Photodetachment of Electrons from Solvated Alkali Metal Anions

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Summary Photolysis of rapidly quenched alkali metal–HMPA solutions (HMPA = hexamethylphosphoramide) produces high concentrations of paramagnetic, solvated alkali atoms; we argue that the precursor metal anion M^-_{solv} species in these vitreous solids is quite noticeably solvated and is best viewed in terms of paired, valence electrons in an expanded outer s-orbital on the metal.

The evidence for a stoicheiometric alkali metal anion species M^- in fluid metal–amine and –ether solutions is overwhelming.[1] However, the degree of solvent involvement in the general-state wavefunction of M^- in these fluid solutions is still a matter of some conjecture.[2–4] Dye and co-workers have argued, primarily on the basis of ^{23}Na n.m.r. data,[3,4] that Na^- in ethylamine and tetrahydrofuran solutions probably exists as a large, centrosymmetric solvated anion with two electrons in the outer 3s-orbital. Unfortunately, n.m.r. spectra of these large anion species in solution appear to be noticeably insensitive[4] to the 'fine-details' of any M^-–solvent interaction.

Here we report the first observation by e.s.r. spectroscopy of solvated alkali metal atoms, generated *via* photodetatchment of electrons from diamagnetic, solvated M^-_{solv} species[5] in quenched metal–HMPA solutions. Since our experiments were performed on vitreous solids some 200 K below the m.p.,[6] matrix reorganisation during the photodetachment process is negligible. The magnetic properties of these generic fragments then provide direct information as to the extent of solvation in the diamagnetic, alkali anion precursor.

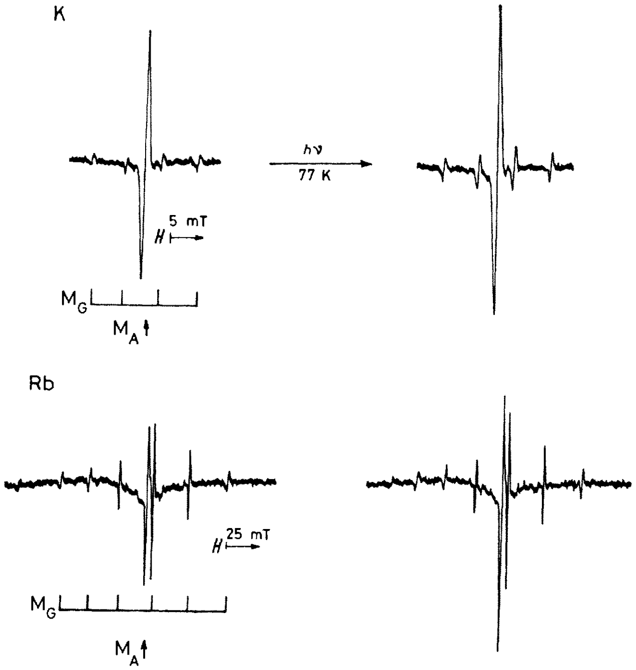

Figure 1. E.s.r. spectra of frozen solutions of potassium and rubidium (77 K) both before and after photolysis.

E.s.r. spectra (Figure 1) of 'dark' quenched solutions of potassium and rubidium in HMPA (HMPA = hexamethylphosphoramide) were identical to those reported previously.[7] The species responsible for the (metal) hyperfine splitting is a solvated alkali metal atom (labelled M_G on a system of nomenclature outlined elsewhere)[6] with an electron population in the outer s-orbital approaching *ca.* 70% of the free atom value. It is widely accepted[6–8] that the decrease in the hyperfine coupling constant (A_{iso}) below the atomic value arises from a measurable degree of solvation of the *S*-state atom. The central singlet (M_A, Figure 1) originates from an electron trapped in the weak coulomb field of a strongly solvated cation; *i.e.*, an ion-pair-like species with *ca.* 1% (electron) spin density in the outer s-level.[7]

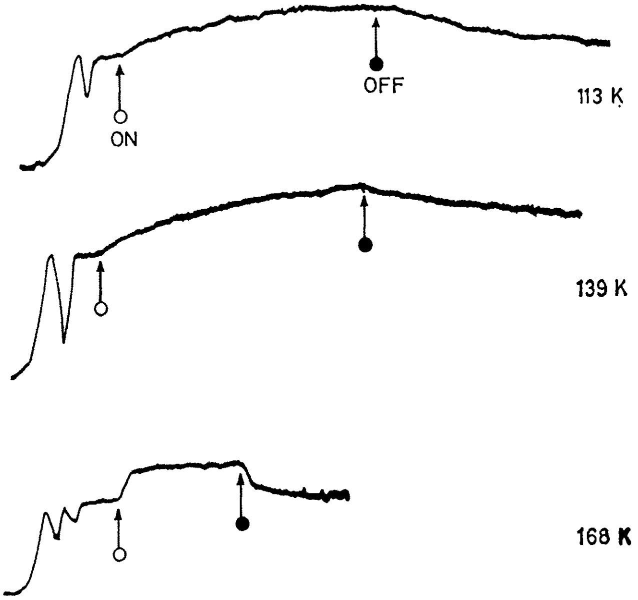

Figure 2. Growth and decay curves for the photoinduced M_A species in frozen K–HMPA solutions. The traces are of the e.s.r. signal intensity during photolysis at fixed magnetic field corresponding to peaks in the first derivative spectrum. Forward/reverse scans before the ON arrow indicate maximization of signal amplitude.

In situ irradiation (Hanovia mercury lamp) of samples in the e.s.r. cavity resulted in a marked increase in both M_A and M_G signals (Figure 1) and Figure 2 shows typical growth/decay curves at three temperatures. The production and decay of these photoinduced resonances were markedly temperature dependent, with rate constants for both processes being notably higher at the elevated temperatures (Figure 2). We stress that the photoinduced fragments M_A

and M_G have *identical* magnetic parameters to the normal (dark) solvated atom and ion-pair species [*e g* , A_{iso} (^{39}K) = 5·480 (± 0·01) mT, *g* = 2·00121 ± 0 0004 (M_G)]

Our results can be accommodated by equations (1) and (2) [9]

$$M^-_{solv} \xrightarrow{h\nu} (M^-_{solv})^* \rightarrow M_G + e_{solv}^- \qquad (1)$$

$$e^- + M^+_{solv} \rightarrow M_A \qquad (2)$$

The primary photochemical step involves the production of a metastable, bound excited state of the metal anion Photodetachment (1) and subsequent transfer (2) of a single electron then occurs to an accessible, fully solvated cation (M^+_{solv}) to yield the ion-pair species (M_A, Figure 1) The remaining paramagnetic fragment (1) is the M_G species

Thus, photolysis of M^-_{solv} in these low temperature glasses results in the detachment of one electron (to give M_A) but the retention of the second (valence) electron in a relatively diffuse s-orbital centred on the metal with all the characteristics of the dark, solvated atom species M_G The results quite clearly indicate a measurable degree of solvent participation in the parent anion wavefunction, without this solvent involvement, photolysis would yield a free-atom, rather than a solvated-atom, fragment in (1) We therefore advocate the description of M^- as a distinct, centrosymmetric species[5] but suggest that, arising from the solvation of M^- in these systems, the paired, valence electrons reside in a slightly expanded metal s-orbital [2]

Independent support for process (2) comes from recent γ-radiolysis studies[10] of frozen HMPA–KBr solutions Grishina *et al* [10] have observed an e s r singlet at low incident power levels which has the same spectral characteristics as the ion-pair species, M_A, observed in frozen K–HMPA solutions (Figure 1) when an electron photodetached from K^- becomes trapped in the weak Coulomb field of a strongly solvated K^+ cation

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