The Oxygen Effect on Electronic Properties of α, α'-Diphenyl-β-picrylhydrazyl

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There is one unpaired electron in each molecule of α, α'-diphenyl-β-picrylhydrazyl. In the study of unpaired spin by means of the method of electron spin resonance (ESR), thereby, this free radical ($g=2.0036\pm0.0003$) is widely used as a standard for estimation of the spin population and also the g-value of the applied specimen. However, it has been already known that the ESR absorption spectrum of free radical changes strongly under the influence

TABLE I. THE ELECTRON SPIN RESONANCE ABSORPTION DATA OF D.P.P.H.

Sample	D.P.P.H.-Single			D.P.P.H.-Free			D.P.P.H.-Ether		
	ΔH_{msl}[1]	ΔH[2]	I[3]	ΔH_{msl}	ΔH	I	ΔH_{msl}	ΔH	I
Evacuated at 80°C(10^{-6} mmHg) for 18 hr.	1.7	3.0	1.0	1.5	2.4	1.0	1.6	2.6	1.0
Exposed to air for 2 hr.	1.7	3.0	1.0	2.25	4.2	0.9	1.75	2.9	1.0
Exposed to air for 2~3 days.	1.9	3.2	1.0	2.5	4.7	0.9	1.75	2.9	1.0

1) ΔH_{msl}: Distance between inflection points on absorption curve in gauss.
2) ΔH: Line width at half power of absorption curve in gauss.
2) I: Integrated intensity (products of ΔH and height of the absoption curve) in arbitrary unit.

of gaseous oxygen[1-3]. Further, the existence of stable addition compound between α, α'-diphenyl-β-picrylhydrazyl and a organic solvent*, such as benzene, cyclohexane or ether, has been reported frequently[4]. In this brief report, we are presenting the effects of oxygen on the spin population and also on the electronic conduction of α, α'-diphenyl-β-picrylhydrazyl itself.

The observation of ESR absorption spectra was carried out at room temperature with association of Hitachi MPS-1 type x-band spectrometer. This prime free radical was made from α, α'-diphenyl-β-picrylhydrazine by oxidation with PbO_2 in ether. The dependence of the line width and of the intensity of ESR absorption spectra on the three different samples have been observed. One of them, recrystallized from carbon disulfide solution, was a solvent free powdered sample (D.P.P.H.-Free). The second sample was a large single crystal (1.3 mg.) grown from carbon disulfide solution (D.P.P.H.-Single) and the third sample was deposited from ether solution (D.P.P.H.-Ether).

We found that the spin populations in these samples, keeping in vacuo, were coincident with each other as shown in Table I. When these materials were exposed to air, the line width of ESR spectrum of D.P.P.H.-Free was spread remarkably. However, no change of the integrated intensity of ESR absorptions was found practically in spite of broadening of their line widths. These results indicate that the interaction between α, α'-diphenyl-β-picrylhydrazyl and applied solvent or gaseous oxygen is physical instead of chemical one.

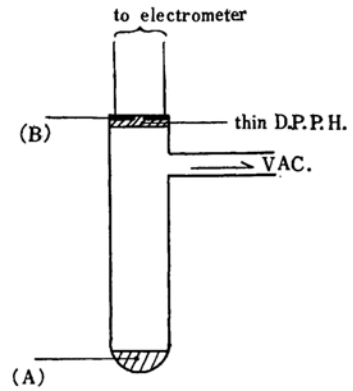

Fig. 1.

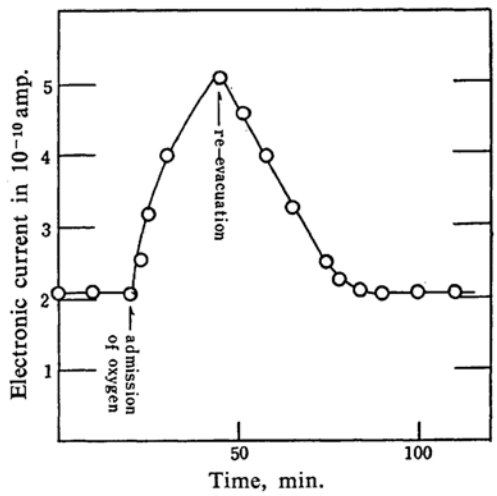

Fig. 2.

We also observed the oxygen effect on the electric conduction of thin D.P.P.H. film. The D.P.P.H. crystal to be evaporated was placed on the bottom (A) of glass vessel as shown in Fig. 1. By heating the vessel, the free radical was evaporated in vacuo to form a continuous thin film inside the top of vessel (B) between the two graphite (colloidal) electrodes. The resistance of this thin film

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2) J. E. Bennett and E. J. H. Morgan, *Nature*, **182**, 199 (1958).
3) A. E. Arbuzov, F. G. Volitova, N. S. Grif'yanov and B. M. Kozyrev, *Doklady Akad. Nauk, S. S. S. R.*, **126**, 774 (1959).
* No addition compound between D. P. P. H. and carbon disulfide is found.
4) J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **16**, 141 (1955).

was observed with association of a vibration-reed electrometer. The admission of oxygen into the vessel caused a marked increase of conduction of the film. However, this effect was reversible as on pumping out the oxygen, then, the resistance of the cell returned to its original value. One of these behaviors is illustrated in Fig. 2. These behaviour also suggests that the interaction between D.P.P.H. and oxygen is almostly phyical. The detail of this work may be submitted in elsewhere.

One of the present authors has already found that the absence of the hydrogen deuterium reaction at the surface of the D.P.P.H. crystals shows that the unpaired electrons in the molecules react with adsorbed hydrogens physically[5].

From these observations, the integrated intensity of ESR absorption of D.P.P.H. is independent on the conditions of preparation and also on the exposing time in the air. Therefore, we can conclude that various sorts of the D.P.P.H. crystals are applied as a standard to estimate the spin population of paramagnetic materials.

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