

## ESR Spectra of Radicals during Photolysis of Chloranil in Solutions

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**Synopsis.** ESR spectra were recorded during photolysis of chloranil in 2-propanol, ethanol, methanol and benzene at room temperature. The spectra observed from solution in alcohols are identified as due to neutral semiquinone radical. It is also suggested that excited chloranil abstracts a hydrogen from benzene.

Principal aims of this investigation are in the identification of electron spin resonance (ESR) spectra of short-lived intermediates formed during photolysis of chloranil (tetrachloro-*p*-benzoquinone) in alcohols and also in the confirmation by ESR method of the possibility that excited chloranil abstracts a hydrogen atom from benzene. Hales and Bolton observed a single line spectrum of 0.80 G width in the photolysis of chloranil in ethanol and methanol and attributed it to chloranil radical anion on the basis of its *g*-value.<sup>1)</sup> Later, Wong *et al.* observed a spectrum of 0.58 G width from the 2-propanol solution and attributed it to neutral semiquinone radical of chloranil mainly on the basis of decay kinetics.<sup>2)</sup> Identification of the spectra seems to be still uncertain because of the lack of hyperfine structure in it.

By a recent study of flash photolysis, optical absorption spectra attributable to both neutral semiquinone radical and radical anion were observed from the solution of chloranil in methanol.<sup>3)</sup> One of the present author (H.Y.) and others studied short-lived intermediates during photolysis of *p*-benzoquinone and its methyl derivatives by ESR and found that both neutral radicals and radical anions are formed in alcohols.<sup>4)</sup> These results also suggest the necessity of re-examination of the single line spectra observed from chloranil in alcohols. In addition, the flash photolysis study showed an interesting result that the neutral semiquinone radical is formed in the solution of chloranil in benzene, which is not believed to be a hydrogen donor. It may be worthwhile to detect ESR spectrum of the neutral radical to confirm this flash photolysis observation.

## Experimental

All chemicals were analytical grade and used as received without further purification except that chloranil was recrystallized from chloroform.

ESR measurements were carried out at room temperature with a conventional X-band spectrometer (JEOL, Model JEX-ME) with a specially designed rectangular TE<sub>102</sub> cavity during photolysis with light from a super-high pressure

mercury arc (Philips, SP 500). Sample solutions were purged with helium gas to remove dissolved oxygen for at least half an hour, flowed through quartz flat cell in the cavity at a 4 ml/min and photolyzed with the light through a grid wall of the cavity.

## Results and Discussion

**Alcohol Solutions.** Figure 1a shows a typical ESR spectrum observed from solution of chloranil in 2-propanol during photolysis. It is a single line spectrum without resolved hyperfine structure, as reported previously,<sup>1)</sup> and its width (peak-to-peak width in derivative curve) is 0.55 G. The lifetime of the spectrum is shorter than the response time of the spectrometer used (0.3 s). No change is observed in the spectral shape and intensity by adding acetic acid to the solution. This fact strongly suggests that the spectrum is due to the neutral semiquinone radical rather than the radical anion, because radical anions are readily transformed to neutral radicals by protonation reaction in acidic solutions in the case of *p*-benzoquinone and its methyl derivatives.<sup>4)</sup>

When chloranil is reduced by sodium methoxide in isopropanol, a stable single line spectrum of 0.43 G width is observed without light. It is attributed to the radical anion of chloranil. The intensity of the

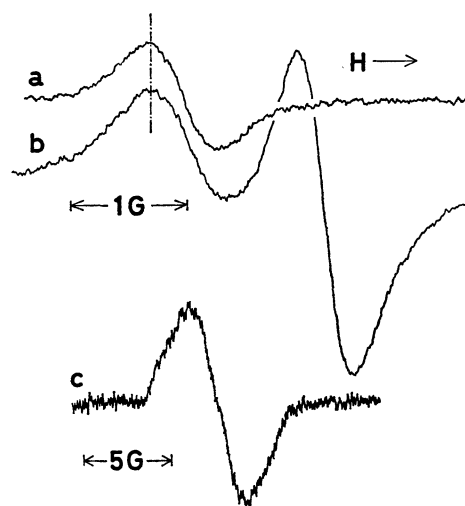


Fig. 1. ESR spectra observed at 20 °C during photolysis of solution of 1 mM chloranil (a) in isopropanol, (b) in 2-propanol with a small amount of sodium methoxide in it, and (c) in benzene. The vertical line gives a base for comparing the magnetic field position of the spectra (a) and (b) relative to each other. The signal curve (c) gives only the spectral shape and no information about the magnetic field position relative to that of (a) and (b).

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spectrum is strong and depends on the concentration of methoxide. Figure 1b shows spectra recorded from the solution of chloranil in 2-propanol in the presence of low concentration of sodium methoxide during photolysis. The spectrum at lower field is the photo-induced unstable spectrum, which corresponds to that in Fig. 1a. The spectrum at higher field is the stable one just mentioned above. Coexistence of the two spectra during the photolysis indicates that the unstable spectrum is attributed to the neutral semiquinone radical formed by the hydrogen abstraction from solvent molecule by excited chloranil.

The  $g$ -value of the chloranil radical anion is smaller by 0.0008 than that of the corresponding neutral radical. This contrasts to the absence of significant difference in  $g$ -value between radical anion and neutral radical formed from *p*-benzoquinone in ethanol (see the spectra in Fig. 1 of Ref. 4 and in 2-propanol.<sup>2</sup>) Chlorine atoms having a large spin-orbit coupling constant may have caused a significant change in  $g$ -value, when the electronic state is modified by the attachment of a proton to the chloranil radical anion to form the neutral radical.

Observations are the same for the solution of chloranil in methanol or ethanol as solvent instead of 2-propanol. The unstable spectrum shows the width of 0.63 and 0.62 G in methanol and ethanol, respectively. The width of the stable spectrum is 0.49 G in methanol and 0.43 G in ethanol. The coexistence of the two spectra indicates that the photoinduced unstable spectrum is due to the neutral semiquinone radical in all alcohols examined.

As a conclusion, the ESR spectra observed during photolysis of chloranil in alcohols are due to the neutral radical regardless of which alcohol is used as solvent. This conclusion does not exclude the assignment of the optical absorption spectra observed by the flash photolysis study that they are due to both the neutral radical and the radical anion,<sup>3</sup> because the time scale of measurements is very much different between these two methods. It may be worth noting that the ESR spectrum of only the neutral radical is observed during photolysis of chloranil, while the spectra of both the neutral radical and the radical anion are simultaneously observed during the photolysis of benzoquinone and its methyl derivatives in the same solvents.

**Benzene Solution.** Figure 1c shows the spectrum observed from solution of chloranil in benzene during photolysis. The spectrum has a width of 3.4 G without

resolved hyperfine structure, which is much wider than the spectrum of neutral semiquinone radical formed from chloranil in aprotic solvent of dioxane.<sup>2</sup> Although the reason why the present spectrum in benzene is so much wider is not known at this moment, it is suggested to be due to the neutral semiquinone radical, because the addition of acetic acid causes no change in the shape and intensity of the spectrum. The integrated intensity of the spectrum is comparable to or somewhat larger than that of the unstable spectrum observed from the alcohol solutions under the measuring conditions unchanged. The presence of dissolved oxygen reduces remarkably the efficiency of radical formation.

The above interpretation of the spectrum may raise a question what the excited chloranil abstracts a hydrogen atom from. Even if 5 vol% of isopropylbenzene is added as hydrogen donor into the solution, no increase is found in the intensity of the spectrum. The photolysis of chloranil in toluene gives the same spectrum as in the benzene solution, the intensity of which is also the same as in benzene. These results infer that the photochemical reactions involved are rather complex but the excited chloranil molecule abstracts a hydrogen atom from the benzene ring. The above interpretation is consistent with the previous flash photolysis study where transient optical absorption bands observed from the solution of chloranil in benzene were attributed to the neutral semiquinone radical.<sup>3</sup>

In addition to the main broad spectrum, spectra composed of several sharp hyperfine lines of 0.25 G width are traced from both the benzene and toluene solutions. However, the spectra are too weak to be recorded clearly. They are believed to be due to free radicals formed from solvent molecules, and their identification, if possible, may give an essential information of the reaction involved.

#### References

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