Electron Spin Resonance Spectra of Frozen Solutions of Potassium and Rubidium in Hexamethylphosphoramide

By RON CATTERALL* and PETER P. EDWARDS

(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT, *Lancs.*)

Summary Electron spin resonance spectra showing the presence of two metal-dependent species in frozen solutions of alkali metals in hexamethylphosphoramide are reported and constitute the first unambiguous distinction between current models for solvated alkali atoms.

IN this note we present e.s.r. spectra (Figure) of frozen solutions of potassium and rubidium in hexamethylphosphoramide (HMPA) which show clearly the presence of two metal-dependent species. One, responsible for the hyperfine splitting, had an electron population in the outer *s* level approaching that of the free metal atom while the other, a central singlet whose width was dependent on metal, had only *ca.* 1% of free atom value. The coupling constants were independent of temperature over the accessible range (77—160 K). The magnetic parameters are summarized in the Table.

Becker, Lindquist, and Alder[1] have suggested that some of the unpaired electrons in solutions of alkali metals in ammonia might be trapped in expanded orbitals on solvated alkali ions. Symons[2] pointed out that such species should give rise to characteristic hyperfine structure in the e.s.r. spectra. Although no such structure has been observed in metal–ammonia solutions,[3] structure attributed to hyperfine interaction with metal nuclei has been reported in amine[4] and ether[5] solutions. The marked temperature dependence of the hyperfine splitting constants in these systems was difficult to reconcile with precise species, and the e.s.r.

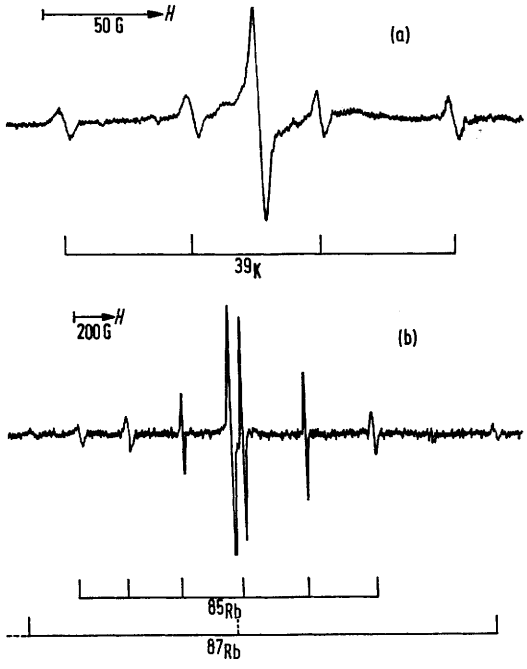

FIGURE. E.s.r. spectra of frozen solutions of (a) K and (b) Rb in HMPA at 77 K.

TABLE

Magnetic parameters for frozen metal–HMPA solutions

Metal isotope	Species	A_{iso}/G	ΔH_{ms}/G	*g*-factor (±0·0005)	Atomic character (%)
^{39}K	1	54·9	—	2·0005	66·7
^{39}K	2	—	4·3	2·0017	<*ca.* 1·5
^{85}Rb	1	251·9	—	1·9985	69·8
^{87}Rb	1	849·0	—	1·9980	69·6
^{85}Rb	2	—	9·5	2·0005	<*ca.* 0·6

spectra have been explained by two conceptually different models. The models proposed are (i) a single species whose structure was markedly temperature dependent[4a,6] and (ii) a dynamic equilibrium between two (or more) species whose structures were independent of temperature.[7] Attempts to distinguish between these two proposals by freezing the solutions were unsuccessful.[4,7,8]

The close similarities between HMPA solutions and those in ammonia,[9] amines,[9,10] and ethers[11] have already been established and hence our spectra constitute the first unambiguous distinction between these models. We conclude that the spectra of fluid amine and ether solutions represent a time-averaged situation resulting from dynamic equilibria between at least two species whose structures are independent of temperature.

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