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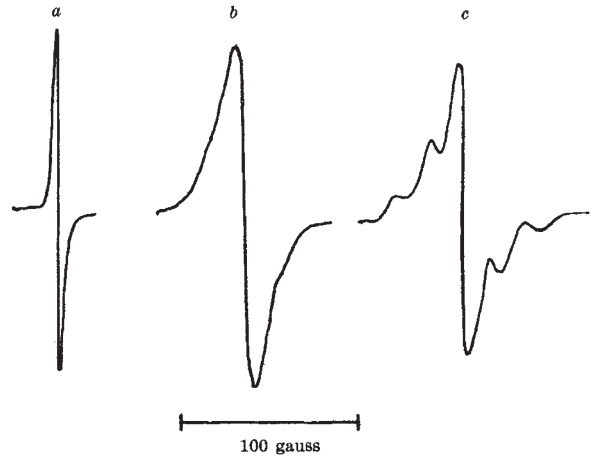

Fig. 1. Electron spin resonance spectra of DPPH in: (*a*) benzene; (*b*) carbon disulphide; (*c*) pyridine, at −196° C

CHEMISTRY

Effect of Micro-crystal Formation on the Electron Spin Resonance Spectra of αα-Diphenyl-β-picrylhydrazyl in Various Frozen Solvents

Despite the very numerous investigations of the electron spin resonance spectra of DPPH (αα-diphenyl-β-picrylhydrazyl) a number of perplexing problems remain. Those relating to its behaviour in various solvents are important because DPPH is used very commonly as a standard for concentration measurements in electron spin resonance and as a radical 'scavenger' in the examination of radiation chemistry.

During an investigation into the suitability of deaerated frozen solutions of DPPH in various solvents as concentration standards at low temperatures[1], it was found that there were wide differences in line width, hyperfine splittings and saturation behaviour, not all of which could be explained. In particular, frozen solutions of DPPH in benzene (10^{-3}–10^{-4} M) gave a strongly exchange-narrowed line about 2 gauss wide, while the very similar solvents, toluene and xylene, gave broad, poorly resolved five-line spectra like broadened versions of the solution spectra.

It was also found that the frozen benzene solutions showed little microwave power saturation, whereas the others all saturated heavily at 77° K. Further investigations showed that the electron spin resonance spectra could be divided into three groups: (*a*) strongly exchange-narrowed (peak to peak line width $\Delta H_{pp} \sim 2$–4 gauss), for example, benzene, naphthalene, quinoline (Fig. 1*a*); (*b*) broader, unresolved lines ($\Delta H_{pp} \sim 10$–20 gauss), for example, acetone, diethyl ether, toluene, carbon disulphide, thiopen (Fig. 1*b*); (*c*) poorly resolved five-line spectra with hyperfine splittings greater than those observed in solution, for example, pyridine, tetrahydrofuran, xylene (Fig. 1*c*).

The spectra of group (*c*) are similar to those observed by Schneider[2] for DPPH in solidified 'Perspex' or polystyrene, and by Lord and Blinder[3] for DPPH and carbazyl in a plastic cement. These latter authors show clearly that the increase in hyperfine splittings and line-width is the result of including anisotropic contributions which are averaged out in solution. It has been suggested[4] that the exchange narrowing of the spectra of group (*a*) results from 'super-exchange' throughout the whole lattice or from crystallization of the solute in the form of micro-crystals.

In order to test this suggestion we have examined thin films of frozen solutions on the cold stage of a high-powered polarizing microscope. A concentration of about 10^{-2} M DPPH was needed for proper observation, and at this concentration micro-crystals of DPPH could clearly be seen in frozen benzene by means of their characteristic extinction properties. By contrast, pyridine solutions gave no evidence of crystallite production; instead, the production of a solid solution on freezing was shown by the retention of the violet colour when viewed with unpolarized light. Thus, although only two solvents have been examined, the evidence supports the view that the exchange-narrowing and, incidentally, the absence of saturation, are caused by the separation of the frozen solution into at least two solid phases, one of which is pure DPPH. The observed line width is almost identical with that of polycrystalline DPPH, which is also known to show negligible saturation. Solvents in group (*b*) may well show more complex behaviour with some DPPH in the form of crystallites and some in a solid solution, but this has not been established. It is, however, clear that there is some correlation between the electron spin resonance spectra and the spatial distribution of DPPH in the solid, which is significant in relation to its efficiency as a radical scavenger.

The spectra were recorded on a Varian *V*-4500 electron spin resonance spectrometer using 100 kc/s modulation. We thank Dr. N. H. Hartshorne, of the Department of Inorganic and Structural Chemistry in this University, for his assistance with the microscopy experiments.

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Reactions of Ammonia and Aliphatic Amines with Sulphur Dioxide

Although much work has been carried out on the reactions of ammonia with sulphur dioxide[1,2], little attention has been directed to spectrochemical measurements of the reactions. Tertiary amines (such as trimethylamine and triethylamine) and aniline derivatives give well-known molecular complexes by addition of sulphur dioxide; and ultra-violet absorption spectra[3,4] for the former and infra-red absorption spectra[5] for the latter have already been examined.

This communication deals with investigations of infra-red and Raman spectra of the reaction products obtained from ammonia and aliphatic amines with sulphur dioxide. The reaction between ammonia and sulphur dioxide