*On the Nature of the Red Adduct of Styrene with Sodium**

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As shown independently by Szwarc et al.[1] and by Meshitsuka and Okada[2], the red complexes or adducts formed between styrene and sodium have an interesting property as chain initiators; i. e., in some suitable solvents, the adducts produce living polymers which can grow when a monomer is added. According to Szwarc, the living polymers result from the dimerized styrene anions with both ends "living":

$$\text{(A)}\quad (:\text{CHX—CH}_2\text{—CH}_2\text{—CHX}:)^{=}$$
$$(\text{X}=\text{C}_6\text{H}_5)$$

this bivalent anion is formed by dimerization of univalent monomer anions,

$$(\text{A}')\quad (:\text{CHX—CH}_2\cdot)^{-}\quad \text{or}$$
$$(\text{A}'')\quad (\cdot\text{CHX—CH}_2:)^{-}$$

which are produced by the electron transfer process from naphthalene anions:

$$\text{Naphthalene}^{-}+\text{Styrene}\rightarrow \text{Naphthalene}+\text{Styrene}^{-}. \qquad (1)$$

However, the proposed formula A as the initiator of the chain polymerization seems to lack firm experimental evidences.

Recently[3] two of the present authors found that there exist two other modifications in styrene adducts, blue and yellow, besides the familiar red one. Comparing the absorption spectra of these adducts with those of α-methylstyrene and *p*-divinylbenzene, not only as a dissolved state but also as a filmy state, they reached some conclusions as to the nature of styrene adducts. The adducts which were used in the research mentioned above were, however, slightly different from those of Szwarc et al. in two points; (a) the adducts** are prepared directly from styrene and metallic sodium immersed in solvents, and (b) the solvents may be non-polar ones, e. g., benzene and toluene as well as polar solvents hitherto reported (dimethylether, tetrahydrofuran, etc.).

In the above paper it is one of the conclusions that the adducts, which dissociate into sodium ions and such anions as shown by the structure A′ or A″, constitute one of the stable red adducts whose absorption maximum is 510 mμ as reported already[2]. It is the object of the present paper to reinforce the conclusion further with the paramagnetic resonance absorption measurement.

Experimental Method

Samples.—The apparatus, as shown in Fig. 1, is used to prepare most of the samples. The details of the operations will be omitted, as it has already been described[4]. Thus it was made possible generally to produce the pure adduct of aromatic hydrocarbons, e. g., styrene which was used in the present paper.

Measurement of the Paramagnetic Resonance Absorption. — The conventional apparatus which was constructed by Professor J. Itoh of Osaka University was used. The details of the measurement will be published elsewhere.

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* The third report of "The research on the adduct of styrene with alkali metals": I., ref. 4, II., ref. 3.

[1] M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*. **78**, 2656 (1956); M. Szwarc, *Nature*, **178**, 1168 (1956), etc.

[2] G. Meshitsuka and Y. Okada, *Chemistry of High Polymers*, (*Kobunshikagaku*), **14**, 33, 37, 123 (1957).

[3] K. Hirota, K. Kuwata, H. Togawa and S. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 602 (1958).

** According to the present method, the sample is free from other substance, when compared with the samples prepared indirectly by the electron transfer method, such as by Eq. 1.

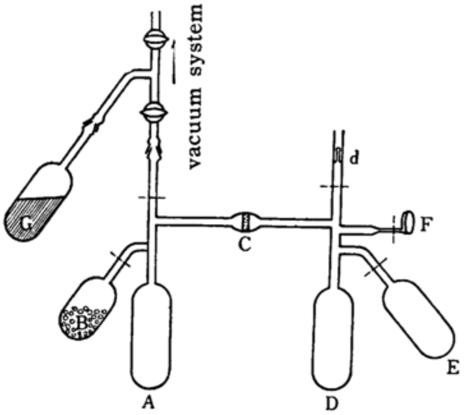

Fig. 1. Apparatus for preparation of samples
A: Reaction vessel, B: Sodium which will be vacuum-distilled into A, C: Glass filter, D: Storage vessel, E: Vessel for waste product, F: Sample cell for P. S. R. measurements, G: Styrene or toluene which will be vacuum-distilled into A, d: Breakable joint.

Results and Discussion

In the previous report[3], the structure A′ or A′′ was assigned to the red adduct of styrene rather than the Szwarc's structure A from the results of absorption spectrometry. Now there will be another method of decision of this problem. Because there exists an unpaired electron in the structure A′ or A′′, the paramagnetic resonance absorption may be observed if it is true, while the absorption will not be observed if the structure A is true. The measurement carried out at 9400 mc by the present writers in tetrahydrofuran solution at the concentration of 10^{-2} molar could confirm the above presumption*. One of the absorption curves is shown in Fig. 2. The Szwarc's structure A, therefore, will not be justified. In sharp contrast with naphthalene anion having seventeen or twenty-three hyperfine splitting[5], the hyperfine structure of the styrene anions seemed to consist of two lines with small intervals, but the decision which is more probable of the two structures, A′ or A′′, could not be reached owing to the poor sensitivity of the apparatus. As the problem is very important in structural chemistry, further research is going on with an improved apparatus**.

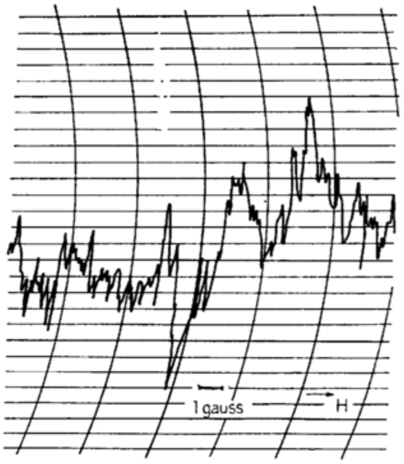

Fig. 2. Paramagnetic Resonance Absorption curve.

Summary

Paramagnetic resonance absorption could be observed on the solution of the pure red adduct, which was prepared according to the method reported by the present writers. The adduct, therefore, produces a radical anion consisting of odd electrons by dissociation. The proposition on the structure of the red adduct in the previous report was thus confirmed.

The writers express sincere thanks to Professor Junkichi Itoh of Osaka University who made the measurement of the paramagnetic resonance absorption possible.

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[4] K. Hirota and K. Kuwata, ibid., **78**, 1421 (1957).

[5] T. R. Tuttle, Jr., R. L. Ward, and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956), (17 splitting). S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

[6] D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

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

** Moreover the absorption may occur owing to the interaction with the proton at para-position, but such a probability will be neglected owing to the reactivity of that position.

Note added in proof: It is found that much more hyperfine structure lines can be observed in the samples made under different experimental conditions.

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