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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON THE EFFECT OF OXYGEN ON PARAMAGNETIC RESONANCE ABSORPTION IN $\alpha\alpha$-DIPHENYL-β-PICRYLHYDRAZYL

(Presented by Academician B. A. Arbuzov on 8 VII 1957)

At a frequency of 127 MHz, by the method described in ([1]), we have found a strong effect of oxygen on the resonance paramagnetic absorption in $\alpha\alpha$-diphenyl-β-picrylhydrazyl (DPPH), taken in the form of freshly ground fine-crystalline powder. When the air pressure above the sample is lowered, the intensity of the absorption line increases and its half-width decreases. Raising the pressure to the initial value leads to restoration of the former absorption line.

Fig. 1. Dependence of ΔH on temperature at a pressure of $9 \cdot 10^{-4}$ mm Hg *(a)* and 760 mm Hg *(b)*

The effect of oxygen on the intensity, width, and shape of the line is especially clearly manifested upon cooling a DPPH sample. The dependences of the half-width ΔH of the absorption lines on temperature in samples that were under air pressures of $9 \cdot 10^{-4}$ mm and 760 mm are given in Fig. 1, and photographs of some of the lines obtained are shown in Fig. 2.

From Fig. 1 it is seen that in the absence of oxygen (curve *a*) only a very slight decrease of ΔH is observed upon heating DPPH from 77 to 395°K, probably connected with a decrease in the effectiveness of local magnetic fields as a result of thermal motion ([2]).

A DPPH sample in contact with air (Fig. 1, *b*) behaves quite differently: in this case the curve $\Delta H(T)$ lies higher, and in the temperature interval from \$ \$300 to \$ \$250°K a sharp increase in the line width is observed. Repeated experiments with the same sample give identical results. Different samples at an air pressure of 760 mm differ somewhat from one another, and the broadening of the line proves to be the greater, the smaller the particle size of DPPH. Thus, in samples prepared by grinding DPPH with sugar, it was possible to obtain a line whose

Fig. 2. Curves of resonance paramagnetic absorption in DPPH.

Figure 2: Fig. 2. Curves of resonance paramagnetic absorption in DPPH.

width at 295°K was $ $3 gauss, and at 77°K approximately 10 gauss. The effect of temperature on ΔH in this case was also reversible. In coarse-crystalline samples, where the surface of contact with atmospheric oxygen is small, the course of the curve $\Delta H(T)$ proved to be close to that in the evacuated sample.

An especially strong change in the absorption line is observed if a finely ground DPPH sample is in direct contact with liquid oxygen. If, however, the sample is brought into contact with liquid nitrogen, then the dependence $\Delta H(T)$ proves to be approximately the same as in the evacuated sample; in this case the line width does not change, even if the sample immediately

after immersion in liquid nitrogen, brought into direct contact with liquid oxygen.

The experiments described show that the change in linewidth is entirely due to oxygen molecules adsorbed by the surface of DPPH. Broadening of the DPPH line was also observed in an atmosphere of NO_2. Thus it turns out that in DPPH, as in coals ([2]), adsorbed paramagnetic gases considerably shorten the time T_2, which determines the linewidth.

Fig. 2. Curves of resonance paramagnetic absorption in DPPH.
a–760 mm Hg, $T = 295$°K; *b*–$9 \cdot 10^{-4}$ mm, 295°K; *v*–$9 \cdot 10^{-4}$ mm, 77°K; *g*–760 mm, 77°K.

The most remarkable fact here is the abrupt change in linewidth near 275°K. It may be caused either by an abrupt change in the adsorption of O_2 on DPPH (for example, by the formation at temperatures < 275°K of a second adsorption layer of O_2 molecules), or by a change in the character of the motion of O_2 molecules on the surface of DPPH. The latter explanation seems more probable. One may suppose that at temperatures above 275°K the adsorbed oxygen has a large freedom of motion on the surface of DPPH, forming, as it were, a two-dimensional gas or liquid; this motion should weaken the effectiveness of the local magnetic fields created by the O_2 molecules; at temperatures below ~ 275°K the motion of the adsorbed molecules is "frozen."

Adsorption of oxygen by the surface of DPPH is the first stage in the oxidation of this free radical; the oxidation itself proceeds slowly: even in very strongly dispersed samples exposed to air, the paramagnetic resonance disappears completely only after several days.

It should be noted that the literature contains rather contradictory data on the linewidth of paramagnetic resonance in DPPH ([3–6]). The temperature dependence of ∇H in DPPH also proves to be different for different authors ([5,7–9]). It seems probable to us that these discrepancies can be explained by the fact that DPPH samples of different degrees of dispersion and of different ages were used, as a result of which the action of oxygen on them was not the same.

In conclusion, the authors express their deep gratitude to F. G. Valitova for preparing the preparation of $\alpha\alpha$-diphenyl-β-picrylhydrazyl.

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Note: Figure translations are in progress. See original paper for figures.