

ELECTRON SPIN RESONANCE ABSORPTION OF DIPHENYLPICRYLHYDRAZYL - ZINC OXIDE MIXTURES¹

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ABSTRACT

Electron spin resonance measurements on mixtures of $\alpha\alpha$ -diphenyl- β -picrylhydrazyl (DPPH) and zinc oxide when compared with corresponding determinations on DPPH itself, and with DPPH - potassium chloride mixtures, indicate that there is a transfer of electrons between the DPPH and the zinc oxide. These observations support earlier published views of Harrison and McDowell, who found that the above mixture was able to enhance the catalysis of the ortho-para hydrogen conversion, and the hydrogen-deuterium exchange reaction.

INTRODUCTION

Mixtures of $\alpha\alpha$ -diphenyl- β -picrylhydrazyl (DPPH) and zinc oxide have been found to be more efficient catalysts of the ortho-para hydrogen conversion (1, 2) than either of the two components alone. This led Harrison and McDowell (2) to postulate that the enhancement of the catalysis was caused by an electron transfer process occurring at the DPPH - zinc oxide interface. More recently Eley and Inokuchi (3) have found evidence for partial transfer processes in the systems DPPH-hydrogen, and also in DPPH - hydrogen sulphide. We here report the results of some experiments on the electron spin resonance absorption of mixtures of DPPH and potassium chloride, and DPPH and zinc oxide. These observations, as do also some less complete ones on DPPH - nickel oxide mixtures, confirm the earlier views of Harrison and McDowell (2) that electron transfer processes occur at the DPPH - zinc oxide interface.

EXPERIMENTAL

Pure non-sintered zinc oxide was prepared by treating a slightly acidic solution of zinc sulphate with metallic zinc to remove heavy metal ions. Ferrous iron was oxidized with hydrogen peroxide and removed by coprecipitation with zinc hydroxide by addition of a small quantity of ammonium hydroxide solution. Zinc oxalate was prepared from thus purified solution of zinc sulphate and calcined at 400° C for 6 hours.

$\alpha\alpha$ -Diphenyl- β -picrylhydrazyl (DPPH) was prepared by oxidation of the corresponding hydrazine, supplied by Eastman-Kodak, with lead dioxide and recrystallized from a mixture of benzene and ligroin. Our sample contained crystalline benzene, but the mole ratio is less than one (6). Therefore, there is to be expected an "oxygen effect" as reported by Bennett and Morgan (5).

DPPH and zinc oxide mixtures were prepared, in a ratio of 1:9 by weight, by grinding the compounds in a mortar. The derivative of the electron spin resonance absorption was recorded on our electron spin resonance spectrometer at a frequency of 9000 Mc/sec. For convenience the distance between points of maximum slope ΔH_{ms} and the peak-to-peak intensity I_p on derivative curve will be used in this paper. The area A under the absorption curve can be estimated by the product of the square of ΔH_{ms} and I_p (3). The value of I_p of DPPH in vacuum is taken as unity.

RESULTS AND DISCUSSION

The DPPH used in this experiment had a ΔH_{ms} of 1.4 oersteds *in vacuo*, and a ΔH_{ms} of 1.45 oersteds and an I_p of 0.66 in air. The value of ΔH_{ms} of crystalline solvent-free DPPH

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has been reported to be 0.85 oersted and that with 0.8 mole of crystalline benzene 4.6 oersteds (3). No electron spin resonance absorption was detected in zinc oxide under the conditions of the present experiments.

A preliminary examination of the interaction between DPPH and zinc oxide was carried out in air without considering the oxygen effect. By grinding the compounds for a few minutes the value of I_p decreased to less than 0.4. A further, more rapid, decrease in I_p was caused by prolonged mixing. I_p was also observed to decrease slowly on standing. These results are shown in Fig. 1.

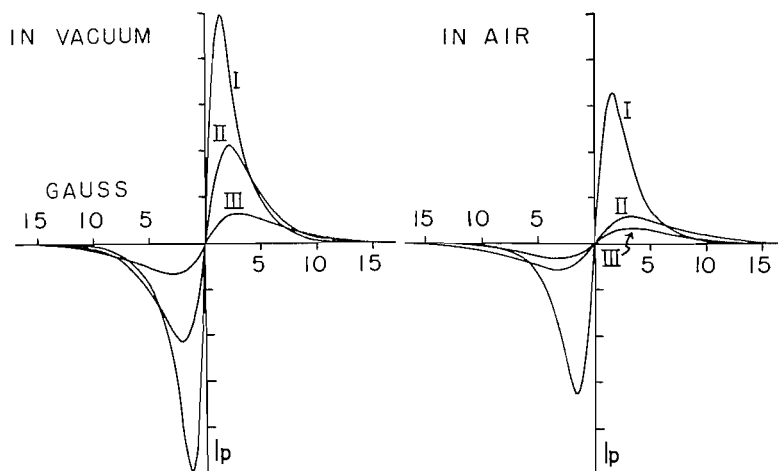


FIG. 1. Electron spin resonance absorption of mixtures of diphenylpicrylhydrazyl and zinc oxide. Curve I refers to DPPH alone; curve II refers to the DPPH-ZnO mixture No. 2 in Table I; curve III refers to the DPPH-ZnO mixture No. 4 in Table I. The value of I_p for DPPH in vacuum is taken as unity.

The variation of I_p with time is shown in Fig. 2. Curves A and B in this figure refer to measurements on the same mixture but at different degrees of admixing (B is the result of prolonged mixing). Although the I_p of DPPH shows a marked decrease by grinding with zinc oxide, the area under the

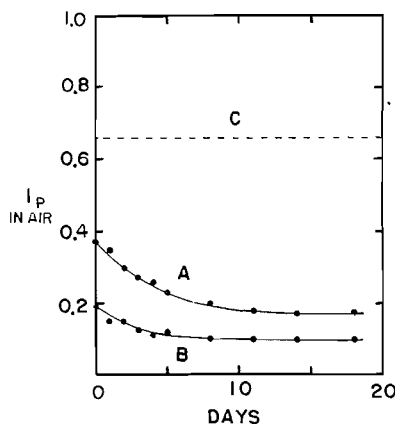


FIG. 2. Variation of the electron spin resonance absorption of mixtures of diphenylpicrylhydrazyl and zinc oxide (1:9) with time. Curves A and B refer to two mixtures with different degrees of admixing (B is the result of prolonged mixing). Curve C refers to a mixture of diphenylpicrylhydrazyl and potassium chloride (1:9); DPPH alone also gives a signal of this magnitude.

absorption curve, which is proportional to the electron spin concentration, does not change so much because of the increase of ΔH_{ms} . No change of g -value was observed.

The results shown in Figs. 1 and 2 indicate that the values of ΔH_{ms} and I_p mixtures of DPPH and potassium chloride (1:9) do not change with time, nor do these data differ from the values for DPPH alone. Therefore, the observed line broadening in DPPH - zinc oxide mixtures suggests that there is a change of environment of the unpaired electrons by some kind of interaction between the DPPH and the zinc oxide. As this solid-solid interaction proceeds fairly rapidly by grinding, it was found quite difficult to prepare homogeneously mixed samples in different stages of the interaction. A few preparations, which could be considered to be well mixed, were examined *in vacuo* and in air. The results are given in the following table.

TABLE I
Electron spin resonance absorption of DPPH-ZnO mixtures

	In vacuum			In air		
	ΔH_{ms}	I_p	A^*	ΔH_{ms}	I_p	A^*
DPPH-KCl	1.4	1.00	1.0	1.45	0.66	0.7
DPPH-ZnO (1)	1.85	0.63	1.1	2.5	0.22	0.7
(2)	2.1	0.43	1.0	3.2	0.12	0.6
(3)	2.2	0.31	0.8	3.2	0.10	0.5
(4)	2.85	0.13	0.5	3.5	0.07	0.4

NOTE: The numbers, for example (1), after the DPPH-ZnO refer to different mixtures.
*Estimated error ± 0.1 .

The data obtained *in vacuo* show that the absorption line is broadened by interaction between DPPH and zinc oxide. The electron spin concentration seems to be constant in the initial stages of mixing, but a permanent decrease is found as time increases. It is not clear whether this apparent loss of spin is due to the real disappearance of unpaired electrons or the fact that some of unpaired electrons are in a different state and show too broad a resonance absorption to be detected. It is, however, apparent that there is some transfer of electrons, though whether this transfer is from the DPPH to the zinc oxide, or vice versa, cannot be deduced from our results.

The decrease of I_p by admission of air is several times larger in DPPH - zinc oxide mixtures than in DPPH alone. This oxygen effect on electron spin resonance absorption is instantaneous and reversible in DPPH (2) and also in DPPH - zinc oxide.

Since zinc oxide is an excess, or n -type, semiconductor, it was of interest to see if the effects observed with mixtures of this compound and DPPH would also occur with a defect, or p -type, semiconductor and DPPH. A few experiments were carried out with DPPH and nickel oxide which is a p -type semiconductor. The nickel oxide was prepared by calcination of the nitrate. The results are shown in Table II.

TABLE II
Electron spin resonance absorption of DPPH-NiO mixtures

	In vacuum			In air		
	ΔH_{ms}	I_p	A^*	ΔH_{ms}	I_p	A^*
DPPH-CCl	1.4	1.00	1.0	1.45	0.66	0.7
DPPH-NiO (1)	1.7	0.22	0.3	2.0	0.18	0.4
(2)	2.8	0.045	0.2	3.1	0.036	0.2

The same trends are observed in the results for the DPPH - nickel oxide mixtures as we found for the DPPH - zinc oxide mixtures. These observations must, therefore, be taken as additional evidence that electron transfer processes do occur at DPPH-oxide interfaces.

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