

A Comparative Study of the Effects of UV and Electron-Beam Irradiation on Diphenylamine by Electron Spin Resonance Technique

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The present work was undertaken in order to investigate intermediate radicals from photolysis and radiolysis of diphenylamine at the temperature of liquid nitrogen by means of electron spin resonance. As a result, ESR spectra corresponding to the diphenylamino and the diphenylamine cation radical could not be observed in the present experiment. Namely, UV-irradiation of diphenylamine exhibited a single line spectrum with ΔH_{msl} of approximately 20 gauss, not showing any anisotropy. Accordingly, this single line spectrum could not be ascribed to either the diphenylamino radical or the diphenylamine cation radical. This single line spectrum was tentatively assigned to a phenyl-type radical which was formed by the cleavage of a C-H bond. Electron-beam irradiated diphenylamine gave a triple-triplet spectrum which exhibited the anisotropy of hfs. This triple-triplet spectrum can be identified as a cyclohexadienyl-type radical which was produced from the addition reaction of a hydrogen atom to the ortho or the para position in phenyl ring.

INTRODUCTION

The present work was undertaken in order to make a comparative study of intermediates produced by exposure of diphenylamine to UV and to ionizing radiation by means of electron spin resonance.

In the previous studies,¹⁾ it has been confirmed that γ and/or electron-beam irradiation of benzene and its derivatives produced the cyclohexadienyl radical from the addition reaction of a hydrogen atom to a double bond in benzene ring. On the other hand, it was also reported that UV-irradiation of a physically adsorbed benzene at 77°K produced benzene cations through the photoionization,²⁾ and that UV-irradiation of polycrystalline benzene at 77°K did not give the spectra from both benzene cation radicals and the cyclohexadienyl-type radical.³⁾

In the present work, a comparative study of effects of UV and ionizing radiation was extended to diphenylamine, the photolysis of which had been assumed to produce the diphenylamine cation radical and the diphenylamino radical by means of optical absorption spectroscopy.⁴⁾ The previous ESR study of the photooxidation of diphenylamine in the frozen solution⁵⁾ has reported the formation of both the diphenylamine cation radical and the diphenylamino radical. In the present investigation, however, it was found that ESR spectra corresponding to the diphenylamine cation radical and the diphenylamino radical could not be

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observed, and that UV-irradiation of diphenylamine at 77°K did not induce the hydrogen addition reaction like the case of UV-irradiation of benzene.

EXPERIMENTAL

Materials: Diphenylamine was obtained from Nakarai Chemical Company, Ltd.; it was recrystallized from the solution in purified ligroin. The single crystal of diphenylamine was prepared from a saturated solution of diphenylamine in ligroin by a spontaneous evaporation method. Di-tert-butylperoxide, obtained from Nakarai Chemical Company, Ltd., was used for the oxidation of diphenylamine. Diphenylamine placed in an i. d. 4 mm. quartz ampoule was degassed on a vacuum line and subsequently it was sealed in vacuo. The photooxidation of diphenylamine was carried out at room temperature by UV-irradiation of diphenylamine in the solution consisting of 10 mg of diphenylamine and 0.2 ml of di-tert-butylperoxide. Before UV-irradiation, this solution put into an i. d. 4 mm. quartz ampoule was degassed through repeated freezing and thawing and subsequently it was sealed in vacuo.

Irradiation: UV-irradiation was performed at the temperature of liquid nitrogen with a Toshiba 400 W highpressure mercury lamp using either UV-25 or UV-D25 as a UV light filter. UV-irradiation for the oxidation of diphenylamine was carried out at room temperature with the same mercury lamp as described above. Electron-beam irradiation was done at the temperature of liquid nitrogen using a van de Graaff accelerator (1.5 MeV, 50-100 μ A).

ESR Measurements: Spectra were recorded on a Varian V-4560 X-band EPR spectrometer with 100 kc/sec modulation at the temperature of liquid nitrogen and/or at room temperature.

RESULTS AND DISCUSSION

Spectra from UV-Irradiation: UV-irradiation of diphenylamine at the temperature of liquid nitrogen showed a single line spectrum with ΔH_{msl} of about 20 gauss as is shown in Fig. 1 (a) and this spectrum disappeared at room temperature in less than approximately 10 min. UV-irradiation of the single crystal of diphenylamine also exhibited a single line spectrum corresponding to the case of powder of diphenylamine as is shown in Fig. 1 (b). Furthermore, the spectrum from a UV-irradiated single crystal did not give both any anisotropy and hfs. It has been previously postulated that the diphenylamino and the diphenylamine cation radical^{4,5)} are produced from the photooxidation of diphenylamine in frozen solutions. The diphenylamino radical could be expected to exhibit a spectrum with both hfs consisting of three lines and an anisotropy arising from the interaction of the unpaired electron with the nucleus of nitrogen atom (N^{14}) by analogy with the diphenylnitric oxide radical.⁵⁻⁸⁾ Also in the present experiment, in order to try an experimental assignment of the present single line spectrum, the single line spectrum from UV-irradiated diphenylamine was compared with the spectra from the diphenylnitric oxide radical, which is known to be produced from the oxidation of diphenylamine.^{9,10)} The diphenylnitric oxide radical, which

Irradiation Effects on Diphenylamine

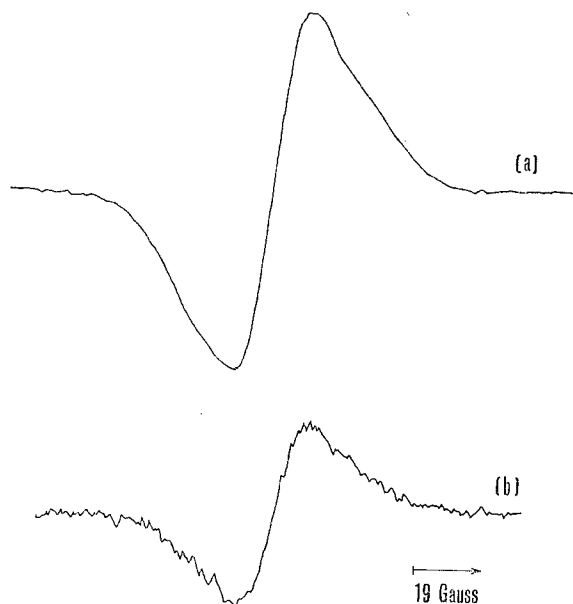


Fig. 1. ESR spectra observed from diphenylamine powder (a) and the single crystal of diphenylamine (b) exposed to UV light, respectively. The spectrum (b), one of spectra obtained from a single crystal, did not show any anisotropic effect, when the single crystal was rotated around the three axes in the external magnetic field.

was prepared from the photooxidation of diphenylamine with di-tert-butylperoxide, showed the three-line spectrum with the splitting value of about 11 gauss, each of three lines being split into extra hfs with the splitting value of approximately 0.9 gauss as is shown in Fig. 2 (a), in the liquid state at room temperature. The above sample frozen at the temperature of liquid nitrogen gave the three-line spectrum, with the splitting value of about 18 gauss, the width of the central resonance line being narrowed due to the isotropic resonance. To consider from the above experimental results, the present single-line spectrum can not be attributed to the diphenylamino radical and it is supposed that this single-line spectrum arises from a radical species other than the diphenylamino radical. Kholmogorov *et al.*⁵⁾ attributed the single line spectrum with ΔH_{msl} of 20 gauss, which was observed from the photooxidation of diphenylamine in toluene at the temperature of liquid nitrogen and gave the maximum optical absorption at $690 m\mu$, to the diphenylamine cation radical. The diphenylamine cation radical also could be expected to show a three-line spectrum and an anisotropic effect by analogy with the triphenylamine cation radical,¹¹⁾ which was observed from triphenylamine adsorbed on decationized zeolites and gave the three-line spectrum with the splitting value of 14 gauss. Furthermore, it has been confirmed that the photoionization of aromatic amines does not proceed from the ejection of a non-bonding electron on the nitrogen atom, but from the ejection of a π -electron in benzene ring.¹²⁾

From the above experimental results, one of the most probable radicals may be due to a phenyl-type radical where hfs could not be observed probably due to the degree of freedom of rotation of the phenyl ring and/or to an effect of the substitution group, although the present spectrum is different from the six-line

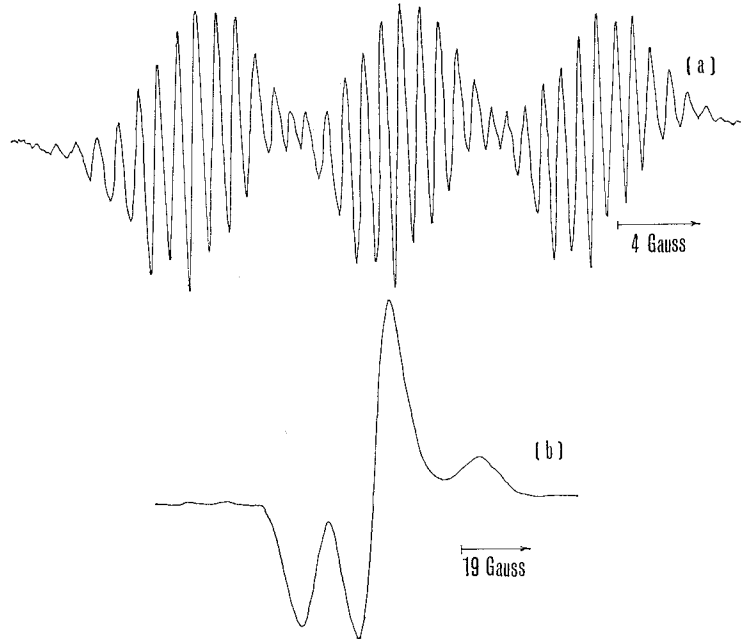


Fig. 2. The dependence of the ESR spectrum of the diphenylnitric oxide radical on temperature. The spectrum (a) and the spectrum (b) were recorded at room temperature and at liquid nitrogen temperature, respectively.

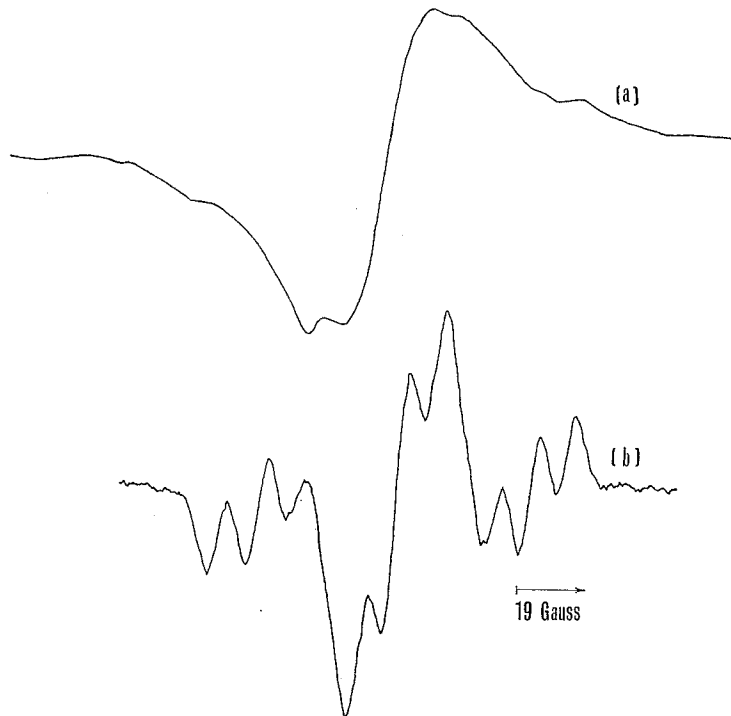


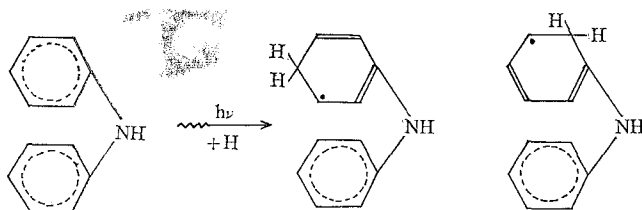
Fig. 3. ESR spectrum from electron-beam irradiated diphenylamine powder. The spectrum (a) was recorded immediately after irradiation and the spectrum (b) after the sample was kept at room temperature for two weeks.

Irradiation Effects on Diphenylamine

spectrum tentatively assigned to the phenyl radical⁹⁾. This suggestion that a phenyl-type radical will be produced from UV-irradiation of diphenylamine seems to be compatible with the production of carbazole from the photochemical reaction of diphenylamine in alcoholic solution.^{13,14)}

The effective wavelengths for observing spectra from diphenylamine were estimated to be in the region approximately from 2200 Å to 2900 Å. This wavelength region corresponds to the wavelength regions of the absorption (max. 285 mμ) by diphenylamine.¹⁵⁾ In the present experiment, the mechanism of photolysis of diphenylamine could not be clarified, although a two-quantum process has been postulated in diphenylamine-sensitized photooxidation in the frozen state.¹⁶⁾

Spectra from Electron-Beam Irradiation: Electron-beam irradiated diphenylamine powder, which was kept at the temperature of liquid nitrogen until just prior to the performance of ESR measurements, showed a poorly resolved three-line spectrum with the overall-spread width of approximately 170 gauss as is shown in Fig. 3 (a). The above sample being kept at room temperature for two weeks, the well resolved triple-triplet spectrum was observed, with the main triplet and substructure triplet having the splitting value of approximately 38 gauss, and 10 gauss respectively, as is shown in Fig. 3 (b). This spectrum can be ascribed to the cyclohexadienyl-type radical which was produced from the addition reaction of a hydrogen atom to either ortho or para position in the phenyl ring as described below.



Electron-beam irradiated single crystals of diphenylamine did not show any anisotropy of g -value, but gave the anisotropy of hfs as is shown in Fig. 4. Namely, it was found that the triple-triplet spectrum in Fig. 3 (b) changed depending on the angle between an axis of a sample and the magnetic field, the splitting value of substructures changing from 10 gauss of the triplet to 19 gauss of the doublet and the splitting value of the main triplet remaining unchanged. This anisotropy is probably due to the anisotropy of the hfs of the cyclohexadienyl-type radical, which has not been observed. Namely, this anisotropy of hfs could be supposed to be induced by the interaction of the unpaired electron with α -H in the cyclohexadienyl radical, although the crystal structure of diphenylamine has not been determined yet.

In the case of electron-beam irradiation, the single-line spectrum appearing in the case of UV-irradiation could hardly be observed. The broadening of ESR spectrum immediately after irradiation is probably responsible for the presence of a single-line spectrum other than the effect of the dipole-dipole broadening.

Comparison of Effects of UV and Electron-Beam Irradiations: UV-irradiation did not induce the addition reaction of a hydrogen atom to a phenyl ring in con-

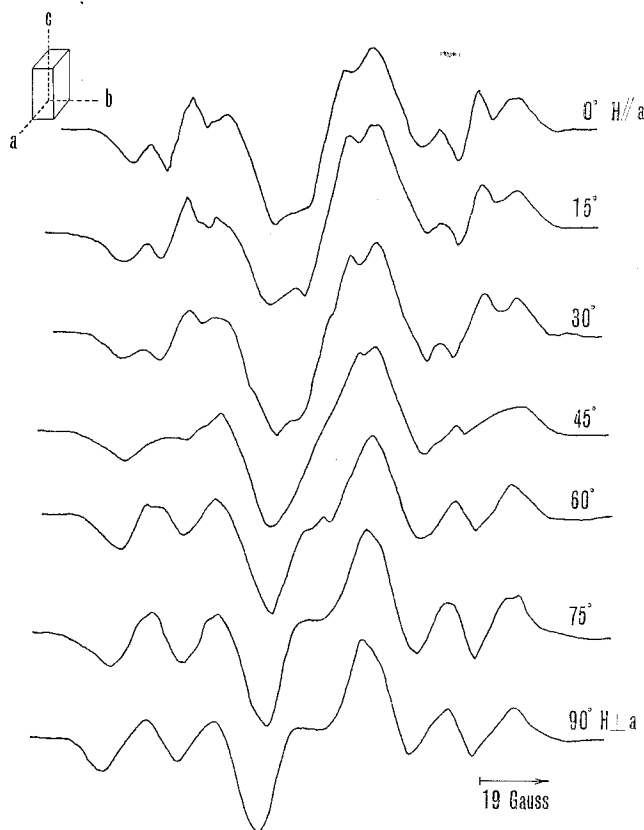


Fig. 4. The angular dependence of ESR spectrum from an electron-beam irradiated single crystal of diphenylamine. The sample was rotated at angular intervals of 15° along the c axis of the crystal represented.

trast with the case of electron-beam irradiation. This phenomenon has been observed similarly in the previous ESR study of benzene.³⁾ The impossibility of UV-irradiation to induce the addition reaction of a hydrogen atom may be interpreted in terms of the activation energy for the addition reaction, and the competition reaction of a hydrogen atom with both other radicals, including a hydrogen atom and intermediate radicals from diphenylamine, and a neutral diphenylamine. The activation energy for the addition reaction of a hydrogen atom has been evaluated to be approximately 10 kcal/mole. The thermal energy corresponding to kT at 77°K is found to be about 0.3 kcal/mole and might be insufficient for the hydrogen addition reaction. On the contrary, the electronbeam could provide the addition reaction with a sufficient thermal energy. The effects of UV-irradiation on solid substances may be restricted to a surface region, and radical species may be more adjacently distributed than those of electron-beam irradiation. Accordingly, it may be supposed that a hydrogen atom produced from the cleavage of C-H bonds is supplied more preferentially to the combination reaction with the other neighboring free hydrogen atoms than to the addition reaction to a phenyl ring.

To summarize the above experimental results, UV-irradiation of diphenylamine

Irradiation Effects on Diphenylamine

exhibited the single line spectrum with ΔH_{msl} of 20 gauss not showing any anisotropic effect and did not provide the evidence of the formation of the diphenylamine and the diphenylamine cation radical. Electron-beam irradiation of diphenylamine gave ESR spectra corresponding to the cyclohexadienyl-type radical, and the formation of the diphenylamino and the diphenylamine cation radical could hardly be recognized as in the case of UV-irradiation. UV-irradiation did not induce the addition reaction of a hydrogen atom to a phenyl ring.

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