BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 273—275 (1971)

An ESR Study of Radicals Produced in γ-Irradiated Allyl Alcohol Glass and Their Photochemical Reaction at 77°K

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(Received May 15, 1970)

The ESR spectrum of γ-irradiated allyl alcohol glass is a composite of four-line and five-line spectra.[1] The four-line spectrum has been assigned to the α-hydroxy allyl radical[1-3] (I), which disappears with UV-irradiation.[1] The five-line spectrum has been assigned to the allyl radical[1-3] (II). Neither coloration nor the ESR spectrum due to the trapped electron has been observed in this system, in contrast with the cases of γ-irradiated alkyl alcohol glasses.[4] In this work we have investigated the fate of the thermal electron, and also the photolysis and thermal behavior of the radicals in allyl alcohol glass.

Experimental

Allyl alcohol and triethylamine (TEA) were purified by fractional distillation. The γ-irradiation and ESR and optical measurements were described previously.[5] Thermal

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[1] M. C. Chachaty, *C. R. Acad. Sci., Paris*, **259**, 2219 (1964).

[2] K. A. Mass and D. H. Volman, *Trans. Faraday Soc.*, **60**, 1202 (1960).

[3] M. Fujimoto and D. J. Ingram, *ibid.*, **54**, 1304 (1958).

[4] A. Ekstrom and J. E. Willard, *J. Phys. Chem.*, **72**, 4599 (1968).

[5] S. Noda, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, **49**, 3287 (1968).

annealing experiments were carried out at various temperatures in the range of 90—140°K by keeping the sample tube in a JES variable-temperature quartz Dewar insert. Photolysis experiments were performed with UV light from a high-pressure mercury lamp. Cut-off filters were employed if necessary.

Results and Discussion

The ESR spectrum of γ-irradiated allyl alcohol glass at 77°K is shown in Fig. 1. The trapped-electron signal was not observed in this system, although ESR measurements were made at microwave powers low enough to avoid power saturation[6,7] and in the dark. Upon γ-irradiation, TEA glass produces a blue color and gives an ESR spectrum consisting of a sharp singlet due to the trapped electron and a broad unresolved signal due to the solvent radical.[7] The ESR spectrum of the γ-irradiated TEA containing 1 mol% of allyl alcohol is shown in Fig. 2a. The five-line spectrum appears with a decrease in the intensity of the central sharp singlet. The illumination of infrared light bleached the trapped-electron signal and increased the intensity of the five-line spectrum (see Fig. 2b). This five-line spectrum is ascribed to the radical(II) on the basis of its ESR parameters. These facts indicate that allyl alcohol reacts with the thermal electron dissociatively to produce the radical(II) and the hydroxy anion:

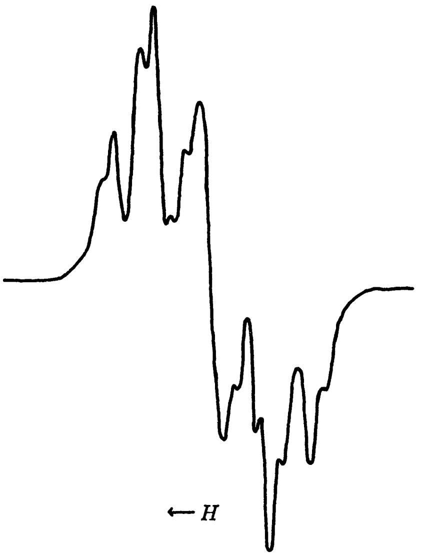

Fig. 1. ESR spectrum of γ-irradiated allyl alcohol glass at 77°K.

$$CH_2{=}CH{-}CH_2OH + e^- \longrightarrow CH_2{=}CH{-}\dot{C}H_2(II) + OH^-$$

Making use of the competitive reaction, the cross section, σ(R–OH), for electron capture by allyl alcohol relative to biphenyl was determined. Optical measurements were made in order to determine the yield of the biphenyl anion (410 nm[8]). The observed ratio, σ(R–OH)/σ(biphenyl), was about 0.3. This agrees with that given by Habersbergerová *et al.*,[9] the ratio of the electron-capture efficiency of allyl alcohol to that of naphthalene in methanol glass being about 0.25. We have also found that other allylic compounds, such as allyl acetate, allyl formate, and allyl nitrile, react with thermal electron dissociatively to produce the radical(II) and the corresponding anion, although detailed studies on these compounds were not carried out.

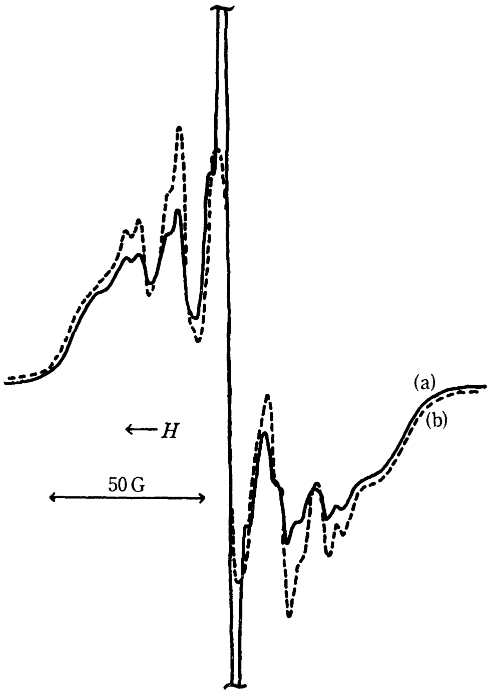

Fig. 2. ESR spectra of γ-irradiated TEA glass containing 1 mol% of allyl alcohol at 77°K, a) before bleaching, b) after bleaching with infrared light.

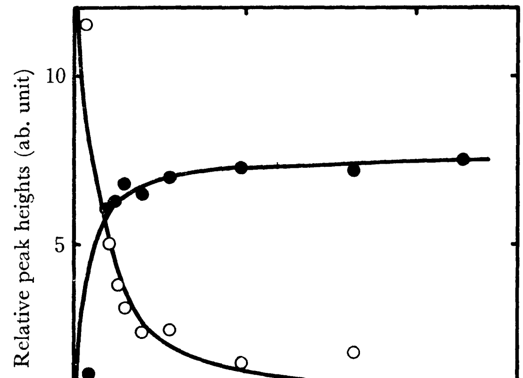

Fig. 3. The plots of relative ESR peak heights against the UV-irradiation time, ●, allyl radical; ○, α-hydroxy allyl radical.

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6) D. R. Smith and J. S. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

7) H. Tsujikawa, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, **47**, 256 (1967).

8) W. H. Hamill, "Radical Ion," ed. by. E. T. Keiser and L. Kevan, Interscience Publishers, New York (1968), p. 321.

9) A. Habersbergerová, Lj. Josimović, and J. Teplý, *Trans. Faraday Soc.*, **66**, 656 (1970).

When the γ-irradiated allyl alcohol glass was warmed to 118°K, the ESR spectrum changed to the pure four-line spectrum.¹⁾ Moreover, UV-irradiation, following the γ-irradiation, caused the ESR spectrum of pure allyl alcohol glass to change from a composite of the four-line and five-line spectra into the five-line spectrum.¹⁾ On warming this sample characterized by only a five-line spectrum, a weak four-line spectrum appeared with the decay of the five-line one. When the same sample was kept in the dark for a few days at 77°K, the spectrum changed to a composite of the four-line and five-line spectra. These facts seem to suggest that the radical(II) abstracts an α-H from allyl alcohol to produce the radical(I) at 77°K as well as at 118°K, but the evidence for this is not conclusive.²⁾

Until now it has not been clear whether or not the radical(I) produces the radical(II) by UV-irradiation. The pure four-line spectrum remaining at 118°K was changed into a composite of the four-line and five-line spectra by UV-irradiation at 77°K, while prolonged UV-irradiation caused the composite spectrum to change completely into the five-line spectrum. The relative ESR peak heights of the four-line and five-line spectra are plotted against the UV-irradiation time in Fig. 3. From these results, it is apparent that the radical(I) decomposes upon UV-irradiation to produce the radical(II). As the mechanism of this photochemical conversion in allyl alcohol, the following process may be proposed:

$$\mathrm{CH_2{=}CH\text{-}CH_2OH + CH_2{=}CH\text{-}\dot{C}HOH\,(I)} \xrightarrow{\mathrm{UV}}$$
$$\mathrm{CH_2{=}CH\text{-}\dot{C}H_2(II) + CH_2{=}CHCOH + H_2O}$$

A spot test¹⁰⁾ of the sample which had been UV-irradiated after γ-irradiation gave evidence of the presence of aldehyde, but we could not identify the aldehyde with acrolein because of the detection limit. Therefore, the scheme proposed above should be regarded as only tentative.

The relative primary yields of radicals in γ-irradiated allyl alcohol glass were obtained. The primary yield of the radical(II) was estimated to be about twice that of the radical(I). Since the radical yields of I and II must be the same if the ionic processes play an important role, the excitation process may also be concerned with the radiolysis of allyl alcohol glass. However, further product analysis is required for a complete understanding of the mechanism of the radiolysis and photolysis of allyl alcohol.

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10) F. Feigel, "Spot Tests in Organic Analysis," Elsevier Publishing Company, Amsterdam (1960), p. 223.