

A Comparative Aspect of Radical Species Produced from Several Benzene Derivatives by Photo and Ionizing Radiations

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Free Radicals produced from ultraviolet, electron-beam, and gamma-ray irradiated benzene derivatives were detected by an electron spin resonance method and discussed about their structures. Distinguishable differences on the structures between both radicals produced by the photo and ionizing radiations were found in these experiments. Both phenyl and hexadienyl radicals were produced when irradiated with ionizing radiation, contrary to only phenyl radicals with ultraviolet irradiation. The results presented useful consideration on mechanisms of direct actions of radiation.

INTRODUCTION

Mechanisms of actions of photo and ionizing radiations on organic compounds in solid state have been of great interest from stand points of photo and radiation chemistry. In elementary process of the radiation effects various radical species have been known to appear on the irradiated compounds by a direct action on solid. The radicals have been considered to have close relationships to successive chemical effects of the radiation.

The radicals produced from the irradiated compounds could be detected using an electron spin resonance spectrometer at low temperature because those were stable relatively at the low temperature and supposed to be analogous to those appeared in a primary course of radiation chemical reactions. Temperature-increasing experiments from, and photo bleaching techniques at, the low temperature would give some information about changes of structure of the radicals in the irradiated solids.

This paper deals with a comparative study on structure of the radicals on solids produced by photo and ionizing radiations. Distinguishable difference on structures of these radicals produced by the photo and ionizing radiations and useful consideration on the mechanisms of direct effects of radiation are described.

MATERIALS AND METHODS

Materials:

Single crystals, polycrystals and amorphous powder of benzene derivatives,

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ethylbenzene, chlorobenzene, azobenzene, polystyrene, hydrazobenzene, phenylcyclohexane, tri-phenylamine, α -naphthol, carbazole and phenylether were used for these experiments. Those were purchased in chemical pure grade from Nakarai Kagaku Co., Kyoto and Wako Junyaku Co., Osaka.

Irradiation :

Irradiation was performed at 77°K and room temperature to 2 to 5×10^7 rads by a 1.5 MeV electron-beam from a van de Graaff accelerator and γ -rays from a cobalt-60 irradiator. Photo irradiation was by a Toshiba 400 W ultraviolet lamp which was used for photo bleaching experiments equipping with the electron spin resonance spectrometer.

Electron spin resonance measurements :

A Varian V-4500 X-band EPR spectrometer with 100 Kc/sec modulation, was used for detection and measurements for electron spin resonance signals of solid radicals produced from organic molecules by irradiation. Estimation of g-values was carried out referring to one of 1, 1-diphenyl-2-picryl-hydrazyl (DPPH) powder.

RESULTS

Radicals produced from benzene derivatives in solid state by photo and ionizing irradiation at low temperature

By means of photo irradiation several radicals were produced from irradiated solids of ethylbenzene, chlorobenzene, azobenzene, polystyrene, triphenylamine, α -naphthol and phenylether in a vacuo sealed tube at 77°K. The radicals of these benzene derivatives showed similar spectra to one of benzene. A spectrum of ethylbenzene was shown in Fig. 1.

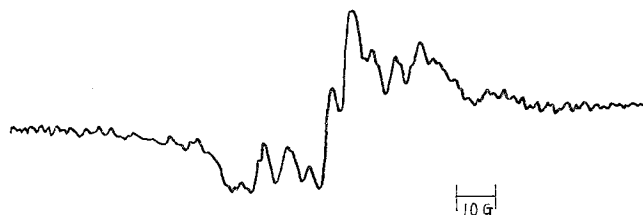


Fig. 1. Electron spin resonance spectrum of ultraviolet irradiated ethylbenzene at 77°K.

It has been reported that a hexadienyl radical was produced from benzene irradiated with ionizing radiation at 77°K (1), and a phenyl radical was produced from ultraviolet irradiated benzene (2). The hexadienyl radical showed a quintet-triplet spectrum splitting at 47.5 gauss in triplet of which intensity of 1:4:1 and every 10.4 gauss splitting, contrary to a singlet of the phenyl radical of which ΔH_{msl} of 25 gauss (3). The singlet radical seems to show a sextet spectrum which was found to be produced from ultraviolet irradiated benzene and to have a splitting constant of 6 gauss. The ΔH_{msl} of the sextet spectrum was about 20 gauss which was similar to the singlet which produced when irradiated with

ionizing radiation. When polystyrene chlorobenzene, azobenzene, phenylether and triphenylamine were irradiated with ionizing radiation both a similar hydrogen additional radical and a phenyl radical were shown to be produced contrary to only a phenyl radical by ultraviolet irradiation without any hydrogen additional radical as shown in Fig. 2.

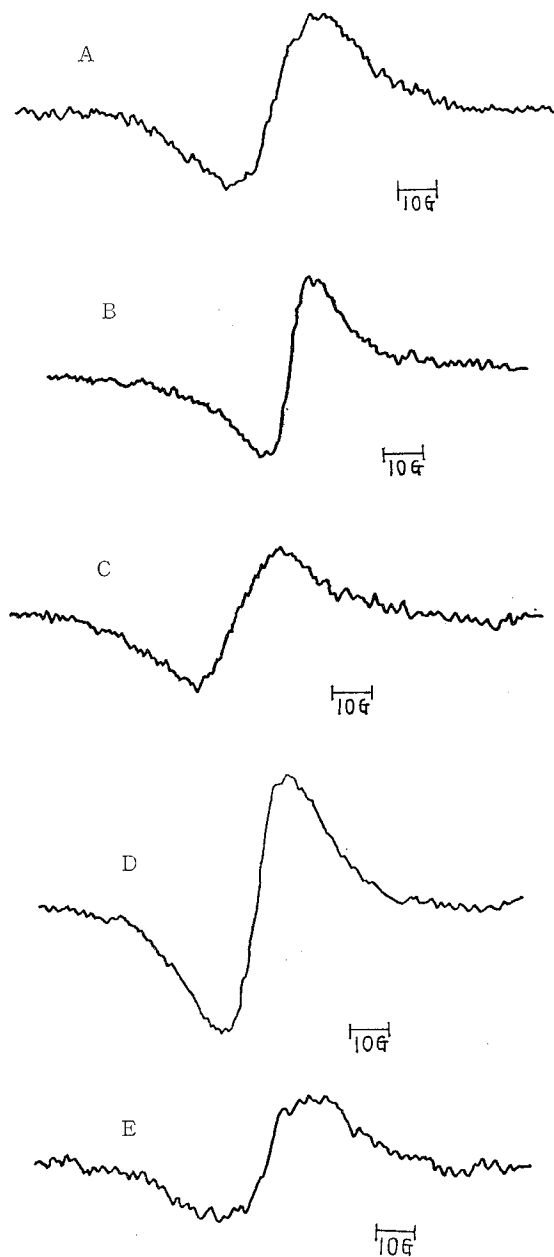


Fig. 2. Electron spin resonance spectra of ultraviolet irradiated several benzene derivatives.

A: polystyrene, B: chlorobenzene, C: azobenzene, D: phenyl ether, E: triphenylamine.

Radicals from Irradiated Benzene Derivatives

Similar results were obtained on several aromatic compounds such as α -naphthol, hydrazobenzene, phenylcyclohexane, and carbazole as shown in Fig. 3.

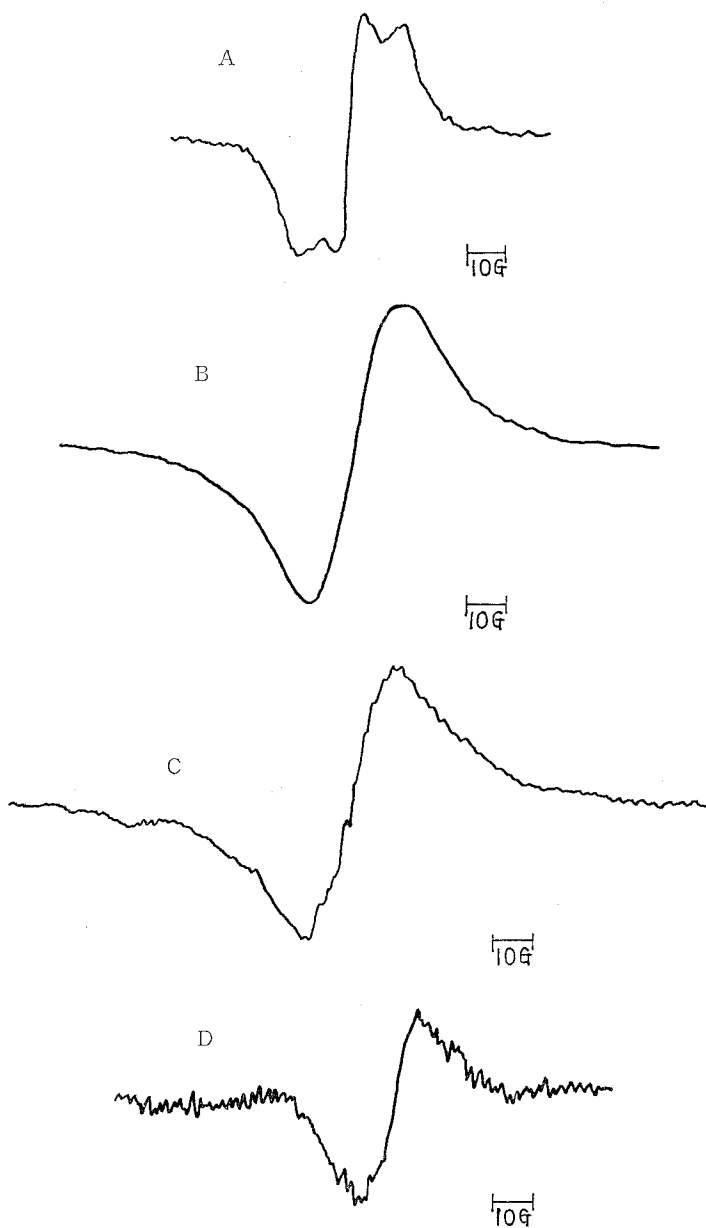


Fig. 3. Electron spin resonance spectra of ultraviolet irradiated several benzene derivatives.

A: α -naphthol, B: hydrazobenzene, C: phenylcyclohexane, D: carbazole.

Ultraviolet irradiated phenylether and triphenylamine did not show any hydrogen additional spectra. Ethylbenzene which has an ethyl group of a side-chain, however, showed a different electron spin resonance spectral behavior from the above compounds.

DISCUSSION

When benzene was irradiated with ionizing radiation, both a hexadienyl radical which was an additive product of a hydrogen atom to the benzene ring, and a phenyl radical which was a splitting product of a hydrogen atom from the benzene ring, were produced where both spectra were found to be duplicated. Contrary to the above case, only a phenyl radical was produced from ultraviolet irradiated benzene. Similar results were obtained on several benzene derivatives such as α -naphthol, phenylether, triphenylamine and ethylbenzene as shown in Figs. 2 and 3. It was pointed out that no additive product radicals such as the hexadienyl radical, was observed on the ultraviolet irradiated benzene derivatives.

Conclusively, photo and ionizing radiation induced effects were observed to occur only on the benzene ring of the derivatives. By ultraviolet irradiation on a carbon-hydrogen bond of the benzene ring was broken, and by ionizing radiation a further additive reaction of a hydrogen atom to a double bond was observed to occur on the benzene derivatives. This difference on the structures of the irradiated benzene derivatives between with ultraviolet and with ionizing radiations would give a useful consideration on mechanisms of radiation effects and reactions of aromatic compounds induced by ultraviolet and ionizing radiations.

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