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Photochemical reaction dynamics of 9,10-phenanthrenequinone and 1,2-naphthoquinone with hydrogen donors in solution

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Abstract

Photoreaction dynamics of 9,10-phenanthrenequinone (PQ) and 1,2-naphthoquinone (NQ) in solution has been studied by laser flash photolysis technique. The real-time transient absorption measurements found out: (1) by excitation at 355 nm in the presence of alcohol, absorption band characteristic to the quinone ketyl radical emerged as the triplet–triplet (T–T) absorption of the quinone submerged, (2) the rise of the absorption of the ketyl radical consisted of two components; the fast and slow ones, where the fast one had the rise rate constant corresponding to the decay rate of triplet quinone, while the slow one rose up much slowly. The experimental fact clearly revealed that the slow reaction should give rise to formation of the ketyl radical following the hydrogen abstraction of triplet PQ and NQ from alcohol, and should be attributed to the hydrogen atom transfer between the parent quinone in the ground state and counter α-hydroxyalkyl radical produced from alcoholic molecule. The reaction mechanism of the ketyl radical formation was thoroughly discussed in the text. The notable reactivity toward hydrogen abstraction of the triplet *o*-quinones was also discussed.

Keywords: *o*-Quinone; 9,10-Phenanthrenequinone; 1,2-Naphthoquinone; Hydrogen atom abstraction; Ketyl radical

1. Introduction

It is known that quinone compounds play important roles in photosynthesis and photobiology, and apparently the interest in their biological function has stimulated basic chemical research in many scientific fields [1]. A large number of studies on photoexcited quinones, especially *p*-quinones, have been carried out; photophysics [2–4] and photochemistry such as cycloaddition, dimerization [5–9], photoreduction involving hydrogen abstraction and electron transfer [10–12]. Photoinduced hydrogen abstraction and electron transfer of quinones are known as the primary processes of various photochemical reactions and key reactions in the development of synthetic and mechanistic photochemistry.

Compared with *p*-quinones, however, little information on photochemistry of *o*-quinones has been reported. Photocycloaddition and photoinduced 1,2- or 1,4-addition reaction of 9,10-phenanthrenequinone (PQ) and 1,2-naphthoquinone (NQ), which are the prototype of *o*-quinones, with olefins, toluenes and aldehydes were investigated by steady-state photolysis and product analysis [13–16]. Photoexcited PQ and NQ were reported to be reduced by alcohols, producing 9,10-dihydroxyphenanthrene (PQH_2) and 1,2-dihydroxynaphthalene (NQH_2), respectively [1,15,17]. Carapellucci et al. performed the steady-state and the flash photolysis studies on the photoreduction of PQ in 2-propanol–benzene mixture [17]. They found that the photoreaction of PQ with 2-propanol gave rise to PQH_2 and acetone, and the quantum yield for the disappearance of PQ was greater than unity (Φ = 1.6 in neat 2-propanol). Several time-resolved techniques were applied to investigate dynamics of excited PQ and NQ. The excited *o*-quinones gave rise to ultrafast S → T intersystem crossing ($k_{ISC} \sim 10^{11}\ s^{-1}$) [18].

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Shimoishi et al. reported by time-resolved ESR and chemically induced dynamic electron polarization (CIDEP) studies that triplet PQ and NQ were reactive with alcohols and amines to produce ketyl radicals and semiquinone anion radicals as reaction intermediates [19,20]. However, the complicated reaction mechanism of photoexcited PQ and NQ has not been elucidated yet.

In this article, we studied on photochemical dynamics of PQ and NQ in the presence of hydrogen donors with a nanosecond laser flash photolysis technique, and elucidated the overall reaction mechanism.

2. Experimental

PQ and NQ (Aldrich) were purified by column chromatography. Acetonitrile, benzene, methanol, ethanol, and 2-propanol (Kanto Chemical, GR grade) were used from freshly-opened bottles. The sample solution was deaerated by bubbling with Ar gas (purity 99.95%) purged by the solvent vapor for half-an-hour before use.

An experimental setup for the transient absorption measurement was described elsewhere [21]. Briefly, a Nd^{3+}: YAG laser (Continuum Powerlite Precision 8010) operated at 355 nm (5–7 ns pulse duration, <450 mJ/pulse, repetition rate 2 Hz) was used as an excitation light source and a Xe flash lamp (Ushio UXL-300DO; 300 W) was used as a monitoring light source. The monitoring light, passing through a cuvette (NSG T-59FL-10; 10 mm optical pass length), was detected by a monochromator (Nikon P-250) and photomultiplier tube (Hamamatsu Photonics R928) combination system. The output signal was recorded on a digital oscilloscope (Sony Tektronix TDS380P; 400 MHz, 2 GS/s) and transferred to a personal computer. The signal was averaged over 30 shots. The sample solution was flowed into the cuvette to remove the influence of photoproducts. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Triplet characterization

Fig. 1a shows transient absorption spectra of PQ in acetonitrile (open circle) and benzene (closed square) immediately after the 355 nm laser irradiation. Two broad absorption bands were observed at around 460 nm and 650 nm, and a sharp band was at around 330 nm in acetonitrile, while two broad absorption bands were observed at around 455 nm and the 300–400 nm region in benzene. The observed absorption bands are in good agreement with the triplet–triplet (T–T) absorption spectra of PQ in the 400–700 nm region reported [22,23]. The spectral differences in between these solutions should result from the T_1 character: $^3\pi\pi^*$ in acetonitrile and $^3n\pi^*$ in benzene [20]. Fig. 1b shows transient absorption spectra of NQ in acetonitrile and benzene. As well as PQ, the

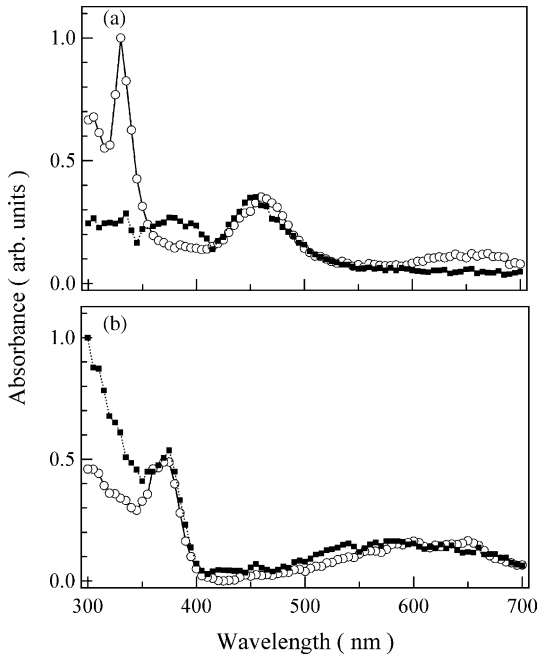

Fig. 1. Transient absorption spectra of (a) PQ and (b) NQ in acetonitrile (○) and benzene (■) obtained immediately after the 355 nm laser irradiation.

bands observed in both solutions were attributed to the T–T absorption of NQ; the T_1 character is $^3\pi\pi^*$ in acetonitrile and $^3n\pi^*$ in benzene [20].

In acetonitrile solution, time profiles of the T–T absorption were observed with various concentrations of PQ and NQ. It was found that the decay rate constants observed under the low laser fluence condition, where T–T annihilation was neglected, depended on the concentration of the ground state quinone ($[^1Q]$). The observed decay rate constant (k_{obs}) for $^3PQ^*$ and $^3NQ^*$ can be expressed as follows:

$$k_{obs} = k_0 + k_{SQ}[^1Q] \quad (1)$$

where k_0 and k_{SQ} are the rate constants for unimolecular decay of the triplet and for self-quenching due to the parent molecule, respectively. Fig. 2 shows the plots of the k_{obs} values as a function of $[^1Q]$ in acetonitrile. From the intercept and the slope of the fitting line obtained by the least squares method, the k_0 and k_{SQ} values were determined (Table 1). Since the k_0 value corresponds to the rate of $T_1 \rightarrow S_0$ intersystem crossing, the triplet lifetimes (τ_T) being immune to the parent molecule were obtained to be 6.7 ± 0.5 μs for PQ and 11.1 ± 0.4 μs for NQ in acetonitrile. Accordingly, the

Table 1
Triplet–triplet absorption and kinetic parameters of PQ and NQ in acetonitrile

	λ_{max} (nm)[a]	k_0 (10^5 s^{-1})[b]	k_{SQ} (10^8 M^{-1} s^{-1})[b]	τ_T (μs)[bc]
PQ	650, 450, 330	1.5	7.2	6.7
NQ	650, 600, 370	0.90	4.0	11.1

[a] The wavelengths of maximum T–T absorption.
[b] Typical errors in the estimated values are less than 5%.
[c] $\tau_T = 1/k_0$.

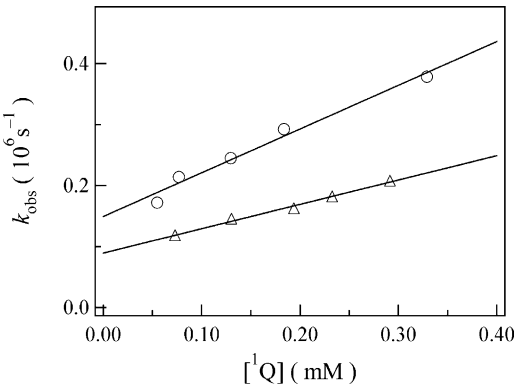

Fig. 2. Lots of the decay rate constant (k_{obs}) of ^{3}PQ* (◯) and ^{3}NQ* (△) as a function of [^{1}Q] obtained by the 355 nm laser photolysis in acetonitrile. Good linear relations were observed. The solid lines denote the best fitting lines determined by the least squares method.

lifetime of ^{3}PQ* was found to be shorter than that of ^{3}NQ*. The shorter lifetime of ^{3}PQ* would be attributed to intersystem crossing of the $T_1 \rightarrow S_0$ accelerated by the interaction of $^3n\pi^*$–$^3\pi\pi^*$. Such an interaction was reported with the ESR measurement [20], while ^{3}NQ* has almost pure $\pi\pi^*$ character in polar solvents.

In benzene solution, the lifetime of ^{3}PQ* and ^{3}NQ* were obtained to be 450 and 500 ns, respectively, and the absorption spectra of the ketyl radicals were observed, revealing the occurrence of photochemical reaction of the triplet quinone with benzene. The high reactivity for triplet *o*-quinones will be discussed below.

3.2. Photochemical reaction with alcohol

3.2.1. The absorption spectrum of the ketyl radical

As mentioned in Section 1, the main products of photoreaction of PQ with alcohol under the deaerated condition are known to be the reduced form of the quinone (PQH_2) and the oxidation form of alcohol. In the case of NQ, the final photoproducts were NQH_2 and the oxidation form of alcohol, as well as PQ.[1] In order to clarify the reaction mechanism, the transient absorption measurement was carried out. Fig. 3a shows transient absorption spectrum of PQ (0.62 mM) in 2-propanol at 0.10 and 4.0 μs after the laser, when ^{3}PQ* completely disappeared. An absorption peak grew up at 380 nm and a bleaching due to depletion of parent PQ appeared at 325 nm gradually. The spectrum agreed with the reported one of the ketyl radical of PQ ($PQH^\bullet$) by the flash photolysis experiment [17]. Thus, the peak will be assigned to the

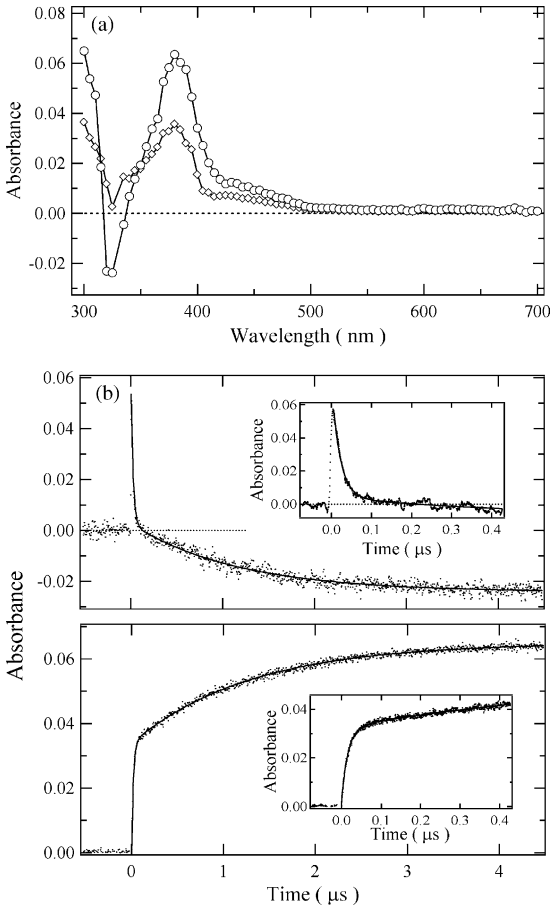

Fig. 3. (a) Transient absorption spectrum of PQ (0.62 mM) in 2-propanol at 0.10 μs (◊) and 4.0 μs (◯) after the laser photolysis. (b) Time profiles of the transient absorption monitored at 325 nm (upper) and 380 nm (lower). The insets show the time profiles in a shorter time region. The time zero corresponds to the end of the excitation laser pulse. At each wavelength, two components were observed. The solid lines are the fitting curves obtained by the least squares fitting with Eq. (2). See text for details.

absorption of $PQH^\bullet$. Time profiles of the transient absorption monitored at 325 and 380 nm are illustrated in Fig. 3b. Two decay components were observed at 325 nm; fast and slow ones. The fast decay component will be due to ^{3}PQ*. At 380 nm, two rising components were clearly observed, indicating two kinds of reaction pathways to produce $PQH^\bullet$.

Accordingly, the time evolution of the transient absorption can be described as follows:

$$OD_t^\lambda = OD_{4.0\,\mu s}^\lambda - C_F \exp(-k_F t) - C_S \exp(-k_S t) \qquad (2)$$

where OD_t^λ is the absorbance at time t, $OD_{4.0\,\mu s}^\lambda$ is the maximum absorbance observed at 4.0 μs, and λ is the wavelength monitored. k_F and k_S are the rate constants of the fast and the slow components, respectively. C_F and C_S are the pre-exponential factors of the fast and slow components, respectively. By analyzing the time profile monitored at 380 nm with Eq. (2), the values of k_F and k_S were successfully determined to be $(5.6 \pm 0.1) \times 10^7$ s^{-1} and $(7.8 \pm 0.1) \times 10^5$ s^{-1}, respectively. The k_F and k_S values obtained at 325 nm were

[1] The orange color of NQ in 2-propanol was clearly bleached and the characteristic absorption bands of NQ disappeared by the stationary visible light irradiation. Shaking the colorless photolyzed solution in the air caused the regeneration of the color and the absorption peaks of NQ were observed again. Colorless NQH_2 was reported to undergo rapid air oxidation to form the parent quinone [15]. Moreover, the characteristic absorption of acetone was observed at 273 nm. Therefore, photoexcited NQ was reduced by 2-propanol to yield NQH_2 and acetone, as well as PQ.

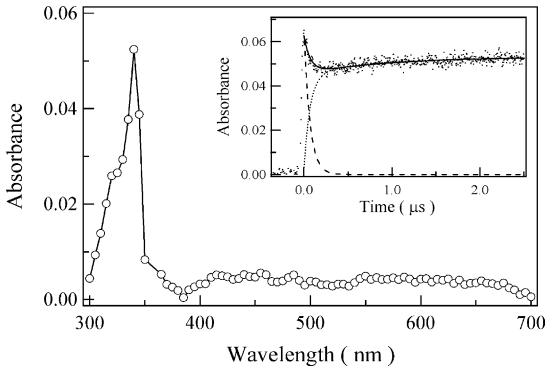

Fig. 4. Transient absorption spectrum of NQ (0.66 mM) in 2-propanol at 2.5 μs after the laser photolysis. The inset shows the time profile of the transient absorption monitored at 340 nm and the analytical results; total absorbance (solid line) and absorbances of ^{3}NQ* (broken line) and NQH• (dotted line).

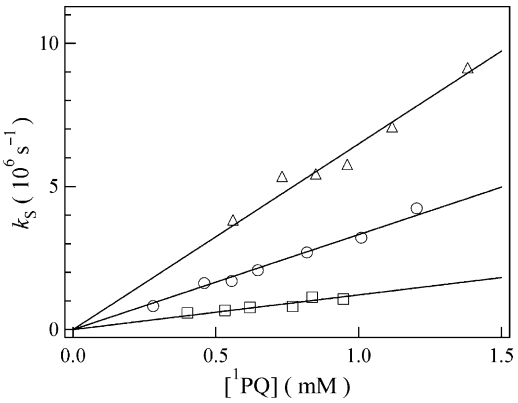

Fig. 5. Plots of the k_S values of PQ in methanol (△), ethanol (◯) and 2-propanol (□) as a function of [^{1}PQ]. Good linear relations were observed. The solid lines show the best fitting lines. See text for details.

excellently identical to those at 380 nm. It is concluded that the fast component at 380 nm should be due to the formation of PQH• produced by hydrogen abstraction of ^{3}PQ* from 2-propanol with the following facts. First, the rise rate constant of k_F at 380 nm corresponded to the decay rate constant of ^{3}PQ* monitored at 325 nm. Second, the transient absorption spectrum at the end of the triplet decay (at 0.10 μs) as well as that at 4.0 μs after the laser was identical to the reported PQH• spectrum. The slow rise component at 380 nm well agreed with the disappearance rate of parent PQ monitored at 325 nm. The appearance of the slow rise component suggests another pathway to produce PQH• besides the hydrogen abstraction reaction by ^{3}PQ*. The similar results were obtained for methanol and ethanol solutions.

Transient absorption measurements were also carried out for NQ-alcohol systems. Transient absorption spectrum of NQ (0.66 mM) in 2-propanol at 2.5 μs after the laser photolysis is shown in Fig. 4. An absorption peak was observed at 340 nm. The CIDEP study [20] revealed that photoexcited NQ was reduced to form a ketyl radical (1-oxy-2-hydroxy semiquinone radical: NQH•) in 2-propanol. Therefore, the absorption band at 340 nm was safely assigned to the absorption of NQH•. A time profile of the transient absorption monitored at 340 nm is shown in the inset of Fig. 4. In a similar analytical treatment for PQ, two processes forming NQH• were found as shown in the inset as the dotted line. The fast one had a rise rate constant (k_F) of 1.4×10^7 s^{-1} in good agreement with the decay rate constant of ^{3}NQ*, while the slow one has a rate constant (k_S) of 1.2×10^6 s^{-1}. In a similar fashion to PQ, another process to form NQH• should exist in addition to the hydrogen abstraction reaction of ^{3}NQ*.

3.2.2. *The slow formation process of the ketyl radical*

The k_S value, the slower formation rate of the ketyl radical, was found to be correlated to the concentration of the ground state quinone. Fig. 5 shows the plots of the k_S value against the concentration of PQ ([^{1}PQ]) in alcohols. Good linear relation was observed, indicating that the parent molecule in the ground state should participate in the formation of the ketyl radical. According to the fact that the oxidation form of alcohol such as acetone was given as the reaction product in alcohol, α-hydroxyalkyl radical should act as a hydrogen source. Therefore, it is suggested that the slower formation process of the ketyl radical should be hydrogen atom transfer from α-hydroxy alkyl radical to the parent quinone molecule in the ground state. The reaction scheme for the formation of the ketyl radical should be written down as follows:

$$^3Q^* + R_2(CH)OH \xrightarrow{k_{HA}} QH^\bullet + R_2\dot{C}OH \quad \text{(i)}$$

$$^1Q + R_2\dot{C}OH \xrightarrow{k_r} QH^\bullet + R_2C{=}O \quad \text{(ii)}$$

where $R_2(CH)OH$ is an alcohol molecule, $R_2\dot{C}OH$ is the α-hydroxyalkyl radical, and $R_2C{=}O$ is the final product from $R_2(CH)OH$. k_{HA} and k_r are the rate constants of reactions (i) and (ii), respectively.

α-Hydroxyalkyl radical is known as an intermediate of photoreaction in ketone–alcohol system, and its reactivity has been investigated by several authors [25–27]. 2-Hydroxypropyl radical, one of α-hydroxyalkyl radical, was produced by the photolysis of acetone in 2-propanol. The radical disappeared by dimerization to produce pinacol and by disproportionation or recombination to produce acetone and 2-propanol. The dimerization is known as the main reaction, and the second order reaction rate constant was reported to be 1×10^9 M^{-1} s^{-1} [25]. With the assumption that the quantum yield of hydrogen abstraction (i) is unity, the upper limit of the concentration of α-hydroxyalkyl radical is roughly estimated to 10^{-5} to 10^{-6} M from the photon density of the excitation light and the absorbance of the sample. This value is two orders of magnitude lower than that of the ground state quinone (10^{-3} M). Thus, reaction (ii) will proceed faster than the bimolecular reactions of α-hydroxyalkyl radical. Under the pseudo-first-order condition, the concentrations of the reaction intermediates can be written down

as

$$[^3Q^*] = [^3Q^*]_0 \exp(-k_T t),$$
$$[QH^\bullet] = p - q \exp(-k_T t) - r \exp(-k_r[^1Q]t),$$
$$[R_2\dot{C}OH] = r\{\exp(-k_r[^1Q]t) - \exp(-k_T t)\} \qquad p = q - r,$$
$$q = \frac{k_{HA}[R_2(CH)OH][^3Q^*]_0 + rk_r[^1Q]}{k_T},$$
$$r = \frac{k_{HA}[R_2(CH)OH][^3Q^*]_0}{k_T - k_r[^1Q]} \tag{3}$$

where k_T is the decay rate constant of the triplet quinone. Since the absorption band of α-hydroxyalkyl radical was not seen in the observed spectral range of 300–700 nm in the case of methanol, ethanol and 2-propanol, the time course of the transient absorption (OD^λ) at the wavelength of λ (nm) can be expressed as

$$OD^\lambda = \{(\varepsilon^\lambda_T - \varepsilon^\lambda_{1_Q})[^3Q^*] + (\varepsilon^\lambda_{QH^\bullet} - \varepsilon^\lambda_{1_Q}][QH]\}d \tag{4}$$

where ε^λ_T, $\varepsilon^\lambda_{QH^\bullet}$ and $\varepsilon^\lambda_{1_Q}$ are the extinction coefficients of the triplet quinone, the ketyl radical and the parent quinone at λ nm. d is the optical path length of the sample cell (d = 1 cm). Finally, the following equation was led by substitution of Eq. (4) by Eq. (3) and comparison with Eq. (2).

$$k_s = k_r[^1Q], \quad k_F = k_T = k_0 + k_{SQ}[^1Q] + k_q[R_2(CH)OH] \tag{5}$$

k_q is the quenching rate constant of the triplet quinone by alcohol. From the slopes of the least squares fitting lines in Fig. 5, the k_r values were successfully determined, and summarized in Table 2. The results obtained for the NQ-alcohol systems were also listed in Table 2. The values of k_r were found to be close to the diffusion-controlled rate (k_{diff}).

The k_q value in acetonitrile was also determined and summarized in Table 2. Since the reaction (i) takes place in the triplet state, the back reaction in a solvent cage is hard to occur due to the triplet multiplicity. So, the k_q value would be regarded as the rate constant of reaction (i) (k_{HA}). The total quantum yield for the formation of the ketyl radical (Φ_{Total}) is expressed by the sum of the yields for reaction (i) and (ii) (Φ_i and Φ_{ii}). The values of Φ_i and Φ_{ii} can be estimated by consideration of the k_T and k_q values and the pre-exponential factors of Eq. (2).

$$\Phi_{Total} = \Phi_i + \Phi_{ii} \qquad \Phi_i = \frac{k_q[R_2(CH)OH]}{k_T},$$
$$\Phi_{ii} = \frac{C_S}{C_F}\Phi_i \tag{6}$$

The Φ_{Total} values in 2-propanol are estimated to be 1.7 for PQ and 1.2 for NQ. The value for PQ is in good agreement with the reported value of the yield for the disappearance of PQ on photoreaction (Φ = 1.6).

It is found that the rate of reaction (ii) is of three orders much faster than the primary reaction (i). The rate of hydrogen abstraction by carbonyl compounds in the $^3n\pi^*$ state is known to be dependent on bond strength of hydrogen donor [28–30]. The bond dissociation energy of O–H bond of α-hydroxyalkyl radical ($D_{dis}(R_2\dot{C}OH)$) can be evaluated as

$$D_{dis}(R_2\dot{C}OH) = \{\Delta H_f(R_2C{=}O) + \Delta H_f(H^\bullet)\} - \Delta H_f(R_2\dot{C}OH) \tag{7}$$

where ΔH_f ($R_2C{=}O$), ΔH_f ($H^\bullet$), and ΔH_f ($R_2\dot{C}OH$) are the heat of formations of the product from alcohol, hydrogen atom, and α-hydroxyalkyl radical. The estimated $D_{dis}(R_2\dot{C}OH)$ values and the dissociation energy of C–H bond of alcohols ($D_{dis}(R_2(CH)OH)$) are listed in Table 3. There are extremely large differences (ca. 65 kcal mol^{-1}) between the values of $D_{dis}(R_2(CH)OH)$ and $D_{dis}(RH^\bullet)$ obtained, suggesting that α-hydroxyalkyl radical would have

Table 3
The bond dissociation energies (D_{dis}) of alcohols and α-hydroxyalkyl radical

Alcohol/RH• radical	$D_{dis}(R_2(CH)OH)$[a]	$D_{dis}(R_2\dot{C}OH)$[b]
2-Propanol/2-hydroxypropyl radical	91.0	26.5
Ethanol/hydroxyethyl radical	94.8	25.7
Methanol/hydroxymethyl radical	96.1	30.2

All the values are in units of kcal mol^{-1}.
[a] Gas phase data at 298 K, taken from Ref. [32].
[b] Estimated by Eq. (7), using the ΔH_f values in gas phase at 298 K. The ΔH_f values are taken from Refs. [32,33]; 2-hydroxypropyl radical = −26.3, acetone = −51.9, hydroxyethyl radical = −13.3, acetaldehyde = −39.7, hydroxymethyl radical = −4.1, formaldehyde = −26.0, hydrogen atom = +52.1 (all in units of kcal mol^{-1}).

Table 2
The quenching rate constant (k_q) of triplet quinone by alcohols, the rate constant of reaction (ii) (k_r), and the diffusion controlled rate constants (k_{diff}) in alcohols

Alcohol	PQ		NQ		k_{diff} (M^{-1} s^{-1})[c]
	k_q (M^{-1} s^{-1})[a]	k_r (M^{-1} s^{-1})[b]	k_q (M^{-1} s^{-1})[a]	k_r (M^{-1} s^{-1})[b]	
2-Propanol	7.6×10^6[d]	1.2×10^9	2.3×10^6[d]	2.6×10^9	3.2×10^9
Ethanol	2.7×10^6[e]	3.3×10^9	1.6×10^5[e]	6.0×10^9	6.1×10^9
Methanol	2.1×10^6[d]	6.5×10^9	–[f]	–[f]	12×10^9

[a] In acetonitrile.
[b] Estimated by Eq. (5) (see text for details). Errors should be within 10%.
[c] At 298 K, from Ref. [25].
[d] From Ref. [23].
[e] This work. Errors should be within 10%.
[f] The k_F and k_S values were too close to be determined separately.

larger degree of hydrogen-donating ability than alcoholic molecule.

Since reaction (i) proceeds via the triplet state, the character and the energy of the triplet quinone should be taken into consideration. As mentioned in Section 3.1, the T_1 character of these quinone in the polar solvent is $^3\pi\pi^*$, and it is expected that the hydrogen abstraction should take place via the $T_2(n\pi^*)$ state which is populated thermally with the $T_1(\pi\pi^*)$ state. In fact, the k_q values of PQ and NQ in the $T_1(^3n\pi^*)$ state ($1.6 \times 10^8\,M^{-1}\,s^{-1}$ for PQ and $6.6 \times 10^6\,M^{-1}\,s^{-1}$ for NQ by 2-propanol [23]) are larger than those in the $T_1(^3\pi\pi^*)$ state (see Table 2). However, these values are smaller than the k_r values. The energies of the lowest $^3n\pi^*$ state of PQ (49.1–50.0 kcal mol^{-1}, affected by solvent polarity [33]) and NQ (though the triplet energy of NQ is unknown because of its non-phosphorescent character, the estimated value by theoretical calculation [22] suggested that it would be slightly lower than that of PQ) are much lower (15–20 kcal mol^{-1}) than the difference of the $D_{dis}(R_2(CH)OH)$ and $D_{dis}(R_2\dot{C}OH)$ values. Consequently, it can be concluded that reaction (ii) proceeds faster than reaction (i) due to the weak bond strength of α-hydroxyalkyl radical, despite of the excess energy of the triplet quinone.

3.3. Reactivity of triplet PQ and NQ

For hydrogen abstraction by carbonyl compounds, the triplet energy is known as one of the important factors to influence the reaction rate [28–30]. The triplet energy of PQ and NQ (see the previous section) are quite low compared with acetone (78 kcal mol^{-1} [24]) and benzophenone (69 kcal mol^{-1} [24]). Surprisingly, the reported quenching rate constants of PQ ($1.6 \times 10^8\,M^{-1}\,s^{-1}$ [23]) and NQ ($6.6 \times 10^6\,M^{-1}\,s^{-1}$ [23]) in the $T_1(n\pi^*)$ state by 2-propanol are larger than those of acetone ($1 \times 10^6\,M^{-1}\,s^{-1}$ [30]) and benzophenone ($1.1 \times 10^6\,M^{-1}\,s^{-1}$ [30]) in the $T_1(^3n\pi^*)$ state. It suggests the high reactivity of triplet PQ and NQ.

We measured transient absorption spectra of PQ and NQ in benzene. The ketyl radicals of PQ and NQ were observed with the 355 nm excitation (the absorption maxima were 390 nm for PQ and 340 nm for NQ), indicating the hydrogen atom abstraction of triplet PQ and NQ take place even from benzene. The reaction rate constant was roughly estimated to be the order of 10^4 to $10^5\,M^{-1}\,s^{-1}$ from the triplet lifetimes of PQ (450 ns) and NQ (500 ns). Rubin and Neuwirth-Weiss [34] reported the formation of biphenyl as a photoproduct with steady-state photolysis of PQ in benzene by means of product analysis. Benzene has been believed and used as an inert solvent, and there have been few reports on hydrogen abstraction for other aromatic ketones from benzene. The inertness of benzene would be explained by the quite high dissociation energy of C–H bond (112.9 kcal mol^{-1} [31]), compared with typical hydrogen donors (91 kcal mol^{-1} for 2-propanol [31]). It also strongly suggests that triplet PQ and NQ should have remarkable high reactivity toward hydrogen abstraction.

The notable reactivity of PQ and NQ would result from their characteristic conformation. The existence of adjacent two carbonyl groups will make the transition state energetically stabilized by doubly hydrogen bonding with the hydrogen donor. Scaiano et al. reported that high reactivity of 1,1,4,4-tetramethyl-1,4-dihydro-2,3-naphtharenedione, whose two carbonyl groups are locked to the *cisoid* conformation compared with biacetyl was attributed to a considerable degree of stabilization of the transition state due to intramolecular hydrogen bonding [35]. Furthermore, higher reactivity of PQ than that of NQ would result from the larger triplet energy, the high symmetry, and the size of π-conjugated system. Therefore, the hydrogen bonding of adjacent two carbonyl groups with the hydrogen donor and the structure of the transition state would affect on the reactivity of *o*-quinones.

4. Conclusion

Photochemical reaction dynamics of PQ and NQ in their triplet states was studied by laser flash photolysis. The T–T absorption spectra of PQ and NQ were affected by the solvent polarity. In the presence of alcohol, the rise of the absorption of the ketyl radical was found to consist of two components, indicating that the two kinds of pathways to produce the ketyl radical exist. The first pathway is the hydrogen atom abstraction of triplet PQ and NQ from alcohol. The other one is the hydrogen atom transfer between the parent quinone in the ground state and α-hydroxyalkyl radical, which has been produced by the hydrogen abstraction of the triplet quinone from the alcoholic molecule. In this study, we carried out the real-time measurement and clarified the reaction mechanism between the α-hydroxyalkyl radicals and the ground state quinones.

Triplet PQ and NQ show remarkably high reactivity with benzene. The notable reactivity would result from their characteristic molecular conformation; namely, the existence of two adjacent carbonyl groups would cause the stabilized conformation in the transition state through doubly hydrogen bonding with the hydrogen donor.

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