

Diphenyl-picrylhydrazyl as a Standard in Electron Spin Resonance

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In the study of free radicals by electron spin resonance α, α -diphenyl- β -picrylhydrazyl (DPH) is widely used as a standard for estimating the number of unpaired electrons present. Recently DPH has become commercially available through Fluka AG. Investigating two separate samples of DPH from this company it was found, that the maximum resonance intensity from one sample was only about one third of that from the other, the line being at the same time correspondingly broader. Subsequent analyses of the samples indicated the presence of substantial amounts of benzene. In view of the importance of DPH as a standard it was thought desirable to investigate the observed effect in some more detail, and especially to ascertain if recrystallization from benzene was responsible for the broadening of the resonance line.

The electron spin resonance spectra were obtained at a frequency of 31.5 Mc/s using a Pound and Knight type spectrometer¹. The magnetic field produced by a pair of Helmholtz coils was modulated at a frequency of 415 cps, and the signals were displayed on a recorder using a phase-sensitive detector. This technique permits the graphic presentation of the first derivative of the absorption as a function of field. The ordinate in the published spectra was calibrated in number of spin centers according to the resonance intensity from a sample of DPH recrystallized from carbon disulfide.

The existence of a stable (1:1) addition complex between DPH and benzene has been mentioned twice in the literature^{2,3}. We prepared the complex both by recrystallization from a mixture of 3 parts benzene and 2 parts cyclohexane, and by slowly evaporating the solvent at room temperature from a solution of DPH in benzene. Microchemical analysis indicated that the ratio of DPH to benzene in the sample used for the investigation was as 1:0.8.

The resonance line of the DPH-benzene complex (Fig. 1) was extremely broad with

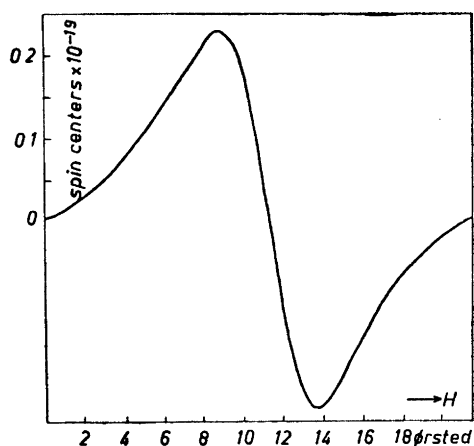


Fig. 1. Electron spin resonance of 60 mg crystalline DPH-benzene complex. (Ordinate is calibrated in spin centers according to resonance intensity from a sample of DPH recrystallized from carbon disulfide.)

a total width of 4.6 oersteds between inflection points of the absorption curve. The peak to peak intensity was only about 1/30th of that observed in a sample of DPH recrystallized from carbon disulfide (Fig. 2), which showed a total width of 0.85 oersteds between inflection points.

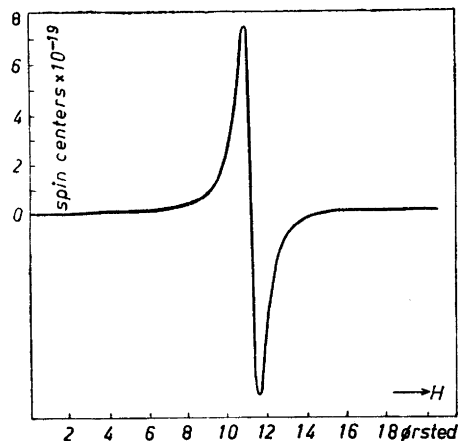


Fig. 2. Electron spin resonance of 50 mg crystalline DPH recrystallized from carbon disulfide.

In accordance with the findings by Müller³ benzene is only very slowly driven away from the complex. Evacuation of the sample for 24 h at 0.1 mm Hg at room temperature had no effect on the spectrum, and after 10 h of vacuum treatment at 60° the peak-to-peak intensity had increased only by a factor of three. It is interesting to note, however, the ease with which the benzene apparently is dispelled by other organic liquids. Only 2 min after the addition of a small amount of cyclohexane to the DPH-benzene complex the peak-to-peak intensity had increased by a factor of five.

Electron spin resonance spectra of solid free radicals are usually characterized by very narrow absorption lines with a half width of less than 10 σ sted. Large intermolecular exchange interaction of the unpaired electrons is mainly responsible for the sharpening of the lines. Some overlapping of the orbitals should occur in order to have exchange narrowing operating. When the distance between the free radicals in the crystal is increased, one may consequently expect, that the exchange effect will be reduced. It seems likely, that the broadening of the resonance line of the molecular addition complex between DPH and benzene may be ascribed to reduced exchange narrowing. A somewhat similar effect has already been observed by Holden and Kittel⁴ in the resonance spectra of di-*p*-anisyl nitric oxide. The resonance lines from this compound was found to have a half width of 15.7 σ sted, whereas a crystalline material in which one part of di-*p*-anisyl nitric oxide was diluted with ten parts of the isomorphous *p,p'*-dimethoxy benzophenone gave a half width of 29.6 σ sted.

It has been pointed out⁵, that the line shape, when exchange narrowing is operating should be of the Lorentzian type, whereas for the case of negligible exchange effects a Gaussian line shape is expected. Weidner and Whitmer⁶ have previously found a Lorentz type resonance line for DPH. Analysis of the resonance line from the DPH-benzene complex showed, that the line could also in this case be closely reproduced by a Lorentz curve. Even though the line of the DPH-benzene complex is considerably broader than in the sample of DPH recrystallized from carbon disulfide, the line shape indicates thus that the line is still sharpened by exchange narrowing. This is not surprising as according to Holden and Kittel⁴, the line width

Table 1.

Sample	a) ΔH_i σ sted	b) I_p	c) A	d) A
DPH recrystallized from CS ₂	0.85	1	1	1
DPH-benzene complex	4.6	0.031	0.9	0.6

a) Distance between inflection points on absorption curve.

b) Peak-to-peak intensity of derivated curve in arbitrary units.

c) Area under absorption curve in arbitrary units, calculated from $(\Delta H_i)^2 \times I_p$.

d) Area under absorption curve in arbitrary units, calculated from the product of the line width and the area under the derivated curve.

in DPH calculated on the basis of dipole-dipole interaction only should be of the order of 100 σ sted.

It is actually the area under the absorption curve, that is a measure of the number of unpaired electrons present in a sample. This area may be estimated either from the product of the square of the line width and the peak-to-peak intensity, or from the line width times the area under the derivated curve. It is seen from Table 1, that using the first method the areas under the absorption curves of the two samples were found to be nearly equal. The lower results on the DPH-benzene complex obtained using the second method of calculation, is probably due to neglect of the area beyond the limits of integration.

A search was made for a suitable solvent for the recrystallization of DPH. It turned out, that the solvent had a pronounced effect on the resonance line. The highest peak-to-peak intensity in the derivated resonance spectrum was obtained from a sample of DPH recrystallized from carbon disulfide. These observations emphasize that great care should be exercised when using DPH as a standard for estimating the number of unpaired electrons present in a system. DPH should preferably be recrystallized from carbon disulfide, and only the area under the absorption curve should be used for the estimate.

So far the observations on the electron spin resonance spectrum of the DPH-

benzene molecular addition complex have been restricted to the radiofrequency region. It is our hope in the near future to extend the work to the microwave region. Work is in progress on the electron spin resonance spectra of other molecular addition complexes of DPH.

The authors wish to express their gratitude to Mr. H. Hognestad, who constructed the electron spin resonance spectrometer. The microchemical analyses were carried out by Dr. Kirsten, University of Uppsala.

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Received July 30, 1958.

Ligand Field Spectrum of Vanadium(II) Hexaquo Ions

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The absorption spectra of hexaquo ions of divalent metals in the first transition group has been one of the most common subjects for ligand field theory. $\text{Cr(II)}^{1,2}$, Mn(II)^3 , $\text{Fe(II)}^{4,5}$, Co(II)^6 , $\text{Ni(II)}^{7,8}$ complexes have all been rather much studied. Only the study of vanadium(II) has been very little performed, due to the strongly reducing character of this oxidation state and the interfering colours of the probable vanadium(III) impurities. Kato⁹ photographed bands at 820, 760, 560, and 540 m μ of a solution in 3 M HCl. However, measurements on a Cary MS-11 recording spectrophotometer has not confirmed the doublet structure in the green, and it is known that the highly varying sensitivity of most photographic plates in this region may produce spurious maxima. Therefore, Ball-

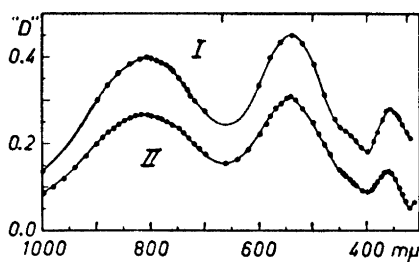


Fig. 1. Reflection spectra of vanadium(II), zinc(II) Tutton salt.

hausen and the present author concluded¹⁰ that the three spin-allowed transitions from 4T_2 to 4T_1 , 4E_g (F), and 4E_g (P) occur at 820, 555, and 378 m μ , respectively. Similar conclusions were drawn previously by Holmes and McClure¹¹, but only published recently.

Fig. 1 gives the reflection spectra (as measured on a Beckman DU) of two samples of $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ into which vanadium(II) is included isomorphically. This happens to be a method of evading the presence of vanadium(III) in the substance. The salt was also dissolved in 2 M H_2SO_4 and measured on the Cary. The band maxima (and shoulders in parentheses) occur at the wavelengths in m μ :

Sample I	Sample II	Solution
810	810	>810
(765)	(760?)	(778)
540	542	563
(430)	(434)	—
355	362	368

The solution has higher wavelengths of all its bands, compared to the solid samples. This may be caused by the presence of sulphate complexes (even though this has relatively little influence on the spectra of other divalent ions), or by partly oxidation to +3 (of which the spectral characteristics is discussed in Ref.¹² p. 79). However, another explanation may be found in the phenomenon⁸ that $\text{Ni}(\text{H}_2\text{O})_6^{++}$ has smaller wavelengths when imbedded in $(\text{NH}_4)_2[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ than in other salts or in solution. Further, the lattice constants of the zinc Tutton salt are so small that $\text{V}(\text{H}_2\text{O})_6^{++}$ may be compressed to some extent¹³.