Paramagnetic Resonance of Radicals of Some Aromatic Vinyl Compounds. I

By Kazuo MORIGAGI, Keiji KUWATA and Kozo HIROTA

(Received January 20, 1960)

Free radicals produced by the reaction of aromatic hydrocarbons with alkali metals have been investigated by the paramagnetic resonance method for several years by Weissman[1] and others. Usually the paramagnetic resonance spectra of these radicals consist of many lines which are coming from the hyperfine interaction of the unpaired electron with protons in these radicals. We have observed the paramagnetic resonance of radicals. We have obtained from the following aromatic vinyl compounds: styrene, α-methyl styrene, p-methyl styrene, 1, 1-diphenylethylene, stilbene and 1, 4-diphenylbutadiene. A part of the experimental results has been already reported briefly[2]. The paramagnetic resonance of the above radicals, except that of stilbene, shows many absorption lines, which are attributed to the hyperfine structure arising from the hyperfine interaction of the unpaired electron with protons in the radicals.

The results obtained by the analysis of these spectra contribute not only to the determination of the unpaired electron density in the radicals, but also give some information about the mechanism of polymerization of these aromatic hydrocarbons, because some of the above compounds polymerize easily by the reaction with monomer, turning into so called "living polymers".

The experimental results and discussion in the case of styrene, α-methyl styrene and p-methyl styrene will de described in the present paper, and the forthcoming paper will describe the results in the case of 1, 1-diphenyl-ethylene, stilbene and 1, 4-diphenylbutadiene.

Experimental

1) Paramagnetic Resonance Spectrometer and Experimental arrangement.—The measurements of paramagnetic resonance of the above radicals were performed at room temperature, except that of styrene radicals which were measured at about −100°C and −40°C besides room temperature. The spectrometer used for the paramagnetic resonance measurements was a transmission type operating at 9300 Mc. The rectangular cavity, which has a

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[1] S. I. Weissman, T. R. Tuttle, Jr. and E. De Boer, *J. Phys. Chem.*, **61**, 28 (1957); T. R. Tuttle, Jr., R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

[2] K. Hirota, K. Kuwata and K. Morigaki, This Bulletin, 31, 538 (1958); **32**, 100 (1959).

hole at the half-point of the narrow side, was excited at the mode of TE_{012}. The sample, being enclosed in a glass tube, was put into the cavity through the hole. By modulating the applied magnetic field at the frequency of 315 c/s, the resonance signal was detected with a phase sensitive detector, and was recorded on a milliampere recorder. The cavity system and the Dewar arrangement for measurement at low temperatures were designed as shown in Fig. 1. The sample enclosed in a small glass-tube was attached with some cement to the end-plane of the inner glass tube of the Dewar inserted into the cavity. The temperature at the position of the sample was measured by a copper-constantan thermocouple, which indicated a temperature of −100°C or −40°C when liquid nitrogen or methanol mixed with dry-ice was filled in the Dewar, respectively, As the outer part of the Dewar was jointed on a copper-head standing out of the cavity on its narrow side, removal of the entire assembly from the cavity for cleaning or using the cavity for measurements at room temperature was done easily. The space between the inner and outer parts of the Dewar and the inside part of the cavity were pumped out to get vacuum by closing the waveguide with thin mica foils in front of and behind the cavity.

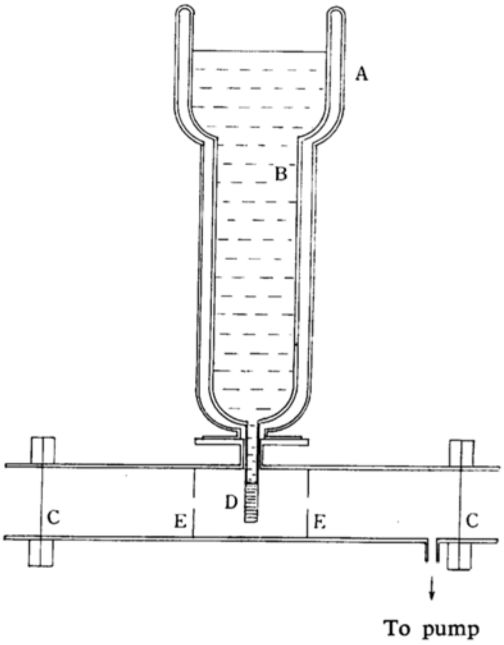

Fig. 1. Cryostat and cavity assembly

(A)	Glass Dewar	(D)	Sample
(B)	Liquid nitrogen	(E)	Iris
(C)	Mica		

2) Preparation of Samples.—The samples used in our experiment were prepared by two ways. One of them may be called the method I, while the other the method II. The latter will be described in details. As shown in Fig. 2, the apparatus for preparing the samples consists of several reaction vessels, all of which can be kept at high vacuum. The samples were prepared using this apparatus as follows. Connecting the entire vessel to the vacuum system, water and oxygen adsorbed on the wall of the glass vessels were excluded by heating and discharging the tube with a tesla coil. The sodium metal contained inside the glass vessel A was distilled into the reaction vessel B under reduced pressure, and the vessel A was sealed off from the system at the part "a". Then the aromatice hydrocarbons and toluene contained in the vessel were distilled into the vessel B under reduced pressure, and the vessels B, D, E and G were taken off from the vacuum system at the part of "b". The reaction vessel B was kept at about 100°C for a long time, in order to change the high-polymerized adduct of the aromatic hydrocarbon, formed inside the reaction vessel B before the heat-treatment, to a low-polymerized one. After the precipitate* inside the reaction vessel B was separated from the solvent, was transfered into the vessel E and was distilled under reduced pressure through the breakable joint, the precipitate was dissolved into the tetrahydrofuran or dioxane which was stored in the vessel G through the breakable joint F. Tetrahydrofuran and dioxane were used here as the solvent in which paramagnetic free radicals were contained as a diluted state. For the measurement of paramagnetic resonance the sample thus prepared was used in the glass tube D, the end part of which was inserted into the cavity. The method II described above was applied to the production of radicals of styrene, α-methyl styrene, p-methyl styrene and 1, 1-diphenylethylene.

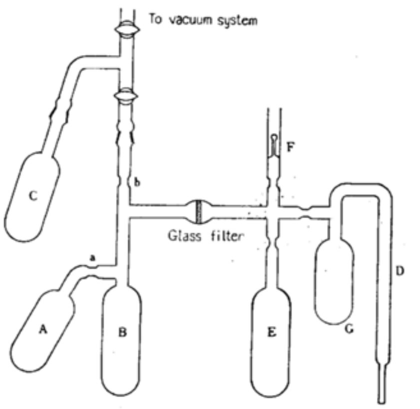

Fig. 2. Apparatus for preparation of sample.

In the method I the aromatic hydrocarbon whose radical was to be produced was reacted directly with sodium metal in tetrahydrofuran or dioxane in a way similar to that of the method II without using toluene. The radicals of styrene, α-methylstyrene, p-methylstyrene, 1, 1-diphenylethylene, stilbene, 1, 4-diphenylbutadiene and isoprene** could be produced by this method.

Determining the concentration of sodium ion in

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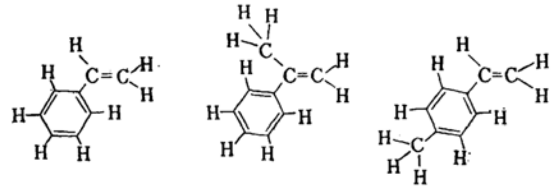
* A strong paramagnetic resonance line was observed in the precipitate of the sodium adducts of styrene. The line width and g-factor were about 2 gauss and 2.002 respectively, and the line shape was Lorentzian.

** Reported briefly: K. Kuwata, K. Morigaki and K. Hirota, This Bulletin, 32, 895 (1959).

sample of styrene by flame spectroscopy, the ratio of radical part to an ionic part was estimated. It was of the order of one tenth. All measurements were carried out in the concentration range of about 10^{-3} to 10^{-4} spin per liter.

In the preparation of radicals described above precautions are taken against contamination of the reaction vessel used, because a trace of water and oxygen, if left in the vessel, may react easily with the adduct of the aromatic hydrocarbon and make the concentration of radicals decrease. Purification of aromatic hydrocarbons, sodium metal and solvents was performed in the following way. The aromatic hydrocarbons purified by the usual method were put in contact with sodium metal so as to remove the remaining water and were purified by vaccum distillation. The solvent purified in the usual way was reacted with stilbene anions or naphthalene anions by utilizing the reactive properties of these anions with the water and oxygen, and then the stilbene or the naphthalene was removed from the solvent by distillation. Naphthalene was used only in the preparation of the first samples of styrene radical. In the other samples, stilbene was used in most cases including the preparation of the styrene radical, because the stilbene anion gave no more than a broad resonance line without any structure even if it remained in the solvent.



Styrene α-Methyl styrene *p*-Methyl styrene

Fig. 3

Results and Discussion

Styrene.—We have observed three kinds of paramagnetic resonance spectra in the styrene radical*. They were i) four lines, ii) nine lines and iii) many complex lines respectively.

i) Four lines.—The four-lines spectrum has been observed in many samples of dilute solution of the styrene adduct with sodium metal, when the solvent is tetrahydrofuran or dioxane. Even if either solvent is used and potassium metal is used in place of sodium metal, almost identical spectra of four lines were given. The above samples were prepared by the methods I and II described in the section 2. The spectrum consists of almost equally spaced four lines of which the intensities of each components are 1 : 3.2 : 3.3 : 1.2 in ratio in order of the strength of the magnetic field corresponding to the resonance lines. From the above results the hyperfine splitting is considered to arise from the hyperfine interaction between the unpaired electron and three equivalent protons. The hyperfine splitting is 4.3 ± 0.5 gauss and the *g*-factor is 2.0031 ± 0.0006.

The line-shape of each components is almost Gaussian with the half-width of about 3.9 gauss as shown in Fig. 5 (**B**).

The spectra observed at low temperatures, −40°C and −100°C, were almost identical with those observed at room temperature. From these results the width of each component is attributed to the unresolved hyperfine interaction with protons.

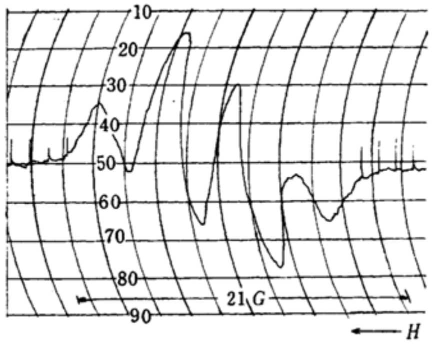


Fig. 4. Paramagnetic resonance spectrum of styrene radical.

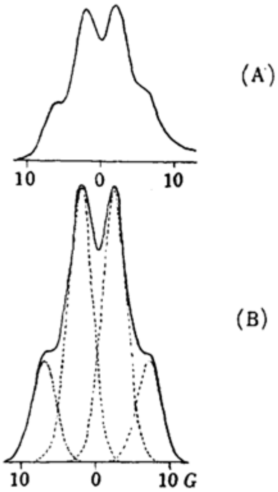


Fig. 5. Paramagnetic resonance spectra of styrene radical.

(**A**) The observed spectrum obtained by numerical integration.

(**B**) The calculated spectrum constructed from four Gaussian shaped lines with relative intensities of 1 : 3 : 3 : 1.

Three equivalent protons contributing to the

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* Besides the three kinds of spectra, the other spectrum similar to that of the naphthalene anion was observed in the styrene radical in the tetrahydrofuran solution prepared by the methods I and II with sodium metal at the first stage of our experiment, which has been already reported briefly[2]. As it has not been reproducible, it will not be described here.

hyperfine splitting and some protons constructing the line-width of each components have not been able to be given a definite correspondence to the protons of the styrene anion.

ii) Nine lines.—The spectrum consisting of equally spaced nine lines has been observed in the styrene radical in the tetrahydrofuran solution prepared by the method I with sodium metal. The spacing between each components was 2.2±0.2 gauss.

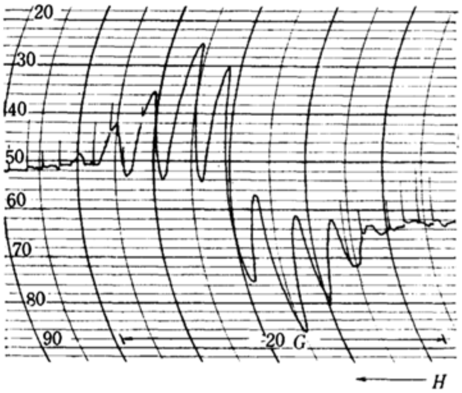

Fig. 6. Paramagnetic resonance spectrum of styrene radical

iii) Many complex lines.—The complex spectrum has been observed in the styrene radical in the tetrahydrofuran solution prepared by the method I with sodium metal. The spectrum extends to the length of 24±3 gauss on the scale of the magnetic field. The g-factor is 2.0028±0.0005.

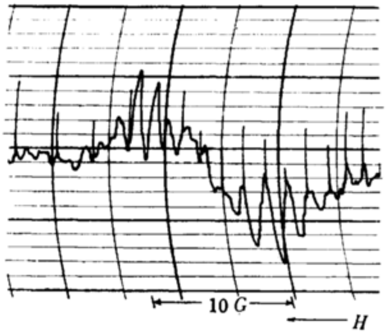

Fig. 7. Paramagnetic resonance spectrum of styrene radical.

The relation among the above three spectra on the point of the preparation of the styrene radical and the magnetic centers corresponding to the spectra have not been found in the present stage, so further experiments will be required to obtain some information about this problem.

On the other hand, we tried to observe the paramagnetic resonance of the styrene radical formed on the film of the vaporized sodium metal, but it gave a negative result*.

α-Methylstyrene.—We have observed the paramagnetic resonance spectrum, as shown in Fig. 8, of the α-methylstyrene radical in the tetrahydrofuran solution prepared by the method I with sodium metal. This spectrum extends to the length of about 32 gauss on the scale of the magnetic field. It may be explained by assuming that the hyperfine splitting is mainly attributed to the hyperfine interaction with three equivalent protons and another two equivalent protons with the coupling constant of 4.2 gauss and 2.5 gauss respectively and some protons contribute to construct the line shape of each components. If the magnetic center corresponding to the above spectrum is assumed to be the unpaired electron being localized on the α-methylstyrene anion, the following assignment might be reasonable on the basis of the unpaired electron density calculated by using the simple LCAO-MO theory: the three equivalent protons and two equivalent protons in the above analysis correspond to the *ortho*, *para*-protons and β-protons respectively, and the *meta*-protons

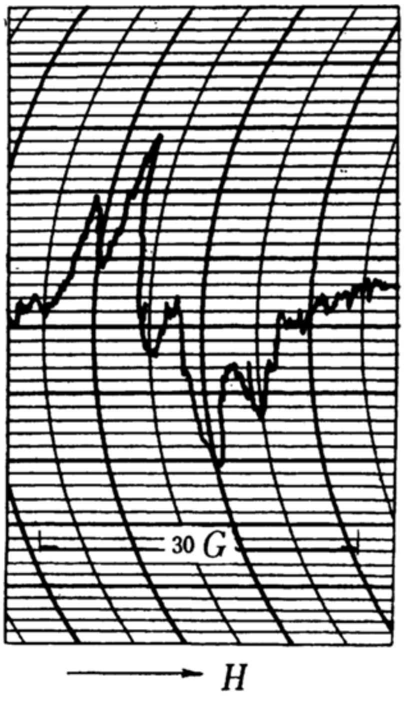

Fig. 8. Paramagnetic resonance spectrum of α-methylstyrene radical.

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* It might be necessary to refer to the Weissman's answer in discussion [*J. Phys. Chem.*, 57, 507 (1953)], that "the paramagnetic resonance absorption in styrene as it is undergoing polymerization initiated by metallic sodium is not reproducible".

and the protons belonging to the methyl-group construct the line width of each components. The simple LCAO-MO calculation gives the following unpaired electron densities on the carbon atom of *ortho*, *meta*, *para*, H_3 and β positions respectively.

$$\rho_o=0.091,\quad \rho_m=0.016,\quad \rho_p=0.149,$$
$$\rho_{H_3}=0.026,\quad \rho_\beta=0.355.$$

***p*-Methylstyrene.**—The observed spectrum of the *p*-methylstyrene radical is shown in Fig. 9. This sample consists of *p*-methylstyrene and *ortho*-methylstyrene with concentration of 60% and 40% respectively. This situation complicates the spectrum. Besides, the proton of the methyl group seems to contribute to the observed spectrum much more than in the case of the α-methylstyrene radical. We have not been able to analyze the observed spectrum.

A few months later than the time of preparation of the samples during which the sample was kept at room temperature, the spectrum became simpler and weaker than that observed immediately after the preparation of the samples. This changes of the spectrum is shown in Fig. 10. No change of the color and viscosity accompained with that of the spectrum were observed. The hyperfine structure of the spectrum exists in the region of the length of about 25 (±5) gauss on the scale of the magnetic field. After this change, the samples always showed the same patterns of the spectrum as the above one, but the intensity of the resonance lines has decreased gradually with time.

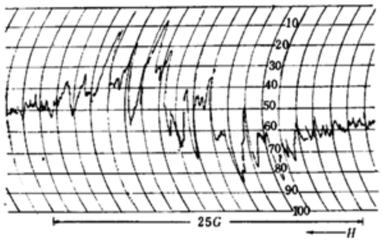


Fig. 9. Paramagnetic resonance spectrum of *p*-methylstyrene radical.

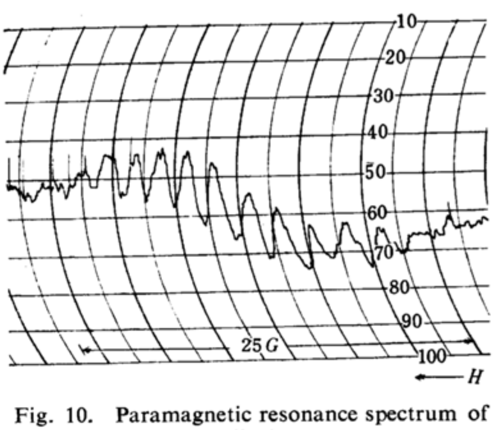
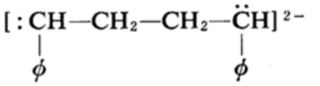


Fig. 10. Paramagnetic resonance spectrum of *p*-methylstyrene radical

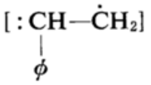
Reaction of the Aromatic Hydrocarbons with Alkali Metals

As described briefly in the section 1, the aromatic vinyl compounds, especially styrene, are initiated to polymerize with alkali metal. This property of styrene adducts with sodium metal as chain initiators was found independently by Szwarc et al.[3] and by Meshitsuka et al.[4] When the monomers of styrene exist in some suitable solvents (toluene, tetrahydrofuran, dioxane etc.), polymerization of them proceeds under existence of the adducts which produce the living polymer. The styrene adducts similar to that in the above case are produced by Scott's method in which naphthalene anions are used as a substitute of alkali metal. In this case, according to Szwarc, the living polymers consist of the dimerized styrene anions with both ends "living",

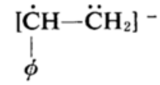


$$[:\underset{\phi}{\underset{|}{CH}}-CH_2-CH_2-\underset{\phi}{\underset{|}{\ddot{C}H}}]^{2-}\quad (\phi=C_6H_5)$$

which is formed by dimerization of univalent monomer anions



$$[:\underset{\phi}{\underset{|}{CH}}-\dot{C}H_2]\quad \text{or}$$



$$[\underset{\phi}{\underset{|}{\dot{C}H}}-\ddot{C}H_2]^-$$

being produced through the following process of electron transfer,

$$\text{naphthalene}^- + \text{styrene}$$
$$\rightarrow \text{naphtharene} + \text{stylene}^-$$

The above situation in the case of polymerization of styrene initiated by the styrene adduct formed through electron transfer which takes place between naphthalene anions and the monomers of styrene will be applied to our cases in which the styrene adducts with sodium metal form the living polymers. Then, the existence of the radical anions will not be detected because dimerization of univalent monomer anions is performed in a very short time in the above process.

On the other hand, two of the present authors found that if the styrene adduct with a high degree of polymerization formed at the first stage of the reaction of styrene with sodium metal reacts with sodium metal still

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[3] M. Szwarc, M. Levy and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1958); M. Szwarc, *Nature*, **178**, 1168 (1956).

[4] G. Meshitsuka and Y. Okada, *Chem. High Polymers* (*Tokyo*), (*Kobunshi Kagaku*) 14, 33, 37, 123 (1957).

more, the dark red precipitates are formed in the solution of toluene as a result of dissociation of the styrene polymer. These precipitates showed a strong paramagnetic resonance line, of which the line width and g-factor were about 2 gauss and 2.002 and the line shape was Lorentzian, and when they were diluted into the tetrahydrofuran, the hyperfine splitting in the paramagnetic resonance spectra was observed as described in the former sections. These spectra were attributed to be coming from monomer anions of styrene or polymer radicals with the low degree of polymerization.

The observations of the paramagnetic resonance of radicals of the aromatic vinyl compounds may be considered to become possible for the following reasons. Under non-existence of the monomer of aromatic vinyl compounds radical anions will exist stably in the polar solvents*, as tetrahydrofuran and dioxane, because they are electrically repulsed by each other in the polar solvent to be obstructed to dimerize.

In the case of the radicals with a high degree of polymerization, it will be difficult to observe their paramagnetic resonance owing to the following two reasons; one of the reasons is that the concentration of radicals in the solution becomes small, and the other is that the motion of such radicals becomes slower than that of monomer radicals or radicals with a low degree of polymerization to extend the line-width of each components of the hyperfine structure by contribution of the anisotropic hyperfine interaction of the unpaired electron with the protons. Indeed, no paramagnetic resonance of the radicals of a highly polymerized styrene diluted in the tetrahydrofuran was observed and the intensity of the resonance lines which were observed in most of the other samples of the aromatic vinyl compounds, described in the present paper, decreased gradually with time in accordance with the progress of polymerization. In some cases the change of patterns of the paramagnetic resonance spectrum was accompanied by decrease of intensity. As an example of such a change of spectrum we can see clearly the tendency in the case of p-methylstyrene as described in the section 3.

In the forthcoming paper, which will describe the results of the paramagnetic resonance of radicals of 1, 1-diphenylethylene, stilbene and 1, 4-diphenylbutadiene, a formulation which describes the process of polymerization will be presented.

Summary

Paramagnetic resonance of radicals of the aromatic vinyl compounds in the tetrahydrofuran and dioxane solutions was observed: styrene, α-methyl styrene and p-methyl styrene. By analyzing the observed spectra the structure of the radicals is discussed. From these results it may be concluded that the reaction of the aromtic vinyl compounds with alkali metal proceeds through two steps; formation of their radical anions, and successive addition of the monomers to this radical anion turning into " living polymers ".

The authors wish to express their sincere thanks to Professor Junkichi Itoh of Osaka University for his continuous encouragement and his helpful discussions throughout this work.

Physics Department (K. M.)
Chemistry Department
(K. K. and K. H.)
Osaka University
Nakanoshima, Osaka

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* We could not observe paramagnetic resonance of the styrene radicals diluted in the solution of toluene which was a non-polar solvent.