SHORT COMMUNICATIONS

*Stable Radicals of a High Molecular Weight Produced by Oxidizing Diphenylamine with Vanadium Pentoxide**

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In a previous report[1] we reported obtaining an absorbed radical very stable, even in air, by oxidizing diphenylamine at 150°C with vanadium pentoxide; we considered this radical to be $(C_6H_5)_2NO\cdot$, because the ESR signal measured at $g=2.0$ showed a hyperfine structure consisting of a triplet.

The absorbates extracted with carbon disulfide and/or benzene were brown and also showed an ESR signal at $g=2.0$, which had a hyperfine structure consisting of a quintet and splitting equally (5 gauss). However, as Fig. 1 shows, this spectrum is different from that of DPPH in solution, although is very similar to the spectra of DPPH in semifluid Duco cement[2]; moreover, the coupling constant of the nitrogen atom is smaller than that of DPPH and diphenyl nitric oxide. These findings suggest the production of a large radical, whose anisotropic hyperfine interaction with two nitrogen nuclei is involved. Therefore, some reaction seems to have occurred in or after the process of dissolution between the radicals adsorbed on the surface.

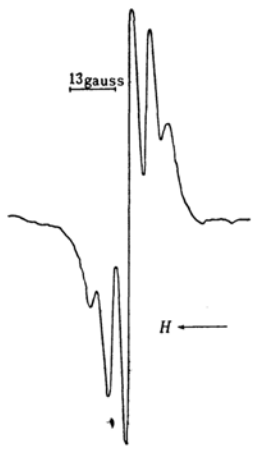

Fig. 1. The ESR spectrum of the products in carbon disulfide solution.

After purification, the solvent was evaporated. A dark brown powder then precipitated which also showed a sharp signal of the Lorentzian type ($\Delta H_{msl}=8$ gauss) at $g=2.0$; its intensity ($10^{19\sim20}$ spins/g.) did not change, even after heat treatment in air at 100°C for more than 300 hr. The cryoscopy in benzene showed the molecular weight to be between 600 and 3000. If the powder was left alone in the solution at 100°C, its molecular weight increased and it became insoluble in solvents. The elemental analysis of a sample (molecular weight: 600~700) showed the composition to be: C, 85.04; H, 5.66; N, 8.36% (total, 99.06%); calculated for $C_{48}H_{38}N_4$: C, 85.92; H, 5.71; N, 8.35%. Therefore, this substance has a composition which corresponds approximately to a condensed product of four diphenylamine molecules. Moreover, the ESR measurements show that one-tenth~one-hundredth of its total molecules are free radicals. The insoluble substance did not melt at 150°C, but slightly sintered at 200°C. It was semiconductive, because its specific resistance was 2.5×10^9 and 8×10^7 ohm·cm. at 20°C and 100°C respectively. The product showed infrared bands at 1270,** 820 and 3420 cm^{-1}, corresponding to ν_{C-N} of a tertiary nitrogen, δ_{C-H} of the hydrogen of a paradisubstituted benzene ring, and ν_{N-H} of the terminal hydrogen respectively.

* A part of this paper was presented at the ESR Meeting, Kyoto, November, 1963.

1) K. Hirota, Y. Kageyama and K. Kuwata, This Bulletin, 36, 875 (1963).

2) N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, 34, 1963 (1961).

** In our measurements, triphenylamine showed a strong band at 1270 cm^{-1} which did not appear in the spectrum of diphenylamine.

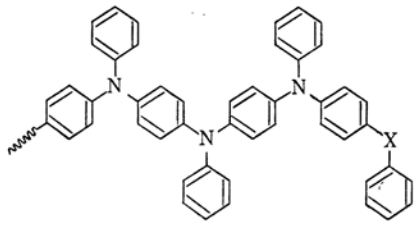

Fig. 2.

In short, the product includes stable radicals of a high molecular weight. Judging from the above discussion, the non-radical and radical structures of the product may be considered to be as shown in Fig. 2, N–H and N· respectively. However, as the radical species, another structure (X=NO·) is possible, for this structure is considered to be more stable.

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