) Adam, W.; Schulte, Oestrich, R. *J. Am. Chem. Soc.* **1992**, *114*, 6031. (i) Samanta, A.; Bhattacharyya, K.; Das, P. K.; Kamat, P. V.; Weir, D.; Hug, G. L. *J. Phys. Chem.* **1989**, *93*, 3651.

(8) (a) Sakamoto, M.; Cai, X.; Hara, M.; Tojo, S.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2005**, *109*, 6830. (b) Sakamoto, M.; Cai, X.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A.* **2006**, *110*, 11800.

(9) Sakamoto, M.; Cai, X.; Hara, M.; Tojo, S.; Fujitsuka, M.; Majima, T. *Chem. Eur. J.* **2006**, *12*, 1610.

(10) (a) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207. (b) Sakamoto, M.; Cai, X.; Hara, M.; Tojo, S.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2004**, *108*, 8147.

(11) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Melco Park, CA, 1978. (b) Suppan, P. *Chemistry and Light*; The Royal Society of Chemistry: Cambridge, U.K., 1994.

(12) Shah, B. K.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem. A* **2004**, *108*, 6087.

(13) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

(14) *Electronic Absorption Spectra of Radical Ions*; Shida, T., Ed.; Physical Science Data 34; Elsevier: Amsterdam, 1988.

(15) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518.

(16) (a) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 398. (b) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9768.

(17) Bietti, M.; Lanzalunga, O. *J. Org. Chem.* **2002**, *67*, 2632.

(18) (a) Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545. (b) Creed, D.; Hoyle, C. E.; Subramanian, P.; Nagarajan, R.; Pandey, C.; Anzures, E. T.; Cane, K. M.; Cassidys, P. E. *Macromolecules* **1994**, *27*, 832.

(19) Arita, T.; Kajimoto, O.; Terazima, M.; Kimura, Y. *J. Chem. Phys.* **2004**, *120*, 7071.

(20) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13387.

(21) (a) Levison, S. A.; Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 4525. (b) Burkhart, R. D.; Wong, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7203. (c) Autrey, T.; Kandanarachchi, P.; Franz, J. A. *J. Phys. Chem. A* **2001**, *105*, 5948. (d) Terazima, M. *Acc. Chem. Res.* **2000**, *33*, 687.

(22) *Handbook of Photochemistry*, 2nd Edition; Murov, S. L., Carmichael, I., Hug, G. L., Eds.; Marcel Dekker: New York, 1993.

(23) Warzecha, K.; Görner, H.; Griesbeck, A. G. *J. Phys. Chem. A* **2006**, *110*, 3356.

(24) Leedy, D. W.; Muck, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4264.

(25) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(26) Lund, T.; Wayner, D. D. M.; Jonsson, M.; Larsen, A. G.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, *123*, 12590.