Bull. Chem. Soc. Jpn., 55, 1705—1709 (1982)

ESR Studies on the Free Radical Intermediates in the Photoreduction of Duroquinone in Alcohol Solutions

Shoji Noda,* Kiyoshi Sanehira, Takahisa Doba, and Hiroshi Yoshida
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

(Received September 9, 1981)

ESR measurements during photolysis of duroquinone (DQ) solutions in ethanol and 2-propanol have revealed the generation of both durosemiquinone anion ($\mathrm{DQ}^{\bar{\cdot}}$) and durosemiquinone radicals ($\mathrm{DQH}\cdot$). Correspondingly, alkoxyl radicals have been detected from the photolyzed solutions by the spin trapping-ESR technique, though the quantum yield of their formation is very low (10^{-3} for the ethanol solution). Main conclusions deduced from the present work are (1) that $\mathrm{DQ}^{\bar{\cdot}}$ is generated through the one-electron reduction of DQ by α-hydroxyalkyl radical and through the photodissociation of (DQ–$\mathrm{DQH_2}$) complex, and (2) that $\mathrm{DQH}\cdot$ is generated through the hydrogen abstraction of $^3\mathrm{DQ}^*$ either from solvent alcohols or from photoproduct durohydroquinone ($\mathrm{DQH_2}$). The one-electron reduction in alcohol solution previously reported for *p*-benzoquinone is a minor pathway of chemical quenching of $^3\mathrm{DQ}^*$. The quantum yield of the $\mathrm{DQH_2}$ formation in an early period of photolysis of a dilute DQ in methanol, ethanol, and 2-propanol has been observed to be 0.12, 0.23, and 0.36 respectively. These values are discussed in terms of the mechanism of the quinone photoreduction.

Despite extensive studies[1–9] on the photochemistry of duroquinone (DQ) in alcohol solutions, there still remains a controvery about the initial photochemical reaction, the chemical quenching of triplet excited duroquinone ($^3\mathrm{DQ}^*$). This reaction can be explained either as a hydrogen abstraction (reaction (1))[1–8] giving a durosemiquinone radical ($\mathrm{DQH}\cdot$), or as a one-electron transfer (reaction (2))[9] giving a durosemiquinone anion ($\mathrm{DQ}^{\bar{\cdot}}$):

$$^3\mathrm{DQ}^* + \mathrm{RR'CHOH} \longrightarrow \mathrm{DQH}\cdot + \mathrm{RR'\dot{C}OH}, \qquad (1)$$

$$^3\mathrm{DQ}^* + \mathrm{RR'CHOH} \longrightarrow \mathrm{DQ}^{\bar{\cdot}} + \mathrm{RR'CH\dot{O}} + \mathrm{H}^+. \qquad (2)$$

$\mathrm{DQ}^{\bar{\cdot}}$ should also be generated through the reduction of DQ by α-hydroxyalkyl radical:[10]

$$\mathrm{DQ} + \mathrm{RR'\dot{C}OH} \longrightarrow \mathrm{DQ}^{\bar{\cdot}} + \mathrm{RR'C{=}O} + \mathrm{H}^+. \qquad (3)$$

The formation of $\mathrm{DQ}^{\bar{\cdot}}$ is thus expected by either mechanism of the chemical quenching. However, no definite detection of $\mathrm{DQ}^{\bar{\cdot}}$ by electron spin resonance (ESR) technique has been reported for the photolysis of DQ in alcohol solutions. The ESR detection of $\mathrm{DQH}\cdot$ has been reported by several research groups,[11–13] but an efficient chemical quenching of $^3\mathrm{DQ}^*$ by durohydroquinone ($\mathrm{DQH_2}$), a main photoproduct,

$$^3\mathrm{DQ}^* + \mathrm{DQH_2} \longrightarrow 2\,\mathrm{DQH}\cdot \qquad (4)$$

may be a dominant source of the detected $\mathrm{DQH}\cdot$. The ESR observations do not seem to have been well explained in the mechanism of photoreduction of DQ in alcohols.

We have demonstrated in the previous ESR study during the photolysis of *p*-benzoquinone in ethanol that the yields of semiquinone radical and semiquinone anion depend on the flow rate of the solution and *p*-benzoquinone concentration.[14] We have also detected ethoxyl and 1-hydroxyethyl radicals by the spin trapping-ESR technique.[14] In contrast, no α-hydroxyalkyl radical has been detected by this technique from the photoreduction of DQ in several alcohols.[15] The spin trapping-ESR detection of α-hydroxyalkyl radicals will depend on the efficiency of the reduction of quinones with the radicals, such as reaction (3).

In order to give further insight into the generation and behavior of semiquinone intermediates, the steady-state ESR measurements during photolysis combined with the spin trapping-ESR measurements are extended in the present investigation to DQ in ethanol and 2-propanol.

Experimental

Chemicals. DQ and $\mathrm{DQH_2}$ from Tokyo Chemical Industry Co. were purified by repeated sublimation. Methanol, ethanol, and 2-propanol of 99.5% purity from Wako Pure Chemical Ind. were used without further purification. Occasionally the effects of purifying the alcohols were examined, but no significant difference was observed in the results. α-Phenyl-*N*-butylnitrone (PBN) was synthesized as described previously[14] and was used as a spin trap.

ESR Measurements during Photolysis. The transient semiquinone intermediates were observed by ESR measurements with a Varian E-109 spectrometer during continuous photolysis of the DQ solution in ethanol or 2-propanol flowing through a quartz flat cell in the resonant cavity, as described in detail elsewhere.[16] The photolysis was carried out with light from a supper-high pressure mercury lamp (Philips, SP-500) or from a mercury-xenon lamp (Conrad-Hanovia 941B0010). Occasionally degassed solutions in a quartz ESR tube were photolyzed in the resonant cavity.

Spin Trapping-ESR Measurements. The DQ solutions in ethanol or 2-propanol containing a small amount of PBN were degassed, sealed in a rectangular quartz optical cell (optical path of 1.0 cm) connected with a Pyrex tube (0.2 cm i.d.) for ESR measurements, and photolyzed with light of 436 nm from a high pressure mercury lamp (Toshiba, SHL-100UV) through filters (Toshiba VY-42 and VV-42).

Optical Absorption Measurements. The decay of DQ and the formation of $\mathrm{DQH_2}$ were followed by observing their absorption spectra with a recording spectrophotometer (Shimadzu, MPS-5000) before and after an intermittent photolysis of the DQ solutions in methanol, ethanol, and 2-propanol sealed in a rectangular quartz optical cell (optical path of 1.0 cm) under a pressure of 10^{-3} Pa. The photolysis was carried out with the light of a sharp resonance line at 254 nm from a low pressure mercury lamp (Toshiba, GL-15) through a glass filter (Toshiba, UVD33S) and an aqueous solution of $\mathrm{NiSO_4\cdot H_2O}$ (500 g $\mathrm{dm^{-3}}$) of 1 cm path length. The intensity of the incident light was calibrated by actinometry with potassium trioxalatoferrate(III).

Results

ESR Detection of Semiquinone Intermediates. ESR spectra observed during photolysis show only semiquinone intermediate(s) as shown in Figs. 1A and B. Dilute DQ solutions ($\leq 10^{-4}$ mol dm^{-3}) in ethanol and 2-propanol flowing in the cell gave only the spectrum of $\mathrm{DQ}^{\bar{\cdot}}$ with thirteen hyperfine lines equally separated with a splitting constant of 0.19 mT (Fig. 1A). Its intensity increased with increasing resident time of the solutions in the resonant cavity up to 1s (with decreasing flow rate of the solutions). This increase is probably due to the accumulation of $\mathrm{DQ}^{\bar{\cdot}}$ during the photolysis of the solution within the effective volume of the cell, and give a rough estimate of the lifetime of $\mathrm{DQ}^{\bar{\cdot}}$ of 1s. The estimated value is of the same order of magnitude as that expected by combining an observed steady-state concentration ($\approx 5\times10^{-8}$ mol dm^{-3}) and a reported second order rate constant for bimolecular decay of $\mathrm{DQ}^{\bar{\cdot}}$, 3.5×10^{6} mol^{-1} dm^{3} s^{-1}.[2] When the DQ concentration is high, a weak spectrum due to DQH· ($7\times7\times2$ line spectrum with hyperfine splittings of 0.48, 0.07, and 0.03 mT)[17] was superimposed on the intense spectrum of $\mathrm{DQ}^{\bar{\cdot}}$. Both spectra decreased in intensity with increase of the resident time.

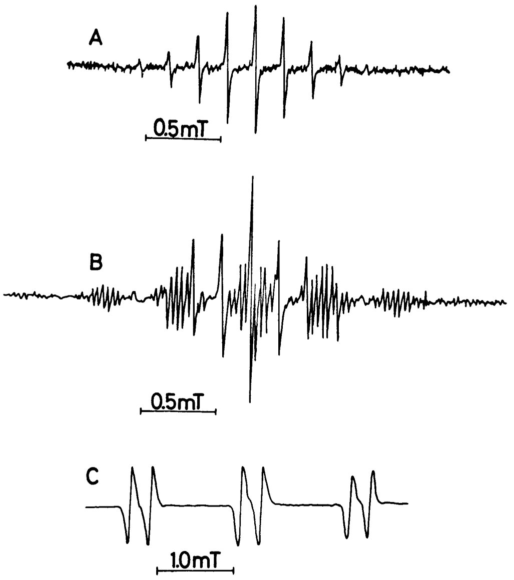

Fig. 1. A: ESR spectrum of a continuously photoirradiated flowing solution of DQ in ethanol. [DQ]$=5\times10^{-5}$ mol dm^{-3} and resident time was one second. B: ESR spectrum of a continuously photoirradiated sealed solution of DQ in ethanol. [DQ]$=50$ mmol dm^{-3}. C: ESR spectrum of spin-adduct radical. [DQ]$=1$ mmol dm^{-3}, [PBN]$=0.1$ mol dm^{-3}.

The concentration ratio of DQH·to $\mathrm{DQ}^{\bar{\cdot}}$ depends on the flow rate of the solutions and the DQ concentration. This varying ratio indicates neither that the acid-base equilibrium between DQH· and $\mathrm{DQ}^{\bar{\cdot}}$ is reached rapidly compared with their lifetime nor that the ratio is determined by the branching ratio of the chemicalquenching processes, (1) and (2). There will exist reaction pathway(s) of generating semiquinone intermediates other than reactions (2) and (3).

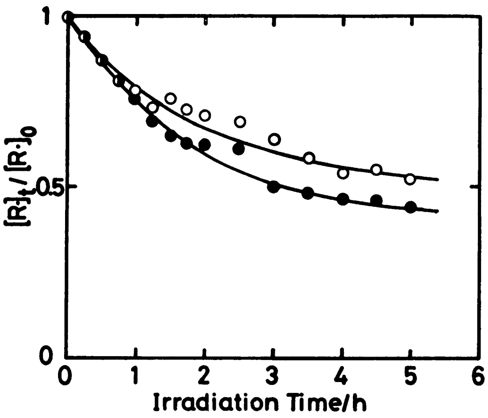

Fig. 2. The variation of $\mathrm{DQ}^{\bar{\cdot}}$ and DQH· yields with irradiation time.
$[\mathrm{DQ}]_0=20$ mmol dm^{-3}, ○: $\mathrm{DQ}^{\bar{\cdot}}$, ●: DQH·.

When the solution of high DQ concentration (50 mmol dm^{-3}) sealed in a quartz sample tube was continuously photolyzed, DQH· was observed with comparatively intense spectral intensity, as shown in Fig. 1B. The ratio of steady-state concentration of DQH· to that of $\mathrm{DQ}^{\bar{\cdot}}$ was initially about 2. As the photolysis was prolonged, both the DQH· and the $\mathrm{DQ}^{\bar{\cdot}}$ gradually decrease in their spectral intensity, and the concentration ratio also decreased as shown in Fig. 2. The former observation is due to the decrease in the DQ concentration. The quenching of $^{3}\mathrm{DQ}^{*}$ by diduroquinone, one of photoproducts in the solution of a high DQ concentration, may also contribute to it.[4,5] The latter observation is not compatible with the rapid acid-base equilibrium. It is interpreted by the quenching of $^{3}\mathrm{DQ}^{*}$ by DQH_2, which competes with the quenching by solvent alcohols, and by the more efficient ionic dissociation of directly photoexcited CT complex (DQ–DQH_2) in the later period of photolysis.

The influence of DQH_2 was examined by photolyzing a flowing 2-propanol solution of a fixed DQ concentration with DQH_2 added to it with various concentrations. The $\mathrm{DQ}^{\bar{\cdot}}$ formation was enhanced in the presence of

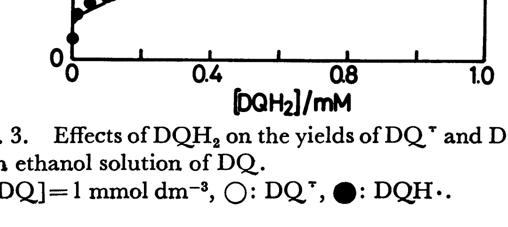

Fig. 3. Effects of DQH_2 on the yields of $\mathrm{DQ}^{\bar{\cdot}}$ and DQH· in ethanol solution of DQ.
[DQ]$=1$ mmol dm^{-3}, ○: $\mathrm{DQ}^{\bar{\cdot}}$, ●: DQH·.

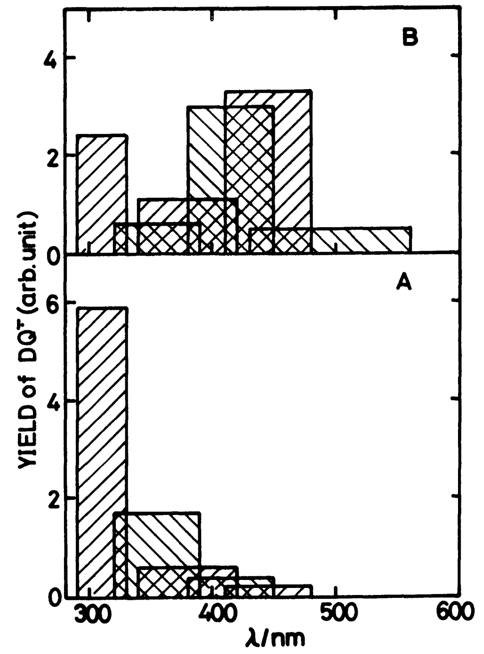

Fig. 4. Wavelength dependence of $DQ^{\overline{\cdot}}$ yield in a flowing solutions (A) of 1 mmol dm^{-3} DQ and (B) of 1 mmol dm^{-3} DQ+1 mmol dm^{-3} DQH_2.

DQH_2 at low concentration, whereas the DQH· yield increased steadily with DQH_2 concentration throughout its concentration range studied, as shown in Fig. 3. DQH· is generated by the quenching of $^3DQ^*$ by DQH_2 in its presence.

In order to see the origin of $DQ^{\overline{\cdot}}$, its yield was examined for the solutions of 1 mmol dm^{-3} DQ with and without 1 mmol dm^{-3} DQH_2 in ethanol and in 2-propanol by photolyzing the light successively cut off with a long-wave pass filter whose 50% transmission wavelength was 310, 350, 390, 420, 450, 480, or 580 nm. The dependence of the yield on the wavelength without DQH_2 agreed qualitatively with the absorption spectrum of DQ, but the dependence of the yield with DQH_2 showed an additional peak of the action spectrum at 400—450 nm, as shown in Fig. 4, for the ethanol solutions. Correspondingly, the ethanol solution of equimolar DQ and DQH_2 showed a weak, broad absorption band extending from 380 to 600 nm with λ_{max} of 410 nm, which is attributed to a (DQ–DQH_2) complex. $DQ^{\overline{\cdot}}$ is generated by the direct excitation of DQ followed by the reactions (1) and (3) or the reaction (2), or by the photodissociation of the complex into ions,

$$(DQ\text{-}DQH_2) \xrightarrow{h\nu} DQ^{\overline{\cdot}} + DQH_2^{+} \qquad (5)$$

depending on the wavelength of light and on the concentration of the coexisting DQH_2. The solutions containing 50 mmol dm^{-3} DQ and 50 mmol dm^{-3} DQH_2 gave no $DQ^{\overline{\cdot}}$ spectrum at all for any wavelength of light between 254 and 600 nm. This will be discussed later.

Spin Trapping of Free Radicals from Alcohols. Although α-hydroxyalkyl radicals have been detected together with benzophenone ketyl radicals from the photoreduction of benzophenone in alcohols by ESR,[16] no ESR spectrum of free radicals generated from solvent alcohols has been observed from the photoreduction of quinones in alcohol solutions. This may be due to the efficient oxidation of α-hydroxyalkyl radicals by quinones (such as reaction (3)). Alkoxyl radicals, if generated, will be rapidly transformed into the α-hydroxyalkyl radicals by the hydrogen abstraction reactions. The alkoxyl radicals, if any, will be difficult to detect, because their spectra are broadened with their short T_1.[18] The spin trapping-ESR technique is useful to detect the transient free radicals generated from alcohols. The technique was first utilized successfully for the photoreduction of quinones in alcohols by McLauchlan and Sealy.[15] The present authors have studied in detail by the same technique the free radicals from solvent ethanol for the photoreduction of *p*-benzoquinone, and observed the formation of both α-hydroxyethyl and ethoxyl radicals.[14] The study has been extended here to the photoreduction of DQ in ethanol and in 2-propanol. PBN has been used as a spin trap, because it reacts efficiently with both α-hydroxyalkyl and alkoxyl radicals.[14]

In the photoreduction of DQ, the observed ESR spectrum is exclusively due to the spin adduct of ethoxyl or isopropoxyl radical, as reported previously.[15] Figure 1C shows the spectrum of the ethoxyl radical adduct with hyperfine constants of 1.46 mT for a nitrogen nucleus and 0.26 mT for a proton, which is the same as that reported previously.[14,15,19] The quantum yield of the spin adduct was determined to be 10^{-3} or less for the ethanol solution, by examining the intensity of the ESR spectrum as a function of the PBN concentration. These quantum yields are much lower than the quantum yield for the conversion of DQ into DQH_2 described later. The quantum yield was still lower for the 2-propanol solution. The dependence of the spin adduct yield on the wavelength was examined by cutting off the photolyzing light in the same way as for the $DQ^{\overline{\cdot}}$ yield, and it was found to agree qualitatively with the absorption spectrum of DQ. The above observations lead to the conclusion that the alkoxyl radicals are generated by the reaction of photoexcited duroquinone, $^3DQ^*$, with solvent alcohols, *i.e.*, *via* reaction (2), though it is a minor pathway for the chemical quenching of $^3DQ^*$.

Yield of DQH_2. In order to compare with the kinetic behavior of the transient intermediates, the conversion of DQ into a major final product DQH_2 was examined by photolyzing dilute solutions of DQ in methanol, ethanol, and 2-propanol with light of 254 nm. The decay of DQ and the formation of DQH_2 were monitored with the intensity of their optical absorption using the reported molar absorptivities.[5] Isosbestic points observed at 233, 279, and 320 nm for the spectral curves during the photolysis indicate that the simple conversion of DQ into DQH_2 is the major consequence of the photolysis. The conversion proceeded linearly with the number of absorbed photons in the very early period of the photolysis, and then the conversion rate gradually decreased as demonstrated previously by Nafisi-Movaghar and Wilkinson for DQ in 2-propanol.[5] The initial quantum yield of the DQH_2 formation was determined from the conversion curves to be 0.12, 0.23, and 0.36 for the methanol, ethanol, and 2-propanol solutions of 8×10^{-5} mol dm^{-3} DQ. This quantum yield determination will be discussed further in the following section.

Discussion

The present investigation was motivated by the following two questions: what is the role of semiquinone anions which we detected by ESR from the photoreduction of quinones in alcohols, and why have the semiquinone anions (especially DQ$^{\cdot-}$) been unobserved in most of the previous photolysis-ESR studies?

The present results clearly show that DQ$^{\cdot-}$ is generated in alcohol solutions either directly from the photoexcited DQ through its chemical quenching with solvent alcohols (reaction (2)) or indirectly from α-hydroxyalkyl radicals through a one-electron transfer (reaction (3)). The former is, however, a minor pathway for the DQ$^{\cdot-}$ formation, because the quantum yield of alkoxyl radicals, the counterproduct of the reaction (2), is much lower than the quantum yield for the disappearance of DQ. Therefore, the DQ$^{\cdot-}$ formation observed significantly in the present ESR study is attributed to the latter reaction pathway. Scheer and Grätzel[9] have reported that in a more polar solvent, *i.e.*, water–ethanol mixed solvent, the chemical quenching of ^{3}DQ* leads almost exclusively to the formation of DQ$^{\cdot-}$, as the solvation of ions favors the ionic dissociation of encounter exciplexes.

In aqueous solution, the acid-base equilibrium

$$\mathrm{DHQ}\cdot \rightleftarrows \mathrm{DQ}^{\cdot-} + \mathrm{H}^+ \quad (6)$$

is reached very quickly. The DQ$^{\cdot-}$ observed in the flash photolysis-optical absorption study has been attributed to the dissociation of DQH·.[2] However, the forward reaction (6) is not significant in alcohols as a reaction pathway for the DQ$^{\cdot-}$ formation. From the acid-base equilibrium of phenol and its analogues in water and in methanol, the relationship of pK_a (methanol) = pK_a (water) + 4.4 has been found experimentally and rationalized theoretically.[20] Provided that this relationship holds for DQH·, the pK_a of DQH· in methanol is estimated to be 9.4 from the reported pK_a of 5 in water.[21,22] The pK_a value will be somewhat larger in ethanol and in 2-propanol. Provided further that the reverse reaction (6) is diffusion-controled ($k_{-6}=10^{10}$ mol^{-1} dm^3 s^{-1}), 4×10^{-10} mol dm^{-3} of K_a leads to the rate of the forward reaction, k_6, being as low as 4 s^{-1}. The dissociation of DQH· is too slow to account for the present ESR observation of DQ$^{\cdot-}$ in the alcohol solutions. The delayed formation of DQ$^{\cdot-}$ in ethanol observed in the previous flash photolysis study cannot be due to the reaction (6) but due to the reaction (3), as pointed out by Amoyal and Bensasson.[8]

An additional path opens for the DQ$^{\cdot-}$ formation, when DQH$_2$ either accumulates in the photolyzed DQ solution or is intentionally added and the absorption band of the (DQ–DQH$_2$) complex is excited. As the pK_a of DQH$_2$ in water is 11.3,[23] the pK_a in methanol will be 15.7. This gives rough estimates of pH, 9.3 and 8.4 for 1 and 50 mmol dm^{-3} DQH$_2$ present in the alcohol solution. Comparison of these values with the pK_a of DQH·, the equilibrium (6) favors very much to the left at the higher concentration of DQH$_2$, so that DQ$^{\cdot-}$ will be readily transformed into DQH·. This is consistent, though qualitatively, with the ESR observation during the photolysis of ethanol solutions of DQ and DQH$_2$ sealed in ESR sample tubes.

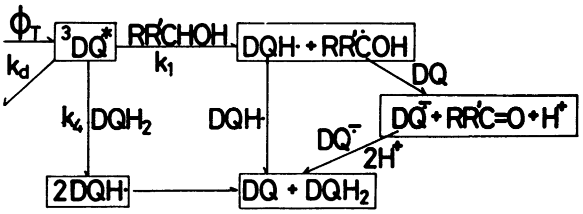

Fig. 5. A photoreduction scheme of DQ in alcohol.

The reaction mechanism of major significance for the formation of the final product, DQH$_2$, has been proposed as shown in Fig. 5 based on the flash photolysis and product analysis results.[5] The quenching of ^{3}DQ* by DQH$_2$ results in the DQH· formation but gives effectively no net chemical change. The steady-state treatment gives the following relationship:

$$\frac{I_\mathrm{T}}{[\mathrm{DQH_2}]} = \frac{k_4[\mathrm{DQH_2}]}{2k_1\phi_\mathrm{T}[\mathrm{RR'CHOH}]} + \frac{k_\mathrm{d}+k_1[\mathrm{RR'CHOH}]}{k_1\phi_\mathrm{T}[\mathrm{RR'CHOH}]}, \quad (7)$$

where I_T is the number of photons absorbed in the unit volume of the solution, ϕ_T is the quantum yield of ^{3}DQ* generation, and k_d is the rate constant of deexcitation of ^{3}DQ* to the ground state.[5] Actually, the present results of the DQH$_2$ formation follow the expected linear relationship between I_T/[DQH$_2$] and [DQH$_2$], as shown in Fig. 6. The quantum yield of the DQH$_2$ formation in the absence of DQH$_2$ is determined, from the inverse of the intercept, to be 0.12, 0.23, and 0.36 in methanol, ethanol, and 2-propanol, respectively. The result for

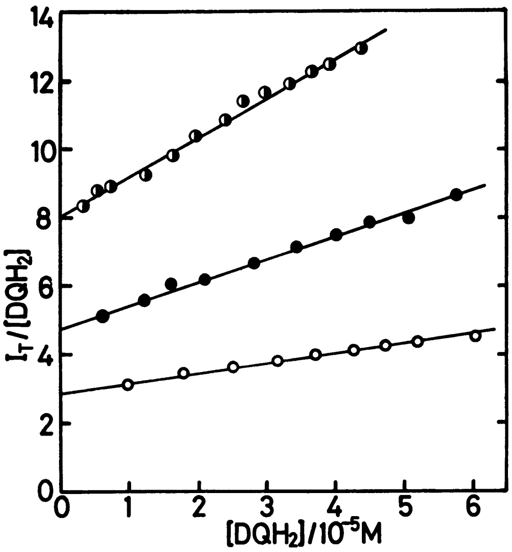

Fig. 6. A kinetic plots of DQH$_2$ formation (see text in detail).

○: 2-Propanol, ●: ethanol, ◐: methanol.

the 2-propanol solution agrees with the previous result obtained in the same way.[5] Combining these values with the pseudo-first order decay rate of $^3DQ^*$, $k_d+k_l[RR'CHOH]$, determined by the laser-flash photolysis experiment, $6.6\times10^4\ s^{-1}$ in ethanol[8] and $1\times10^5\ s^{-1}$ in 2-propanol,[3] k_d and k_l can be determined separately, as $\phi_T=1.0$.[5,6,8] The results are $k_d=5.2\times10^4$ and $6\times10^4\ s^{-1}$, and $k_l=8.1\times10^2$ and $3\times10^3\ mol^{-1}\ dm^3\ s^{-1}$ for ethanol and 2-propanol. The chemical quenching of $^3DQ^*$ is three times as efficient in 2-propanol as in ethanol, whereas the physical quenching is independent of the alcohols.

According to the reaction scheme, $DQ^{\cdot-}$ and $DQH\cdot$ should be generated with an identical yield during the photoreduction of DQ into DQH_2 in alcohols, if the efficient chemical quenching of $^3DQ^*$ by DQH_2 is not predominant. Actually, $DQ^{\cdot-}$ could be detected by the present steady-state ESR measurements, when photolyzed solutions were refreshed by flowing. The comparatively weak ESR spectrum due to $DQH\cdot$ (or its absence) is attributed to the lifetime of $DQH\cdot$ much shorter than that of $DQ^{\cdot-}$: The steady-state concentration of $DQH\cdot$ in the fresh DQ solutions is too low for its ESR detection. The rate constant for the disproportionation of $DQH\cdot$ has been reported to be $3.7\times10^8\ mol^{-1}\ dm^3\ s^{-1}$ which is larger by two order of magnitude than that of $DQ^{\cdot-}$.[2] The previous ESR studies of DQ in alcohols have shown the spectrum to be due exclusively to $DQH\cdot$. The $DQ^{\cdot-}$ spectrum has not been observed even in the absence of a hydrogen donor. This seems to have been caused by the inevitable contamination with DQH_2 of the solution photolyzed for a long time. A small amount of oxygen in a solution resulting from an insufficient degassing should reduce the $DQ^{\cdot-}$ yield because of an efficient electron transfer from $DQ^{\cdot-}$ to O_2.[21] The ESR observations on $DQH\cdot$ cannot necessarily be a proof for the hydrogen abstraction of $^3DQ^*$ from alcohols (reaction (1)) before excluding a possible occurrence of reaction (4).

In conclusion, the present investigation has shown the correct location of the semiquinone intermediates observed by ESR in the reaction scheme of the DQ photoreduction in alcohol solutions. In addition, the present ESR study has indicated three reaction pathways for the $DQ^{\cdot-}$ formation: The photoinduced one-electron transfer from alcohol to DQ, though the quantum yield for it is very small, the one-electron transfer from α-hydroxyalkyl radical to DQ, and the ionic dissociation of a photoexcited CT-complex (DQ–DQH_2), which becomes important at high DQH_2 concentrations with irradiation by an incandescent light.

References

1) N. K. Bridge and G. Porter, *Proc. R. Soc. London, Ser. A*, **244**, 259 (1958).

2) N. K. Bridge and G. Porter, *Proc. R. Soc. London, Ser. A*, **244**, 276 (1958).

3) F. Wilkinson, G. M. Seddon, and K. Tickle, *Ber. Bunsenges. Phys. Chem.*, **72**, 315 (1968).

4) H. Hermann and G. O. Schenck, *Photochem. Photobiol.*, **8**, 255 (1968).

5) J. Nafisi-Movaghar and F. Wilkinson, *Trans. Faraday Soc.*, **66**, 2257 (1970).

6) J. Nafisi-Movaghar and F. Wilkinson, *Trans. Faraday Soc.*, **66**, 2268 (1970).

7) D. R. Kemp and G. Porter, *Proc. R. Soc. London, Ser. A*, **326**, 117 (1971).

8) E. A. Amouyal and R. Bensasson, *Trans. Faraday Soc.*, **72**, 1274 (1976).

9) R. Scheere and M. Grätzel, *J. Am. Chem. Soc.*, **99**, 865 (1977).

10) R. L. Willson, *Trans. Faraday Soc.*, **67**, 3020 (1971).

11) A. J. Elliot and J. K. S. Wan, *J. Phys. Chem.*, **82**, 444 (1978).

12) A. D. Trifunac and J. R. Norris, *Chem. Phys. Lett.*, **59**, 140 (1978).

13) Y. Kambara and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **50**, 1367 (1978).

14) S. Noda, T. Doba, T. Mizuta, M. Miura, and H. Yoshida, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 61.

15) K. A. McLauchlan and R. C. Sealy, *J. Chem. Soc., Chem. Commun.*, **1976**, 115.

16) H. Yoshida and T. Warashina, *Bull. Chem. Soc. Jpn.*, **44**, 2950 (1971).

17) T. Warashina, O. Edlund, and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **48**, 636 (1975).

18) B. Brocklehurst, *J. Chem. Soc., Faraday Trans. 2*, **75**, 123 (1979).

19) A. Ledwith, P. J. Russel, and L. H. Sutcliffe, *Proc. R. Soc. London, Ser. A*, **332**, 151 (1973).

20) C. H. Rochester and B. Rossal, *J. Chem. Soc., B*, **1967**, 986.

21) K. B. Patel and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1*, **1973**, 814.

22) R. L. Willson, *J. Chem. Soc., Chem. Commun.*, **1971**, 1249.

23) G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solutions," Butterworth, London (1961).