BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3369—3372 (1969)

An ESR Study of Photochemical Intermediates from Rigid Organic Solvents Containing Benzene*[1]

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(Received March 10, 1969)

The present work was undertaken in order to examine a photochemical intermediate from benzene using rigid organic matrices: EPA (a mixture of E: diethyl ether, P: isopentane, and A: ethyl alcohol, 5 : 5 : 2, v/v), diethyl ether, and isopentane. The UV irradiation of EPA, diethyl ether, and ethyl alcohol at 77°K, in wavelength regions from approximately 2200Å to 2600Å, gave ESR spectra which can be ascribed to the ethyl and/or the ethanol radical, even when a solute was not added. On the contrary, the UV irradiation of isopentane under similar conditions did not show any ESR spectrum. However, the UV irradiation of isopentane containing benzene in concentration regions from 10^{-1} to 10^{-2} M gave two kinds of ESR spectra, ascribed to phenyl and *tert*-pentyl radicals. This reaction may be interpreted as a sensitized photodecomposition brought about by an excitation and/or a photolytic degradation of benzene.

In previous papers,[1,2] we reported a study of photochemical intermediates from benzene in the solid state and in an adsorption state on silica gel using the electron spin resonance technique. Migirdicyan[3] reported the sensitized photodecomposition of a methylcyclohexane rigid matrix by the addition of benzene, but they did not observe a spectrum arising from benzene.

In the present work, we attempted to examine a photochemical intermediate from benzene using rigid organic matrices of EPA, diethyl ether, ethyl alcohol, and isopentane, which have been used for the study of photochemical intermediates by electronic spectroscopy since the pioneering work by Lewis and Lipkin.[4] From the present experiments, it was found that the rigid matrices of EPA, diethyl ether, and ethyl alcohol not containing benzene were decomposed by UV irradiation in the wavelength regions longer than approximately 2200Å, and that one could not observe a photochemical intermediate from benzene because of the superposition of spectra arising from the solvents. On the other hand, it was confirmed that the UV-irradiated isopentane matrix gave no ESR signal, and that, when benzene was added to isopentane, the photodecomposition of its "isopentane-benzene mixture" was induced to exhibit ESR spectra attributable to phenyl and *tert*-pentyl radicals. This phenomenon can be interpreted as being an example of the sensitized photodecomposition of isopentane, accompanied by the photodegradation of benzene.

Experimental

Materials. An EPA (E: diethyl ether, P: isopentane, A: ethyl alcohol) solvent was prepared in the mixing ratio of 5 : 5 : 2 v/v. The diethyl ether was Nakarai Chemicals' pure grade; it was dried over calcium chloride in a nitrogen atmosphere and then passed through an activated alumina column. Isopentane from Nakarai Chemical Co., Ltd., Kyoto, was distilled in the presence of metallic sodium; no further purification was made. Ethyl alcohol (Special Grade) from the Nakarai Chemical Co., Ltd., was purified by the following procedure; it was distilled in the presence of sulfuric acid, and then its distillate was boiled for several hours in the presence of silver nitrate before further distillation. The distillate was distilled over calcium oxide and passed through a newly-activated silica gel column. The final purification was performed using a Widmer refining column. These solvents were purified immediately before use and were kept in the dark. The benzene was Merck's spectro-grade, which had been purified according to the method described in a previous paper.[2] The EPA, ethyl alcohol, and isopentane solutions containing benzene were prepared in the concentration regions from 10^{-1} to 10^{-4} M.

The solution was added to a 4-mm-i.d. quartz ampoule by the use of a syringe, and was degassed through repeated freezing and thawing on a vacuum line at the temperature of liquid nitrogen.

Irradiation. The UV irradiation was performed at the temperature of liquid nitrogen using either a Toshiba 400 W high-pressure mercury lamp or a low-pressure mercury lamp (germicidal lamp). In some

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*[1] This paper was read at the Symposium on Redoxidation in Nonaqueous Media sponsored by the Chemical Society of Japan, Kyoto, 1968.

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2) T. Tanei, *ibid.*, **41**, 833 (1968).

3) E. Migirdicyan, *J. Chim. Phys.*, **43**, 543 (1966).

4) G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 2801 (1942).

experiments, mainly in the case of a high-pressure mercury lamp, we used a UV filter, either Toshiba UV-25 or UV-D25. γ-Irradiation was carried out with Co-60 (750 Ci) at the temperature of liquid nitrogen.

ESR Measurements. The ESR spectra were recorded using a Varian V-4560 EPR spectrometer operating at X-band frequency and with a 100 kc/sec field modulation, over the temperature region from the temperature of liquid nitrogen to about 130° K. Temperature control was done by means of a Varian variable-temperature accessory.

Results and Discussion

The UV irradiation of the matrices of EPA, diethyl ether, and ethyl alcohol containing no benzene gave ESR signals which can be ascribed to ethyl and to ethanol radicals. This phenomenon made it impossible to observe the ESR spectra from benzene in these rigid solvents. Namely, the UV irradiation of both EPA, and diethyl ether rigid matrices containing no benzene showed a prominent four-line spectrum, with a splitting value of about 27 gauss and an intensity ratio of approximately 1 : 3 : 3 : 1 at 77°K, as is shown in Fig. 1(a) and Fig. 2(a). This spectrum was easily observed just after UV irradiation, but it completely disappeared within about 20 hr when the sample was kept at the temperature of liquid nitrogen.

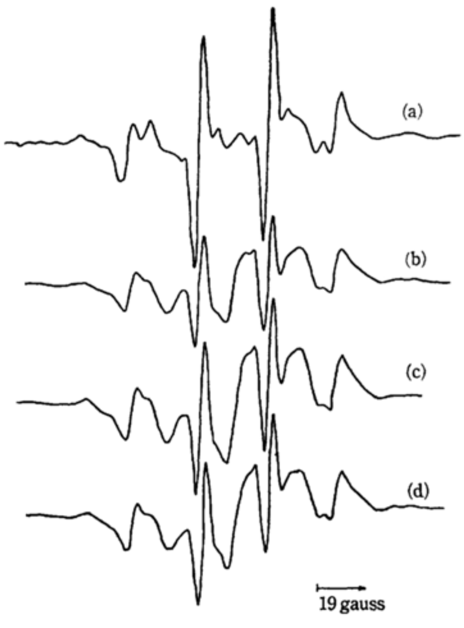

Fig. 1. ESR spectra from UV-irradiated EPA, and " EPA-Benzene " mixtures at 77°K. UV-Irradiation was performed for 15 min at liquid nitrogen temperature. Alphabetical marks correspond to the following samples: (a) EPA, (b) EPA containing benzene in the concentration of 1×10^{-4} M, (c) EPA containing benzene in 1×10^{-3} M, and (d) EPA containing benzene in 1×10^{-2} M.

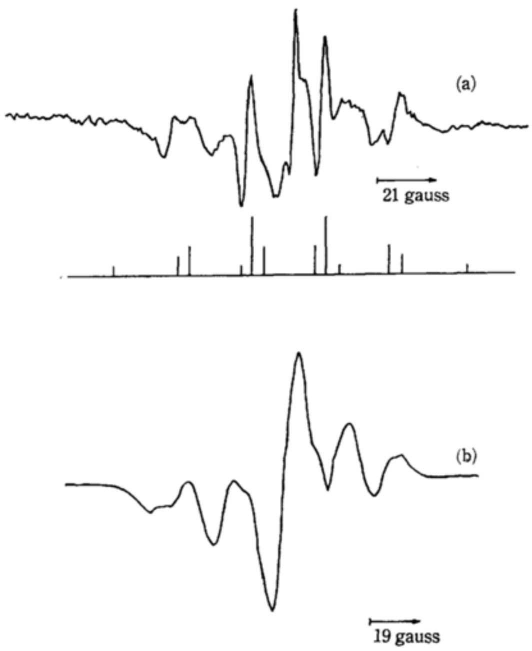

Fig. 2. (a) ESR spectrum from UV-irradiated diethyl ether at 77°K. UV-Irradiation was carried out at liquid nitrogen temperature for 15 min. The lines in the drawing below the spectrum represent the position and the intensity of the resonance lines expected for the radical ($CH_3\dot{C}H_2$). (b) ESR spectrum from UV-irradiated ethyl alcohol at 77°K. UV-Irradiation was performed at liquid nitrogen temperature for 15 min.

The present four-line spectrum can be ascribed to the ethyl radical,[5,6] which is theoretically expected to show four isotropic resonance lines in a reconstruction based on the two α-H with the coupling constant of 22 gauss, and the three β-H with the coupling constant of 27 gauss. The UV irradiation of ethyl alcohol gave a five-line spectrum with a splitting value of about 20 gauss. The five-line spectrum can be ascribed to the ethanol radical($CH_3\dot{C}HOH$) with the α-H coupling constant of 22 gauss and the β-H coupling constant of 27 gauss. The UV irradiation of an "EPA-benzene mixture," which contains benzene in the concentration regions from 10^{-1} to 10^{-4} M, produced ethyl radicals overlapping with ethanol radicals, as is shown in Fig. 1(b)—(d), but no photochemical intermediates from benzene could be observed.

Isopentane-Benzene Mixture. A prolonged irradiation (120 min) of the isopentane rigid matrix did not show any ESR signal, in contrast with the

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[5] Sr. Patricia, J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 159 (1964).

[6] H. S. Judeikis and S. Siegel, *J. Chem. Phys.*, **43**, 3625 (1965).

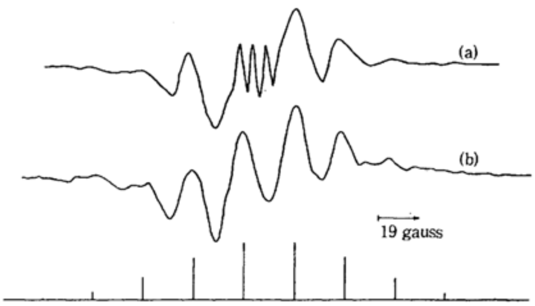

Fig. 3. ESR spectrum from UV-irradiated "isopentane-benzene mixtures," (a), and γ-irradiated "Isopentane," (b), at 77°K. The lines in the drawing below the spectrum represent the position and the intensity of the resonance lines expected for the radical $((CH_3)_2\dot{C}CH_2CH_3)$. UV-Irradiation was performed for 30 min at 77°K. γ-Irradiation was carried out at 77°K using Co-60 (750 Ci) under the following condition: dose rate of 6×10^5 r/hr, and total dose of 3×10^5 R.

cases of EPA, diethyl ether, and ethyl alcohol.

The UV irradiation of the "isopentane-benzene mixture," which contained benzene in the concentration region from 10^{-1} to 10^{-2} M, gave an apparent eight-line spectrum, with a splitting value of about 23 gauss, in addition to three other central lines with approximately a 6-gauss separation, as is shown in Fig. 3(a). On gradually raising the temperature of the above "isopentane-benzene mixture" from the temperature of liquid nitrogen up to about 113°K, the eight-line spectrum showed a rapid decay, and then the three central lines changed to a six-line spectrum with approximately a 6-gauss separation, as is shown in Fig. 4.

The apparent eight-line spectrum showed a very good accordance with the eight-line spectrum observed from γ-irradiated isopentane at 77°K, as is shown in Fig. 3(b). This eight-line spectrum seems to be coincident with that from γ-irradiated *t*-pentyl iodide which was previously reported by Ayscough and Thomson.[7] Accordingly, the apparent eight-line spectrum in the present "isopentane-benzene mixture" can be ascribed to the *t*-pentyl radical$((CH_3)_2\dot{C}CH_2CH_3)$, in which one estimates the hyperfine coupling constant of both six protons of two methyl groups and the one proton of the CH_2 group, and that of another proton of the CH_2 group, at 23 and 46 gauss respectively.

The six-line spectrum observed after the disappearance of *tert*-pentyl radicals is in complete accordance with that of the tentatively-assigned phenyl radical which was previously observed in UV-irradiated polycrystalline benzene at 77°K.[1] Furthermore, it was observed that phenyl radicals did not induce any abstraction reaction of hydrogen atoms from a surrounding isopentane mloecule. This fact seems to suggest that phenyl radicals remaining after the disappearance of *tert*-pentyl radicals may be trapped on the surface of the quartz ampoule. The present experiment failed to observe the formation of benzene cation radicals such as have already been observed upon the UV irradiation of both benzene adsorbed on silica gel[2] and that dispersed in an acidic matrix.[8] This is probably because the isopentane matrix could not provide a site suitable for trapping both benzene-ion radicals and electron ejected from benzene.

An Aspect of the Mechanism of the Photodecomposition of Isopentane. From the above-described experiments, it is evident that the presence of benzene is responsible for the photodecomposition of isopentane. The photolysis of isopentane can be explained in terms of the energy transfer from an excited benzene ($^3B_{1u}$) to isopentane molecules, while one may also suppose the possibility of the photodecomposition of benzene dispersed in the isopentane matrix bringing about the abstraction reaction of hydrogen atoms from the surrounding isopentane molecules. On analogy with the behavior of benzene in the isopentane matrix, one may suppose that the photodegradation of rigid matrices of diethyl ether and ethyl alcohol is induced through an energy transfer from aromatic impurities unremoved by the present purification.

From the above experimental results, we may conclude that: (1) EPA, diethyl ether, and ethyl alcohol are not inert to UV light in the wavelength regions longer than approximately 2200Å, probably because of the presence of unremoved aromatic impurity, and this leads to the failure to observe intermediates from benzene, and (2) isopentane is inert to UV light in the wavelength regions

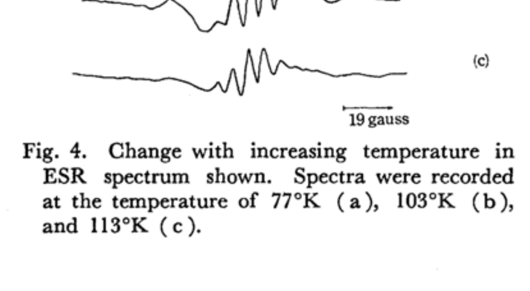

Fig. 4. Change with increasing temperature in ESR spectrum shown. Spectra were recorded at the temperature of 77°K (a), 103°K (b), and 113°K (c).

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[7] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

[8] M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47** 292 (1967).

longer than approximately 2200Å. The UV irradiation of the "isopentane-benzene mixture" induced the sensitized photodecomposition of isopentane and produced phenyl radicals, and *tert*-pentyl radicals from benzene and isopentane respectively.