ESR Studies of the Reactions of Triphenylamine with Alkali Metals

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In secent years, many organic radicals have been prepared by reactions of the conjugated compounds with alkali metals in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and in solvents with similar properties.1) Most of these radicals have been shown to be anion radicals formed by the transfer of an electron from the alkali metals to the conjugated compounds, and ESR studies of these radicals have yielded much interesting information about these molecules.

This work was undertaken to study the reactions of triphenylamine with alkali metals in DME and THF by ESR techniques. It has been found that the reactions are not simple one-electron reductions but that they proceed through the cleavage of C-N bonds and the subsequent recombination to yield a biphenyl anion radical as one of the reaction products.

Experimental and Results

The reactions of triphenylamine with alkali metals (lithum, sodium and potassium) were undertaken in THF or DME as a solvent in vacuo. The reactions at −70°C and at room temperature gave the same results. It was observed that, if a solution of triphenylamine in THF or DME was allowed to contact with an alkali metal, a deep green solution was obtained, a solution which exhibited an ESR absorption as is shown in Fig. 1. The measurements of ESR spectra were carried out with a Hitachi X-band ESR spectrometer, model MPU-3B, employing a field modulation at a frequency of 100 kc./s.

The spectrum can be explained by the couplings with three sets of equivalent protons, via., the coupling with two equivalent protons with the coupling constant of 5.33 gauss, four equivalent protons which have half the coupling of the former, and four equivalent protons with a smaller coupling constant, 0.43 gauss. Namely, the hyperfine structure can be interpreted as arising from the protons of two benzene rings, and no structures resulting from a nitrogen nucleus and the remaining five protons are evident. Recently, Hanna2) has

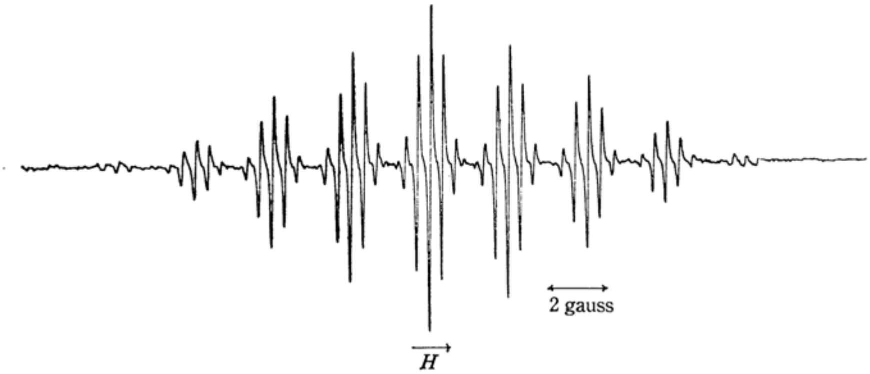

Fig. 1. ESR spectrum of the reaction product of triphenylamine with potassium in DME.

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1) A. Carrington, *Quart. Revs.*, **17**, 67 (1963).

2) M. W. Hanna, *J. Chem. Phys.*, **37**, 685 (1962).

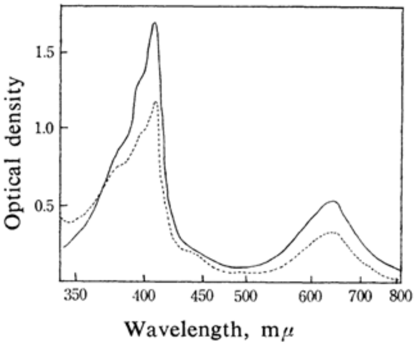

Fig. 2. Electronic absorption spectra of the reaction product of triphenylamine with potassium (----) and biphenyl anion radical (——) in THF.

reported that the odd-electron distribution in the triphenylphosphine anion is restricted to one benzene ring, and that the ESR spectrum can be interpreted by assuming the couplings with a phosphine nucleus and only four protons. He attributed this to the Jahn-Teller distortion. In the case of triphenylamine, because of its threefold symmetry, its anion radical was expected to be subjected to the Jahn-Teller distorsion. However, the ESR spectrum of the radical formed from triphenylamine agrees well with that of the biphenyl anion radical already reported by Carrington et al.[3)]

We also observed the electronic absorption spectrum of the product formed upon the reaction of triphenylamine with potassium and that of the biphenyl anion radical obtained by the reduction with potassium using THF as a solvent. As Fig. 2 shows, the two spectra resemble each other very closely except that the spectrum of the reaction product triphenylamine exhibits an additional absorption at 430 mμ.

Gilman et al.[4)] have reported that triphenylamine is cleaved by lithium at reflux in THF to yield, upon carbonation, diphenylamine in a low yield. However, from the agreement of the ESR and the electronic absorption spectra of triphenylamine with those of the biphenyl anion radical, it seems most reasonable to conclude that the radical formed on the reactions of triphenylamine with alkali metals under our experimental conditions was the biphenyl anion radical, though the mechanism of the reactions is unknown to us at the present time. The additional absorption band at 430 mμ of the reaction product of triphenylamine must be due to some other species.

Also, in the case of tri-*p*-tolylamine, the radical formed on the reactions with alkali metlas was the anion radical of the biphenyl derivative, the p,p'-bitolyl anion radical; its ESR spectrum, which is shown in Fig. 3, was identical with that of the p,p'-bitolyl anion radical previously reported by Ishizu.[5)]

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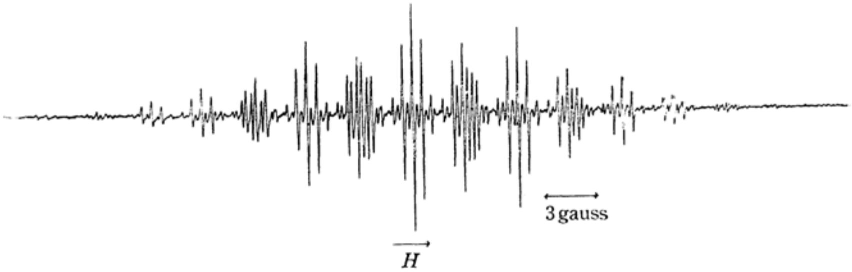

Fig. 3. ESR spectrum of the reaction product of tri-*p*-tolylamine with potassium in DME.

[3)] A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, 5, 21 (1962).

[4)] H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **80**, 380 (1958).

[5)] K. Ishizu, This Bulletin, 36, 938 (1963).