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Photoreduction of Quinones. I. One-electron Transfer to *p*-Benzoquinone in Ethanol Studied by ESR during Continuous Photolysis

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Electron spin resonance was examined during the continuous photolysis of a flowing solution of *p*-benzoquinone in ethanol at room temperature. It was found that both semiquinone anions and semiquinone radicals were generated, but their relative yields changed depending on the experimental conditions. The semiquinone anion was generated in a comparatively high yield at low concentrations of *p*-benzoquinone and at high flowing rates. Its formation was, however, quenched by the addition of acetic acid without transformation to the semiquinone radical. The semiquinone radical was generated efficiently at high *p*-benzoquinone concentrations and at low flowing rates. Its formation was enhanced by the addition of hydroquinone. These results, as well as the previous results on the effect of the wavelength of light, indicate, in contrast with the currently accepted view, that there is effectively no equilibrium in ethanol between the semiquinone radical and the semiquinone anion under the present experimental conditions, and that the latter is formed by a photoinduced one-electron transfer from solvent to *p*-benzoquinone. The semiquinone radical seems to arise from the hydrogen abstraction of excited *p*-benzoquinone from the hydroquinone formed as a product during photolysis.

One of the main interests in photobiology is associated with the naturally occuring quinones mediating in the electron-transport mechanism in photosynthesis.[1] Such a biological function of quinones seems to have attracted the interest of chemists in studying the photochemistry of simple quinones, such as *p*-benzoquinone and duroquinone, by means of the flash photolysis-optical absorption technique[2–7] as well as the photolysis-electron spin resonance (ESR) technique.[8–14] The flash photolysis studies have stressed the hydrogen-abstraction reaction of simple photoexcited quinones since the pioneering works by Bridge and Porter.[2] The transient optical absorption due to the semiquinone radical and the semiquinone anion was observed in hydrogen-donating solvents such as ethanol or in the presence of hydrogen donors; the formation of the latter has generally been attributed to its equilibrium with the former, generated primarily by the hydrogen-abstraction reaction:

$$Q^* + CH_3CH_2OH \longrightarrow \dot{Q}H + CH_3\dot{C}HOH \qquad (1)$$

$$\dot{Q}H \longrightarrow Q^- + H^+. \qquad (2)$$

This seems to be the currently accepted reaction mechanism,[15] and it seems to have been supported also by ESR studies,[10–13] because only the ESR spectrum of semiquinone radicals, presumed to be generated primarily through Reaction 1, has been detected from solutions of quinones in alcohols.

However, our previous ESR study seems to conflict with the above mechanism, because the ESR spectra of both semiquinone radicals and semiquinone anions were observed from a solution of *p*-benzoquinone and its methyl derivatives in ethanol or methanol during continuous photolysis and the effective wavelength of the photolyzing light was found to be different between the semiquinone anions and the semiquinone radicals.[16] The results suggested that the semiquinone anions might be generated primarily from photoexcited quinones, but not by Reaction 2. However, this was not conclusively proven, because the observed ESR signals depended very much on the experimental conditions and we could not verify the factors controlling the yields of both the semiquinone anions and the semiquinone radicals.

The previous study of detecting semiquinone intermediates by ESR has now been extended to verify the factors controlling their yields and to give firm indications against Reactions 1 and 2. The advantage of such an ESR study is that semiquinone anions and semiquinone radicals are clearly distinguished from each other,[16] while the spectra of semiquinone anions, radicals, and triplet quinones overlap each other, and so it is not easy to study the kinetic behavior of the semiquinone intermediates separately in flash photolysis-optical absorption studies.

Experimental

Chemicals. The *p*-benzoquinone (BQ) was purified by sublimation three times. The purified BQ showed a melting point of 387—389 K, identical with that quoted in chemical handbooks. The hydroquinone (BQH$_2$) was sublimed twice under a vacuum, volatile impurities being removed by means of a liquid nitrogen trap. Ethanol with a claimed purity of 99.5% was generally used without further purification. Occasionally, however, it was purified further by distilling it after reflux with sodium hydroxide and zinc powder to remove the acetaldehyde, by refluxing it with magnesium ethoxide prepared from magnesium and absolute ethanol in the presence of ethyl bromide to remove the water, and by then distilling it again. However, such additional purification of the ethanol caused no difference in the results. The acetic acid was used as received. All the chemicals used were of an SG grade and were supplied by Wako Pure Chemical Ind., Ltd.

Photolysis and ESR Measurements. The experimental instrument has already been described elsewhere:[17] it is essentially the same as that developed first by Livingston and Zeldes.[18] Sample solutions were purged with helium gas for at least half an hour under dimmed room light. This procedure was essential to obtaining reproducible results. The solutions were allowed to flow at a rate of from 0.014 to $5.0\ \mathrm{cm^3\ s^{-1}}$, which gave a resident time of 3.6 s to 10 ms of the flowing solution within the effective volume of the ESR

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resonant cavity. Photolysis was carried out at room temperature with unfiltered light of a wavelength longer than 270 nm from a super-high-pressure mercury lamp (Philips, SP-500). The intensity of light gradually changed in the shorter-wavelength region, thus causing a scattering of the results. Therefore, each series of data shown in one figure was obtained at one time. The solution was warmed during photolysis, but its temperature immediately after photolysis was found to be 290±2 K except when the flow rate was extremely slow.

Results

The ESR signal observed from the ethanol solution of BQ generally consisted of a spectrum of benzosemiquinone radicals (triplet of double triplet, with hyperfine separations of 0.51, 0.19, and 0.03 mT) and one of benzosemiquinone anions (quintet, with a separation of 0.24 mT). These spectra are essentially the same as those reported previously.[8,16,19] The most prominent finding was that the relative intensities of both spectra changed depending on the experimental conditions. For instance, Fig. 1 shows the ESR signals recorded for two different concentrations of BQ, the other experimental conditions being unchanged. The dependence of the observed yield for both the benzosemiquinone radical (BQH·) and the benzosemiquinone anion (BQ$^-$) on the BQ concentration is shown in Fig. 2 for two different resident times of the solutions. BQH· was generated only at high BQ concentrations, whereas BQ$^-$ was observed to form in a high yield even if the concentration was lowered to 0.01 mmol dm^{-3}.

Fig. 1. ESR signal recorded during photolysis of *p*-benzoquinone in ethanol flowing at a resident time of 0.5 s at 293 K. Concentration of quinone, (A) 10 and (B) 1.0 mmol dm^{-3}.

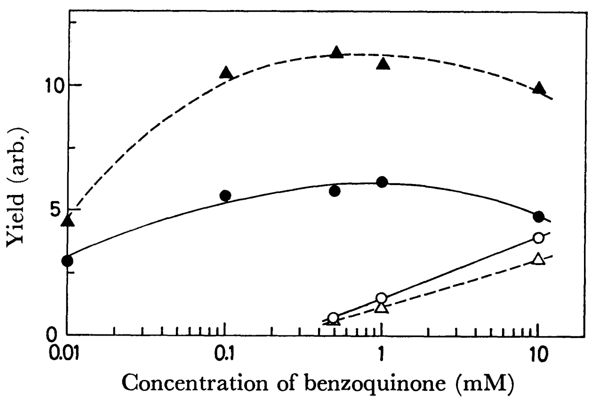

Fig. 2. Dependence of yield of benzosemiquinone anion and benzosemiquinone radical observed during photolysis of *p*-benzoquinone in ethanol on the benzoquinone concentration. Benzoquinone anion at resident time of (●) 1 s and (▲) 0.5 s, benzosemiquinone radical at resident time of (○) 1 s and (△) 0.5 s.

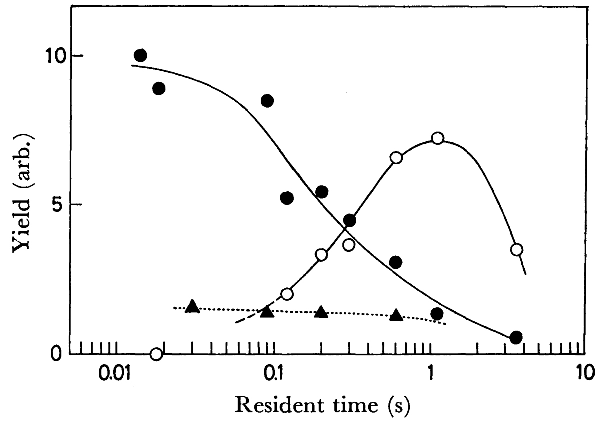

Fig. 3. Dependence of the yield of (●) benzosemiquinone anion and (○) benzosemiquinone radical observed during photolysis of flowing solution of 1.0 mmol dm^{-3} *p*-benzoquinone in ethanol, and (▲) that of the yield of benzosemiquinone anion from the solution of 0.01 mmol dm^{-3} *p*-benzoquinone on the resident time of the solutions within the effective volume of cell. No benzosemiquinone radical was detected from the diluted solution.

The observed yields of BQH· and BQ$^-$ are plotted as functions of the resident time in Fig. 3 for particular BQ concentrations. BQH· was observed only at long resident times for the higher BQ concentrations; its yield increased with the resident time up to about 1 s. On the other hand, the BQ$^-$ yield showed no increase with the resident time. Rather, it remained constant for the lower BQ concentrations, or it decreased from the highest value observed at the shortest resident time examined for the higher BQ concentrations.[20] These observations agree qualitatively with the results obtained independently for the relationship between the yield and the BQ concentration, as is shown in Fig. 2.

Since BQH· is generated appreciably only at high BQ concentrations and at long photolysis times, it seems essential to study the effect of a photoproduct, BQH$_2$, on the formation of BQH· and on that of BQ$^-$ as well. The yields of BQH· and BQ$^-$ were examined by intentionally adding BQH$_2$ to a solution of 1 mmol dm^{-3} BQ under conditions where both BQH· and BQ$^-$ were generated without added BQH$_2$. The yield of BQ$^-$ remained unchanged, whereas that of BQH· increased with the concentration of the added BQH$_2$, as is shown in Fig. 4. Although both BQH· and BQ$^-$ were found to form in the BQH$_2$ solution in ethanol, the increase in the BQH· yield shown in Fig. 4 cannot be attributed simply to the photodissociation of the added BQH$_2$ to BQH·, because the effect of the added BQH$_2$ is prominent at its low concentrations. It should noted that the

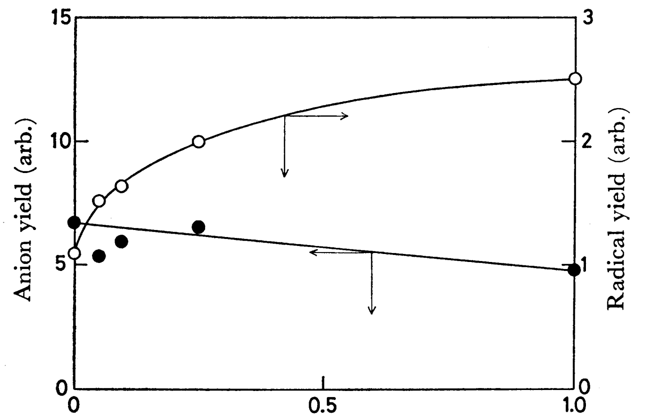

Fig. 4. Effect of the addition of hydroquinone into the solution of 1.0 mmol dm^{-3} *p*-benzoquinone in ethanol on the yield of (●) benzosemiquinone anion and (○) benzosemiquinone radical observed during photolysis at resident time of 1 s.

BQ$^-$ formation from BQ is not affected by the addition of BQH$_2$.

Previously the addition of acids to the solution was found to eliminate the ESR spectrum of BQ$^-$. This was interpreted as being due to the protonation to BQ$^-$, resulting in the transformation of BQ$^-$ into BQH·.[16] In the present study, however, it was found that the addition of acetic acid in increasing amounts up to 16 mmol dm^{-3} caused only a decrease in the BQ$^-$ yield to zero, but no increase in the BQH· yield. When the BQ concentration was so low that only BQ$^-$ was detected, the addition of acetic acid totally eliminated the ESR signal, indicating the absence of the transformation of BQ$^-$ to BQH·.

Discussion

Although the ESR spectra of semiquinone anions have been recorded from halogenated benzoquinones[21,22] and anthraquinone,[9] the spectra recorded from BQ in fluid alcoholic solutions have been almost exclusively those of BQH·.[9,10,12,13,23,24] On the basis of the present results (Figs. 2 and 3), the absence of the BQ$^-$ spectrum in the previous studies may be attributed to the effects of the BQ concentration and the photolysis time, since the solutions with comparatively high BQ concentrations were sealed in a sample tube and photolyzed for a long time or repeatedly by light pulses to overcome a poor signal-to-noise ratio. Pedersen *et al.* observed the coexistence of BQ$^-$ and BQH· in an ethanol solution of BQ at a low concentration during photolysis by recycling a large volume of the solution.[14] This and our own previous studies[16] have been the only cases where evidence of the BQ$^-$ formation was obtained by means of the ESR technique.

BQ$^-$ was found to be generated at short resident times and/or at low BQ concentrations, while no BQH· at all was observed under the same experimental conditions. This strongly suggests that BQ$^-$ is generated directly from BQ through a photoinduced one-electron transfer from the solvent ethanol. Although the above view of the BQ$^-$ formation is not in accord with the currently accepted reaction mechanism for the photoreduction of quinones,[2,15] it is consistent with Tollin's interpretation of the observation of BQ$^-$ by photolyzing BQ in a low-temperature ethanol matrix.[25] McLauchlan and Sealy applied the spin-trapping technique to the photochemical reaction of quinones including BQ in fluid alcoholic solutions and detected no 1-hydroxyethyl radical generated by Reaction 1, though they did detect alkoxyl radicals.[26] These radicals seem to have been generated through the deprotonation of the molecular cation of the alcohols primarily formed by the one-electron transfer between the quinones and the alcohols. The photoinduced electron transfer was demonstrated by Davis *et al.* by means of product analysis to occur from the alkoxide ion to amino anthraquinone derivatives.[27] They postulated that this reaction involves the charge-transfer lowest excited state.

One would anticipate that BQ$^-$ might be generated from the primary intermediate, BQH·, by Reaction 2, which was so rapid that the primary intermediate could not be observed under the present experimental conditions. However, if the BQ$^-$ formation is directly correlated to the BQH· formation by the rapid equilibration between these semiquinone intermediates, their relative yields should not depend on the BQ concentration. It can also be expected that the decrease in the BQ$^-$ yield caused by the addition of acetic acid should be followed by an increase in the BQH· yield. Even if the equilibration was not rapid enough compared with the lifetime of the semiquinone intermediates, the primary intermediate should be observed comparatively more readily than the secondary one at short resident times. None of the present results, then, give any indication of a reaction mechanism comprising Reactions 1 and 2 for the BQ$^-$ formation.

We found previously that BQH· was effectively generated with light of wavelengths of 260—300 nm, whereas BQ$^-$ was generated with light of wavelengths around 460 nm.[16] The study of the wavelength effect on the formation of semiquinone intermediates is very undeveloped, but early in 1960 Bridge found, in his flash photolysis study, that the quantum yield of the durosemiquinone anion was the largest for the light of 350—400 nm, the longest wavelength examined.[28] This is consistent with our previous results.[16] The different wavelengths effective for the formation of BQ$^-$ and BQH· support the view that the formation of the former is independent of that of the latter.

Some comments may be needed here on the BQH· formation, because it has thus far been believed to be the principal semiquinone intermediate in the photoreduction of BQ into BQH$_2$. The enhancement of the BQH· formation caused by the addition of a small amount of BQH$_2$ (see Fig. 4) seems to indicate that the hydrogen abstraction of photoexcited BQ from BQH$_2$ is one of the main sources of BQH·. This reaction reasonably interprets the observed dependence of the BQH· yield on the resident time and on the BQ concentration; the increase in the concentration of the photoproduct, BQH$_2$, during the photolysis of which the rate is the higher for the higher BQ concentration, results in the observation of BQH· at long resident times from the solutions with higher BQ concentrations. It has been already observed in the flash photolysis study of duroquinone in ethanol[3,5,7] that the triplet excited quinone abstracts hydrogen from durohydroquinone with a diffusion-controlled rate, but from solvent ethanol only very slowly. However, we should reserve other possible sources for BQH·, especially for that observed at long resident times, because BQ is readily depleted under the present experimental conditions. In a separate experiment, for example, 1 mmol dm^{-3} BQ was found by optical absorption study to have been almost entirely transformed into BQH_2 and other unidentified stable products after the photolysis and ESR measurements at the resident time of 0.5 s. Therefore, the photodissociation of BQH_2 and the other products may be responsible for the BQH· formation in the later period of photolysis at a long resident time. Photolysis with light of selected wavelengths would give an insight into the detailed mechanism for the BQH· formation, but it could not be done mainly because of the limited sensitivity of the experimental method used.

In conclusion, the present ESR investigation revealed that the primary step in the photochemical reaction of BQ in ethanol is the one-electron transfer giving BQ^-:

$$BQ^* + CH_3CH_2OH \longrightarrow BQ^- + CH_3CH_2OH^+. \quad (3)$$

A question may arise as to the role of BQ^- in the photoreduction of BQ; is it really involved in the reduction process? In order to answer this question, we examined, though qualitatively, the optical absorption of the BQ solutions after the photolysis and ESR measurements under the conditions where BQ^- was exclusively formed, and found that a fraction of BQ had been transformed into BQH_2, giving an absorption band with its maximum at 295 nm. We are inclined to believe that BQ^- but not BQH· is involved in the photoreduction of BQ in ethanol, for which we propose the following reaction scheme based on the present results:

$$CH_3CH_2OH^+ + CH_3CH_2OH \longrightarrow CH_3CH_2\dot{O} + CH_3CH_2OH_2^+, \quad (4)$$

$$CH_3CH_2\dot{O} + CH_3CH_2OH \longrightarrow CH_3CH_2OH + CH_3\dot{C}HOH, \quad (5)$$

$$CH_3\dot{C}HOH + BQ \longrightarrow CH_3\overset{+}{C}HOH + BQ^-, \quad (6)$$

$$CH_3\overset{+}{C}HOH + CH_3CH_2OH \longrightarrow CH_3CHO + CH_3CH_2OH_2^+, \quad (7)$$

$$2BQ^- \longrightarrow BQ + BQ^{2-} \quad (8)$$

$$BQ^{2-} + 2CH_3CH_2OH_2^+ \longrightarrow BQH_2 + 2CH_3CH_2OH. \quad (9)$$

The above reaction scheme is only a matter of speculation. However, Reaction 4 is consistent with the detection of alkoxyl radicals by the spin-trapping technique applied to the photoreduction of quinones in alcohols.[26] Reaction 6 gives a reason why the hydroxyethyl radical was not observed in the present investigation, though it had been detected in a similar ESR study of the photoreduction of benzophenone in ethanol.[17] It was inferred in Willson's pulse radiolysis work[29] to occur as a route for the formation of the semiquinone anion. The disproportionation of semiquinone anion, Reaction 8, has been observed in the flash-photolysis study of duroquinone in an alkaline ethanol–water mixture.[2] This reaction, together with Reaction 9, explains the route without the participation of BQH· for the formation of BQH_2.

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