ESR Studies of the Photoreduction of Quinones. II. The Reinterpretation of Semiquinone Intermediates from Halogenated *p*-Benzoquinones in Ethanol

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A reinterpretation was made of the electron spin resonance spectrum of semiquinone intermediates during the photolysis of a flowing solution of tetrachloro-*p*-benzoquinone (chloranil) in ethanol. The photoinduced spectrum with a width of 0.06 mT with an unresolved hyperfine structure was found to be identical with the spectrum of the semiquinone anion generated by reducing chloranil in an alkaline ethanol solution. This and other observations indicated that the photoinduced spectrum was due to the chloranil semiquinone anion formed primarily by the one-electron transfer to chloranil from the solvent ethanol, rather than to the semiquinone radical. The photoinduced one-electron transfer reaction was found, though qualitatively, to proceed more efficiently for chloranil and fluoranil, with a larger electron affinity, than for *p*-benzoquinone and dichloro-*p*-benzoquinones.

Because of the interesting nature of semiquinone intermediates and their important role in biological systems, the photochemistry of quinones has attracted much attention.1) One of the quinones, tetrachloro-*p*-benzoquinone (chloranil), had thus far been studied by means of the flash-photolysis and the electron spin resonance methods.2–6) However, controversy still remains as to the identification of semiquinone intermediates upon photolyzing chloranil in alcoholic solutions. Kemp and Porter observed an optical absorption at 420 nm in their laser-flash-photolysis study of the ethanol solution and attributed it to the semiquinone radical resulted from the hydrogen abstraction of the triplet excited chloranil from the solvent.2) Wong *et al.* observed an ESR spectrum with an unresolved hyperfine structure by flash-photolyzing chloranil in 2-propanol and attributed it also to the semiquinone radical,4) mainly by the analogy to other simple quinones, such as *p*-benzoquinone and duroquinone, from which semiquinone radicals has been inferred to be the photoinduced intermediates in alcoholic solutions.7–9) On the contrary, Hales and Bolton assigned a similar ESR spectrum recorded from the solution in ethanol or methanol to the chloranil semiquinone anion on the basis of the measured *g*-values.3) In the flash-photolysis study, Kawai *et al.* reported the formation of both the semiquinone anion and the radical from chloranil in ethanol.5)

We also found the generation of the ESR spectra of both the anion and the radical recorded during the continuous photolysis of *p*-benzoquinone and its methyl-substituted derivatives in methanol and ethanol,10–11) and have recently revealed that the *p*-benzosemiquinone anion is generated by a photoinduced one-electron transfer from the solvent to the quinone and that the *p*-benzosemiquinone radical results from a subsidiary reaction between the quinone and hydroquinone.12) These results raised a question as to our previous interpretation of an ESR spectrum observed during the photolysis of chloranil in alcoholic solutions6)—that the transient intermediate involved was the semiquinone radical.

Our primary concern in the present investigation is the reinterpretation of the ESR spectra of chloranil semiquinone intermediates. Experimental evidence will be given that the photoinduced one-electron transfer takes place for chloranil and other halogenated *p*-benzoquinones in ethanol, just as for *p*-benzoquinone.12)

Experimental

Chloranil, fluoranil (tetrafluoro-*p*-benzoquinone), 2,5-, and 2,6-dichloro-*p*-benzoquinones of an analytical grade were purified by sublimation several times, and their purity was checked from their melting point. Ethanol of a specrtoscopic grade was usually used as received, without further purification. Occasionally ethanol was purified as has been described before,12) but the purification of the solvent caused no change in the results. Sodium ethoxide of an analytical grade was used as received.

The photogenerated semiquinone intermediates were studied by observing their ESR spectrum during the continuous photolysis of a solution of the quinones (usually 1×10^{-3} mol dm^{-3}) flowing through a flat quartz cell in the ESR resonant cavity after being purged with helium gas for at least half an hour to remove any dissolved oxygen. The photolysis was carried out with unfiltered light from a super-high pressure mercury arc (Philips, SP-500), except when otherwise mentioned. The effective volume of the cell was 0.045 cm^3, which results in the total photolysis time of 30 ms when the solution flows, for example, at the rate of 1.5 cm^3 s^{-1}. A more detailed description of the experimental apparatus has been given in our previous papers.12,13) The solution sealed in a quartz sample tube was studied under photolyzing light, but no good ESR signal could be recorded because of the rapid depletion of the quinones.

Results and Discussion

Photolysis of Chloranil. Figure 1A shows a typical ESR spectrum recorded during the photolysis of chloranil in neutral ethanol. It indicates no resolved hyperfine structure with a spectral width (peak-to-peak in the derivative spectral curve, ΔH_{msl}) of 0.06 mT, and agrees with the spectra in our previous investigation, where the widths were precisely determined to be 0.055, 0.062, and 0.063 mT in 2-propanol, ethanol, and methanol respectively.6) It is essentially the same as

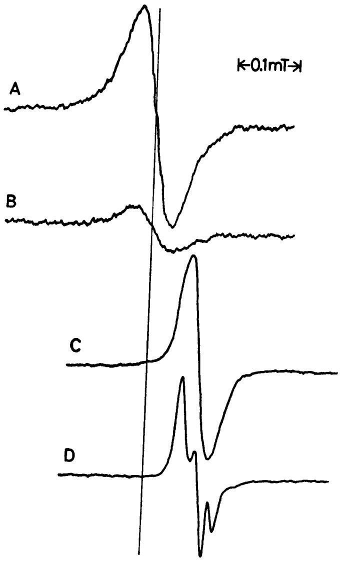

Fig. 1. ESR spectra of semiquinone intermediates generated from chloranil (1×10^{-3} mol dm^{-3}) in ethanol at room temperature (A) during photolysis, or by the addition of (B) 1×10^{-3}, (C) 3×10^{-3}, or (D) 1×10^{-2} mol dm^{-3} of sodium ethoxide. Solutions are flowing at the rate of 0.15 cm^3 s^{-1} for (A) and (B), and are sealed in sample tubes for (C) and (D).

the spectrum reported by Wong *et al.* (0.058 mT in 2-propanol)[4] and that reported by Hales and Bolton (0.08 mT in ethanol and methanol).[3]

When the solution was made alkaline with a small amount of sodium ethoxide, it gave an ESR spectrum without photolyzing light, as is shown in Fig. 1B. This "dark spectrum" showed a *g*-value and width exactly identical with those of the photospectrum in the neutral solution. Successive ESR recording under the photolyzing light, the other conditions being the same, gave a much more intense spectrum without any change in the *g*-value and the width, and confirmed the identity of the dark spectrum with the photospectrum. Thus, the photospectrum is attributable to the chloranil semiquinone anion, the same entity as that in alkaline ethanol,[3,14] resulting from photoinduced one-electron transfer from the solvent ethanol to chloranil. Previously we assigned the photospectrum to the semiquinone radical resulting from the hydrogen abstraction of excited chloranil from the solvent, on the basis of the observed difference in *g*-value between the photospectrum and the dark spectrum.[6] However, such an assignment has been found to be incorrect, as will be described below.

When the solution was made acidic with acetic acid, the photospectrum did not change in shape, but only decreased in intensity. Dissolved oxygen also reduced the intensity. By analogy with the semiquinone anion formation from *p*-benzoquinone previously studied,[12] these observations may be interpreted in terms of the inhibiting effect of oxygen and acid on the photoinduced one-electron transfer to chloranil, and in terms of the protonation of the semiquinone anion being too slow to compete with its decay reaction. When the flow rate was changed from 2 to 0.15 cm^3 s^{-1}, the intensity decreased monotonically. This result indicates a lifetime of the semiquinone anion equal to, or less than, some tens miliseconds under the present conditions. Otherwise, the intensity should have increased as a result of the accumulation of the generated semiquinone anion during the longer photolysis time. The observed decrease in the intensity may be attributed to the depletion of chloranil. Some stable photoproduct seems to have been deposited on the cell surface and to have screened the solution from the photolyzing light at low flow rates, so that no quantitative measurement could be made of the effect of the flow rate.

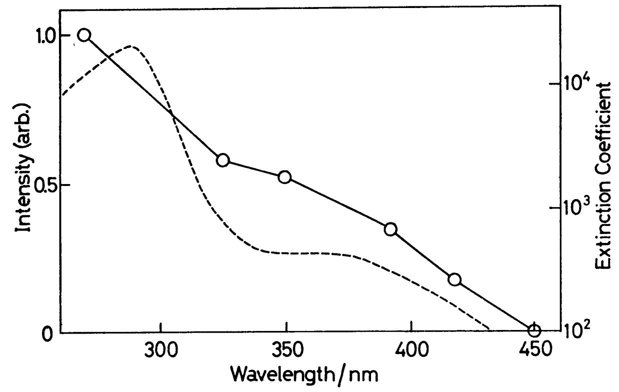

Fig. 2. Dependence of the intensity of ESR spectrum observed during the photolysis of flowing (0.15 cm^3 s^{-1}) solution of 1×10^{-3} mol dm^{-3} chloranil in ethanol on the wavelength of photolyzing light examined by discriminating the light with long-pass filters. Optical absorption spectrum of chloranil in ethanol reported in Ref. 15 is shown by dashed line for comparison.

When the shorter wavelength region of the light was successively descriminated by long-pass filters, the intensity of the spectrum decreased as is shown in Fig. 2. The intensity observed without a filter was plotted at 270 nm, which was effectively the shortest wavelength of the light source used. The plot at 325 nm shows the intensity observed with a filter of a 50% transmission at this wavelength, and so forth. The light of wavelengths longer than 450 nm is found to be ineffective to generate the photospectrum. The optical absorption spectrum of chloranil in ethanol was studied with a conventional recording spectrophotometer, and was found to agree with that reported by Shcheglova *et al.*,[15] though it gradually changed even in the absence of light under oxygen-free conditions. Taking into account this optical absorption spectrum and the spectral distribution of the light sourse supplied by the manufacturer, the relative quantum efficiency of the semiquinone anion formation can be calculated from the data in Fig. 2:

Wavelength (nm)	Efficiency
295—330	0.1
330—370	0.02
370—405	1.0
405—450	0.8

Admitting the uncertainty in the above values mainly caused by the tailing of the filters (though this uncertainty was taken into account in calculating the efficiency), one can notice that the longer-wavelength region of the absorption spectrum is effective for the semiquinone anion formation. This observation is consistent with the previous result that the *p*-benzosemiquinone anion was the most efficiently generated by the light of wavelengths at the nπ^* band of *p*-benzoquinone.[12)]

Chloranil in Alkaline Ethanol. The dark formation of the chloranil semiquinone anion by adding sodium ethoxide was studied in more detail for a fixed concentration of chloranil, 1×10^{-3} mol dm^{-3}, sealed in sample tubes under a vacuum. For concentrations of sodium ethoxide lower than 2×10^{-3} mol dm^{-3}, the ESR spectrum was the one due to the semiquinone anion. However, the spectrum changed, as is shown in Fig. 1C, when the ethoxide concentration was raised to 3×10^{-3} mol dm^{-3}. It narrowed to the width of 0.04 mT and was shifted to a resonant field higher by 0.09 mT (the *g*-value was smaller by 0.0006). We had assigned this shifted spectrum incorrectly to the chloranil semiquinone anion.[6)] The increase in ethoxide concentration caused a further change in the spectral shape, it becoming complex, as is shown in Fig. 1D.

Sasaki *et al.* studied the reduction of chloro-*p*-benzoquinone by ethoxide and found that the semiquinone anion primarily formed was further transformed into the diethoxy-*p*-benzosemiquinone anion.[16)] The present spectral change in the reduction of chloranil may be interpreted analogously: the substitution of one of the chlorine atoms in the chloranil semiquinone anion with an ethoxyl group may have caused the narrowing and shift of the spectrum. Further substitution resulted in the complex and resolved hyperfine structure shown in Fig. 1D, though no exact interpretation has been made. Because chlorine isotopes make the hyperfine structure complicated and unresolved, the decrease in the number of chlorine nuclei involved should resolve the hyperfine structure. Because of the large spin-orbit coupling of the chlorine atom, it is also conceivable that the loss of the chlorine nucleus caused the change in the *g*-value and, therefore, the shift in the resonant magnetic field.

Assignment of Semiquinone Intermediates. Hales and Bolton compared spectral parameters between the photoinduced ESR spectrum in neutral alcohols and that of the semiquinone anion generated from chloranil in alkaline alcohols in the dark, and concluded that the photoinduced spectrum was also due to the semiquinone anion.[3)] Later Wong *et al.* argued that the difference in the *g*-value between the semiquinone anion and the semiquinone radical might be too small to give an unequivocal identification of semiquinone intermediates.[4)] In the present investigation, however, the identity of the photospectrum with that of the authentically generated semiquinone anion was proven almost unequivocally, especially by the photolysis of the alkaline solution, where the semiquinone anion was present even in the dark. In addition, it was strongly suggested that the photoinduced one-electron transfer took place between an ethoxide ion and chloranil.

Wong *et al.* assigned the photospectrum to the chloranil semiquinone radical by analogy with other simple quinones, such as *p*-benzoquinone and duroquinone.[4)] Since Porter's pioneering work by the flash photolysis-optical absorption method,[7)] the photochemical generation of semiquinone radicals from these quinones in alcohols has been widely accepted. ESR studies seem to have supported such a view by detecting photospectra unquestionably attributable to the corresponding semiquinone radicals from their resolved hyperfine structure.[8,9)] Recently, however, we reported ESR evidence that the semiquinone anion is a unique intermediate generated by photolyzing the fresh solution of the simple non-halogenated quinones in alcohols, and that the ESR spectra of the semiquinone radicals may, when observed, have resulted from a subsidiary reaction between the quinones and the corresponding hydroquinones.[10,12)] Therefore, we believe that the photochemical analogy mentioned above is no longer pertinent.

Naturally it is a difficult task to identify an ESR spectrum without a resolved hyperfine structure, such as shown in Fig. 1A. Perhaps the ENDOR study will give a firm answer to the question of whether the photoinduced semiquinone intermediate is an anion or a radical, when the measurements are carried out during the photolysis, by proving the absence (or the presence) of a proton hyperfine splitting. In such a study, attention should be paid to eliminate the perplexing effect of the corresponding hydroquinone in the chloranil solution.

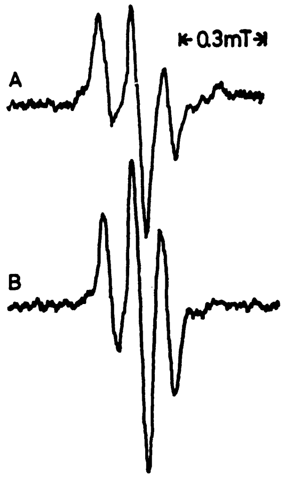

Fig. 3. ESR spectra of semiquinone intermediates observed during the photolysis of the solution, flowing at a rate of 1.5 cm^3 s^{-1}, of 1×10^{-3} mol dm^{-3} (A) 2,5-dichloro-*p*-benzoquinone or (B) 2,6-dichloro-*p*-benzoquinone in ethanol at room temperature.

Photolysis of Other Halogenated p-*Quinones.* When 2,5- and 2,6-dichloro-*p*-benzoquinones were photolyzed in ethanol at a comparatively high flow rate of the solution, the spectra with three hyperfine lines shown in Fig. 3 were recorded. The observed hyperfine splittings were 0.23 and 0.20 mT, essentially the same as those determined for the 2,5- and 2,6-dichloro-*p*-benzosemiquinone anions generated by the air oxidation of the corresponding hydroquinones.[17)] Therefore, the semiquinone anions are believed to form from these dichloro-*p*-benzoquinones, as from chloranil, by photoinduced one-electron transfer reactions. With a decrease in the flow rate, the spectra decreased in their intensity and were distorted simply because of an overlapping of the broad spectrum without a resolved hyperfine structure. The latter spectrum is thought to be due to the semiquinone radicals, which are generated preferentially at a low flow rate through the photoreaction between dichloro-*p*-benzoquinones and their corresponding hydroquinones, because of the depletion of the quinone concentration and the increase in the concentration of the product hydroquinones. Such a dependence on the flow rate is just the same as that reported previously for *p*-benzoquinone.[12)]

The *g*-values for the authentically generated semiquinone aions of chloranil, 2,5-, and 2,6-dichloro-*p*-benzoquinones and *p*-benzoquinone have been reported to be 2.00568, 2.00516, 2.00503, and 2.00468 respectively.[18)] The spectra assigned to these semiquinone anions in this and previous[12)] investigations were all consistent with the reported *g*-values. Evidently the increasing number of chlorine atoms in the semiquinone anions results in an increase in the *g*-value because of the large spin-orbit coupling in the chlorine atom. Keeping in mind the negligible difference in the *g*-value between the *p*-benzosemiquinone anion and the *p*-benzosemiquinone radical, one might be convinced that the shift of the spectra to the higher field (*i.e.*, to the smaller *g*-value) in the solution of chloranil in the highly alkaline ethanol is attributable to the elimination of some of the chlorine atoms by ethoxy-substitution.

Fluoranil in ethanol gave, under the photoillumination, a spectrum with five hyperfine lines of the binomial intensity ratio, just as has been reported previously by Hudson and Lewis.[19)] They interpreted this spectrum as being due to a rapid proton transfer between the two oxygen atoms of the semiquinone radical, which was presumed to be the primary intermediate in the photoreduction of fluoranil in ethanol. However, the spectrum was found to decrease in its intensity without changing its shape if the solution was made highly acidic by adding water and sulfuric acid. The interconversion between the semiquinone anion and the radical, which was a part of proposed rapid proton transfer, is believed to be slow for fluoranil, as for *p*-benzoquinone.[12)] There is no reason why the observed five-line spectrum cannot be attributed to the fluoranil semiquinone anion generated primarily by the photoinduced one-electron transfer.

No spectrum attributable to the semiquinone radical was observed from either fluoranil or chloranil, even by decreasing the flow rate of solution. In contrast, the superposition of the spectrum of the semiquinone radical on that of the semiquinone anion was observed at a low flow rate for *p*-benzoquinone[12)] and dichloro-*p*-benzoquinones. The generation of the *p*-benzosemiquinone radical was found previously to be the result of the hydrogen abstraction of the quinone from hydroquinone, the concentration of which became high enough because of the long photolysis time. The electron affinity increases in the order of *p*-benzoquinone, dichloro-*p*-benzoquinones, fluoranil and chloranil.[20)] The photoinduced one-electron transfer is slow for quinones of a low electron affinity, so that the hydrogen abstraction reaction competes. The one-electron transfer for quinones of a high electron affinity, such as fluoranil and chloranil, proceeds so rapidly that their semiquinone anions are exclusively observed by ESR during the photolysis.

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