Spectroscopic Studies on Potassium Nitrobenzenide

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THE solid, free-radical, potassium nitrobenzenide was prepared under vacuum by a variation on the method of Russell *et al.*,[1] and shown by magnetic susceptibility measurements to contain 88 ± 7% of the paramagnetic species at room temperature.

The solid was slightly soluble in dry 1,2-dimethoxyethane under vacuum and the resulting solution gave an electron spin resonance spectrum in which a quartet splitting of 0·23 gauss due to the potassium ion was clearly resolved. The other splittings agree quite well with those reported by Ward,[2] but the presence of the previously unreported potassium splitting demonstrates that the species is present as a contact ion-pair.

The diffuse-reflectance spectrum of the powder shows a band at 462 mμ in agreement with reports that the free nitrobenzene anion in dimethylformamide and the sodium nitrobenzenide solvent shared ion-pair in acetonitrile absorb at 465 mμ[3] and 435 mμ[4] respectively. There appears to be a discrepancy between these results and those of Nagakura *et al.*,[5] whose experimental results and calculations suggest that the species present in 1,2-dimethoxyethane is the free ion, absorbing at 560 mμ. In the light of the present results it would appear that the explanation of this discrepancy as due to a solvent shift[3] is unlikely. Further experiments and calculations are being performed in order to clarify this matter.

The proton magnetic resonance spectrum of the powder (Figure) under vacuum at room temperature consists of a narrow line with features on either side. These are interpreted as being due to a Knight shift, the low-field line being characteristic of the *m*-protons, on which the spin density is positive, and the high-field of the *o*- and *p*-protons, on which the spin density is negative. No further resolution of the high-field line into separate features due to the *o*- and *p*-protons could be achieved at temperatures down to −60°, though further experiments are being performed at lower temperatures with this aim. The electron spin resonance proton splittings calculated from this spectrum were $A_{2,4,6} = -3{\cdot}88$ gauss, $A_{3,5} = +2{\cdot}18$ gauss, These splittings, which obey the Curie Law between room temperature and −60°, are comparable with those obtained directly from the electron spin resonance spectra of solutions of the radical. The differences which do exist may be partly due to experimental error, which in this particular experiment was of the order of ±10%, but are probably due in the main to solid state effects.[6]

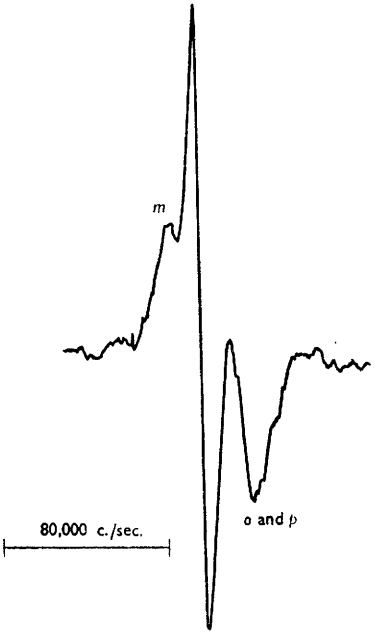

FIGURE. *Proton magnetic resonance spectrum of potassium nitrobenzenide powder.*

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