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114. Mamoru Kamiya, Keiichiro Hatano, and Takao Kwan: Electron Spin Resonance Studies of Photo-sensitized Decomposition of Methyl Alcohol in the Presence of *p*-Benzoquinone.

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Photo-sensitized decomposition of methyl alcohol in the presence of *p*-benzoquinone has been investigated by electron spin resonance method at a frozen state. Four kinds of ESR spectrum were distinguished; these were CH_2OH, CHO, CH_3 and probably *p*-benzosemiquinone radical.

Inspection of the developing pattern of these spectra has led to a result that CHO and CH_3 radicals are secondarily produced rather than photoprimarily. The methyl radical was found to be less stable compared with the other radicals. The decay of methyl radical was investigated and found to obey the second order rate law.

Photo-sensitized decomposition of ethyl alcohol was investigated additionally.

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Literatures[1,2] show that methyl alcohol frozen at 77° K decomposes to give several species of fragment radicals when irradiation of lights of 2537 and 1849 Å is made by a low pressure mercury lamp. Little is known, however, on the photo-sensitized decomposition of alcohol.

We have found that *p*-benzoquinone (*p*-BQ) is a good sensitizer for the fragmentation of frozen methyl alcohol; several species of radicals were readily observed upon irradiation of lights having wavelengths longer than 3000 Å.

The formation of radicals as well as their decay was investigated mainly at 77° K by electron spin resonance (ESR) methods. The results will be reported and discussed in the present paper.

Experimental

p-BQ was purified by sublimations and then recrystallizations from petroleum ether. Methyl alcohol of guaranteed grade supplied by Koso Kagaku Co. was used without purification.

A sample of methyl alcohol containing $10^{-1}\sim10^{-3}M$ *p*-BQ was put in a Pyrex tube of 2 mm. diameter and degassed by several repetitions of freezing and melting on a high vacuum line. The tube was then inserted in the cavity and kept at liquid nitrogen temperature (77° K). The temperature of the sample was allowed to change, when necessary, up to 223°K by means of the cooling nitrogen gas.

All irradiations were made with a 500 W high pressure mercury lamp, and a Matsuda glass filter UVD2 was employed to remove the lights of wavelengths shorter than 3000 Å and greater than 4000 Å.

A JEOL type P-10 X-band spectrometer was used to detect the radicals formed and to follow the changes in their spectra after interupting the lights. The g-values of the spectra were evaluated in reference with the signal obtained by Mn^{++} in MgO.

Results and Discussion

When lights having wavelengths 3000～4000 Å were irradiated on frozen methyl alcohol or ethyl alcohol in the absence of *p*-BQ, no ESR signal could be detected. On the other hand, in the presence of *p*-BQ ($10^{-1}\sim10^{-3}M$) the same irradiation readily gave rise to ESR spectrum. A typical ESR spectrum obtained for methyl alcohol is shown in Fig. 1.

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1) L.H. Piette, W.C. Landgraf: J. Chem. Phys., **32**, 1107 (1960).

2) P.J. Sullivan, W.S. Koshi: J. Am. Chem. Soc., **84**, 1 (1962); *Ibid.*, **85**, 384 (1963); *Ibid.*, **86**, 159 (1964).

Fig. 1. ESR Spectrum for Radicals produced by *p*-BQ Photo-sensitized Decomposition of Methyl Alcohol.

a : CHO *b* : CH_3 *c* : CH_2OH

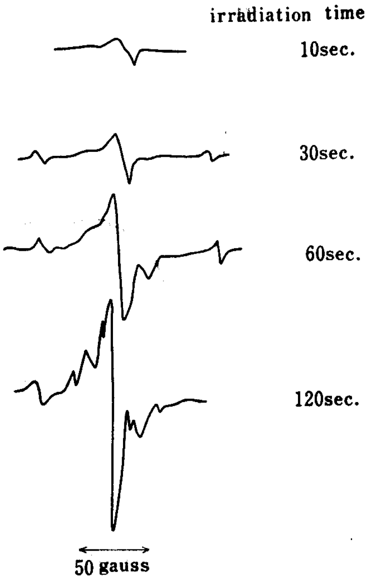

Fig. 2. Change in ESR Spectra for *p*-Benzosemiquinone-like-Radical.

The asymmetric doublet signal (*a*) of Fig. 1, with 128 gauss splitting may be assigned as formyl radical, CHO.[2,3] The 1:3:3:1 sharp quartet signal (*b*) with 22.5 gauss splitting reveals the expected intensity ratio as well as hyperfine splitting if it is assigned as methyl radical, CH_3. This quartet signal could easily be discriminated from the other signals due to its remarkable instability.

The triplet (*c*) underlying the CH_3 quartet may tentatively be correlated with CH_2OH radical. This radical is known to be formed during the photo-sensitized oxidation of methyl alcohol in the presence of *p*-BQ.[4] However, the high intensity of the central line and the weak shoulders of the signal (*c*) prevented to recognize the 1:2:1 triplet intensity of the CH_2OH radical. The signal overlapping of this sort was found to be enhanced with increasing the concentration of *p*-BQ. Hence, there may exist another signal, probably originated from *p*-BQ, superimposed on the central line of the CH_2OH triplet.

The change in the ESR spectra during the irradiation was investigated to get some information on this problem. The results are shown in Fig. 2. The signal obtained after 10 sec. irradiation was asymmetric singlet ($g=2.008$) with 12 gauss peak-to-peak width. This signal appeared to develop on further irradiation and finally was found to overlap with the gradually developing CH_2OH triplet. This seems to suggest that the signal in question is attributable to a semiquinone radical produced by the reaction between photo-excited *p*-BQ and methyl alcohol.

The expected pattern of the signal, when corrected for of the CH_2OH triplet, was a symmetrical singlet with 15 gauss peak-to-peak width. Such a signal was obtained when irradiations were made on benzene containing $5.6\times10^{-2}M$ *p*-benzohydroquinone frozen at 77° K. Therefore, the signal may probably be due to *p*-benzosemiquinone radical. The latter signal is shown in Fig. 3. According to Land, *et al.*[5] a spectroscopic

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[3] I. Miyagawa, W. Gordy : J. Am. Chem. Soc., **83**, 1036 (1961).

[4] B. Atkinson, M. Di : Trans. Faraday Soc., **54**, 1331 (1958).

[5] J. Land, G. Porter, E. Strachan : *Ibid.*, **57**, 1185 (1961).

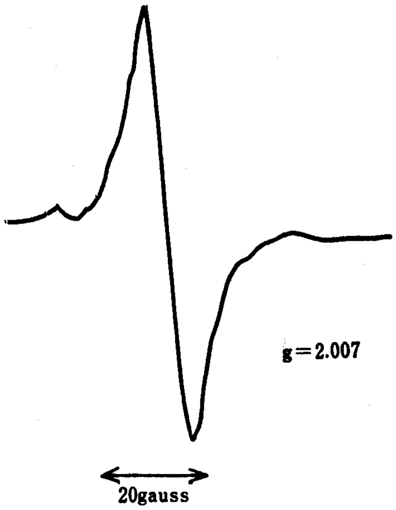

Fig. 3. ESR Spectrum for Radical produced by Irradiating Benzene Containing *p*-Benzohydroquinone.

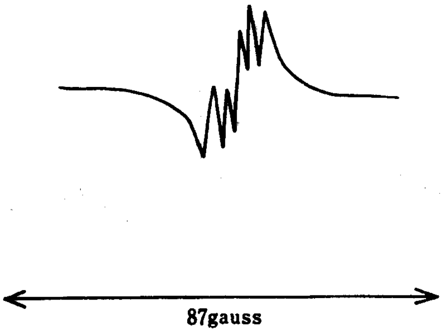

Fig. 4. ESR Spectrum for Irradiated *p*-BQ-CH_3OH Sample

absorption of such species was found to appear when ultraviolet lights were irradiated on *p*-benzohydroquinone dissolved in an inert glassy matrix.

On irradiation at 213° K, the *p*-BQ-CH_3OH sample gave a small but suggestive spectrum as shown in Fig. 4. The spectrum may be considered as the surviving one since other radicals were all found to decay very rapidly around this temperature. The observed quintet with 2.6 gauss splitting may suggest the existence of *p*-benzosemiquinone radical.

Now, let us investigate the kinetics of the formation and decay processes of the radicals. The development pattern of radicals, the part of which is shown in Fig. 2, indicated that the appearance of signals was of the successive order: CH_2OH, CHO and CH_3. The initial formation of CH_2OH may be compatible with the reported mechanism[2] which assumes the secondary formation of CHO according to $CH_2OH \rightarrow CHO + H_2$.

In Fig. 5 (*a*) is shown the developing process of CH_3 as represented by the intensity of one of the two strong lines of the CH_3 quartet. The other curve (*b*) of Fig. 5 indicates that of the CH_2OH triplet. The curve (*b*) can shift depending on the radical concentration without changing the shape. It is apparent from Fig. 5 that the formation of CH_3 has an induction period and the concentration, when initiated, steadily increases with prolonged irradiation whereas the concentration of CH_2OH reaches a saturation.

This may imply that the formation of CH_3 is secondary, for instance from CH_2OH. The methyl radical would probably be formed by the reaction of CH_2OH with H.

The CH_3 radical formed is so unstable in frozen methyl alcohol that it decays soon after interupting lights. The decay was found to obey the second order rate law. The result is shown in Fig. 6. According to Sullivan,[2] the decay was of the first order at lower concentrations of CH_3.

A similar *p*-BQ photo-sensitized decomposition of ethyl alcohol was investigated. The main ESR spectrum obtained from the sample was assigned as the ethyl radical, it gave a quartet of triplet with 22 gauss α-proton splitting and 28 gauss β-proton splitting as shown in Fig. 7. This signal was found to decay also according to the second order rate law. However the rate was much slower than CH_3.

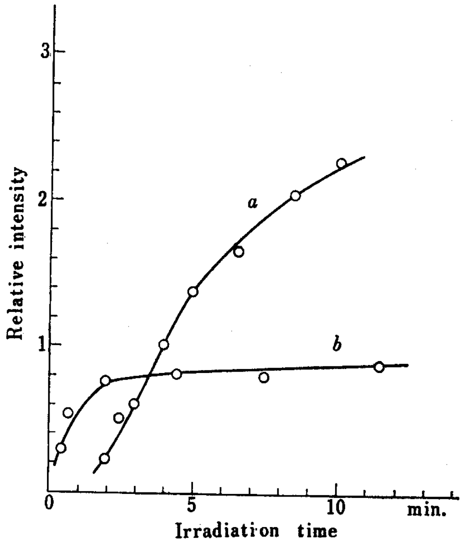

Fig. 5. Relation between Signal Intensity and Irradiation Time

a : CH_3 *b* : CH_2OH

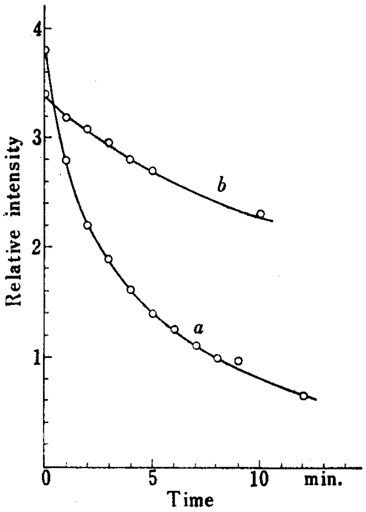

Fig. 6. Decay Curve for Methyl and Ethyl Radicals.

a : CH_3 *b* : CH_3CH_2

The radical decay was sensitively temperature dependent. If the recombination of radicals is rate-controlling, the activation energy should be almost zero. Since the decay process is temperature dependent, it may be considered to be determined by the diffusion of radical in matrix. The mobile nature of the two radicals may also be judged from their relatively sharp resonance lines as compared with CH_2OH or CHO. The tumbling and rotating motions of radical will make narrower the resonance line. On the other hand, the oxygen-containing radicals do not seem to behave like this. Their motion is likely to be restricted by the hydrogen bonds with the surrounding methyl alcohol molecules.

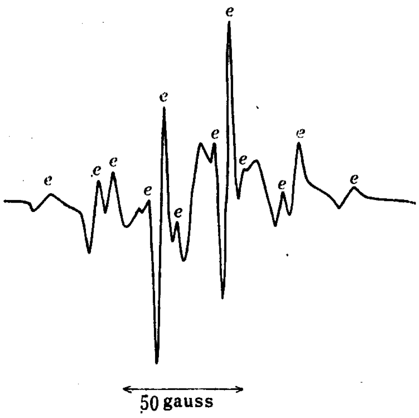

Fig. 7. ESR Spectrum for Radicals produced by *p*-BQ Photo-sensitized Decomposition of Ethyl Alcohol.

e : CH_3CH_2

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