Paramagnetic Susceptibilities of Para-substituted Hydrazyl Free Radicals

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The static magnetic susceptibilities of the stable free radicals, 2,2-diphenyl-1-picrylhydrazyl(DPPH) and 2,2-bis(*p*-chlorophenyl(*p*-bromophenyl, or *p*-methoxyphenyl))-1-picrylhydrazyl(abbreviated to DCl_2(DBr_2 or $D(CH_3O)_2$)[*1], were measured in the temperature range from 10°K to 300°K. The measurements were made by the Faraday method. About 10 mg of the polycrystalline samples were placed in a cylindrical quartz cell (diameter 7mm, height 8mm) suspended by a quartz string from the arm of a vacuum balance. All the measurements were carried out in an oxygen-free helium atmosphere of 30 mmHg.

The paramagnetic susceptibility, χ_p, of DPPH followed the Curie-Weiss law, $\chi_p=Ng^2\beta^2S(S+1)/3\boldsymbol{k}(T-\theta)$, with a Weiss constant, θ, of -24°K between 70°K and room temperature. DPPH is known to have several crystal modifications. Our sample is the one recrystallized from CS_2 and may belong to the DPPH (III) crystal modification, according to Weil *et al.*[1] The observed Curie constant corresponded to a spin concentration of 74%.

The susceptibility, χ_p, of DCl_2, recrystallized from benzene, followed the Curie law over the entire temperature range, and no co-operative phenomenon was observed. The spin concentration was estimated from the Curie constant to be 82%.

DBr_2, which was recrystallized from benzene, was found to have a susceptibility maximum at 15°K, while at higher temperatures it followed the Curie law, with a spin concentration of 82%. The magnetic susceptibility of $D(CH_3O)_2$ had its maximum at 21°K (Fig. 1). The numerical results were analyzed on the basis of the singlet-triplet model;

$$\chi_p=\frac{N/2g^2\beta^2S(S+1)}{3\boldsymbol{k}T}\cdot\frac{3}{3+\exp(J/\boldsymbol{k}T)}+\frac{C}{T} \tag{1}$$

where J is the singlet-triplet energy separation and where the second term represents the contribution of an assumed isolated paramagnetic "impurity." If we take $J/\boldsymbol{k}=33.8$°K and assume the impurity concentration to be 8.7%, Eq. (1) reproduces fairly well the experimental results shown in Fig. 1. The electron spin resonance measurements were made on this sample between 77°K and room temperature. The absorption spectrum was very sharp, the $\varDelta H_{msl}$ value being smaller than 1 gauss. As the absorption shape did not change with the temperature, the peak heights of the first derivative curves are thought to be proportional to the absorption intensity. These values are in good agreement with the static susceptibility data, as may be seen in Fig. 1. Of the four compounds, $D(CH_3O)_2$ has the smallest hyperfine coupling constants of the nitrogens,[2] showing that the unpaired electron in this compound delocalizes most extensively over the phenyl rings. The large intermolecular interaction observed in $D(CH_3O)_2$ can be attributed to this delocalization of the unpaired electron.

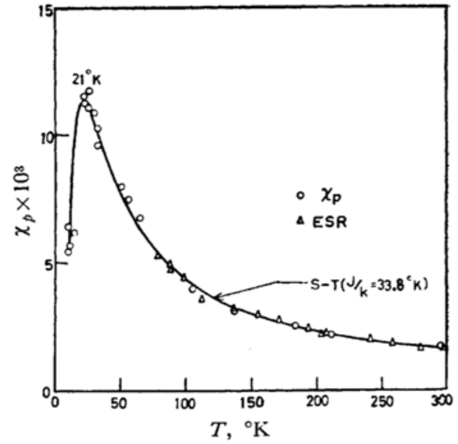

Fig. 1. Paramagnetic molar susceptibility of $D(CH_3O)_2$. The data have been corrected for an assumed impurity paramagnetism. The solid-line curve is the theoretical fit with $J/\boldsymbol{k}=33.8$°K. The ESR data (arbitrarily normalized at 300°K) are also plotted.

[*1] These three compounds were kindly provided by Professor R. I. Walter, Haverford College.

1) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, **1965**, 5567.

2) M. M. Chen, K. V. Sane, R. I. Walter and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961).