1231. *Unstable Intermediates. Part XXXIII.*[1] *Solvated electrons: Electron Spin Resonance of Solutions of Potassium in Ethylamine*

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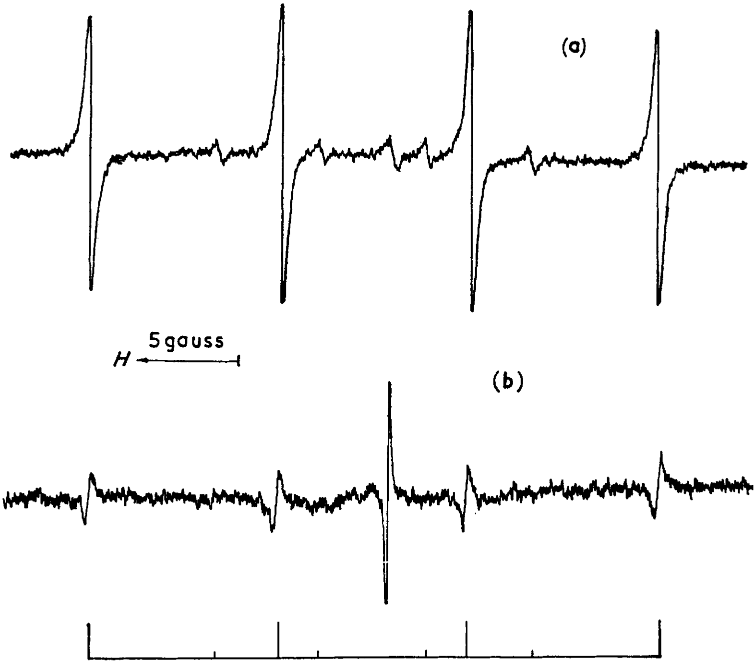
THE electron spin resonance spectrum of solutions of potassium in ethylamine consists of four equally spaced lines[2] ($A_{\text{iso}} = 9{\cdot}1$ gauss at 21°) of equal intensity, and width ($\Delta H_{\text{ms}} = 0{\cdot}5$ gauss). The spectrum was attributed to hyperfine splitting from a single ^{39}K nucleus in an "expanded metal monomer"[3] species ($K_{\text{exp.}}$). A significant point was the absence of any absorption from the solvated electrons ($e^-_{\text{solv.}}$) assumed to be in equilibrium with $K_{\text{exp.}}$.

$$K^+ + e^-_{\text{solv.}} \rightleftharpoons K_{\text{exp.}} \qquad (1)$$

We have re-examined these solutions and find important differences:

(1) Freshly prepared solutions at 21° have electron spin resonance spectra consisting of two quartets ($A_{\text{iso}} = 9{\cdot}85$ and $5{\cdot}4$ gauss, $g = 2{\cdot}00139 \pm 0{\cdot}0002$, $\Delta H_{\text{ms}} = 0{\cdot}2$ gauss).



Electron spin resonance spectra (*X*-band) of solutions of potassium in ethylamine (a) *ca.* 10^{-5}M. (b) *ca.* 10^{-6}M.

The relative intensities and the ratio of the splittings conform closely to those expected for the two naturally occurring potassium isotopes, thus confirming Bar-Eli and Tuttle's interpretation. The outer lines of the more intense quartet were slightly broadened as gauged by their amplitude. However, in addition to the hyperfine structure, a weak singlet ($\Delta H_{\text{ms}} = 0{\cdot}2$ gauss, $g = 2{\cdot}00194 \pm 0{\cdot}0002$) was also observed (see Figure). The difference between the g-factors is $0{\cdot}00055 \pm 0{\cdot}00002$. The optical spectra of these

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[1] Part XXXII. J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Tinling, *J.*, 1965, 6504.

[2] K. Bar-Eli and T. R. Tuttle, jun., *J. Chem. Phys.*, 1964, **40**, 2508.

[3] E. Becker, R. H. Lindquist, and B. J. Alder, *J. Chem. Phys.*, 1956, **25**, 971.

solutions consisted of a band ($\nu_{\text{max.}}$ 15,800 cm.$^{-1}$) asymmetrically broadened on the high-energy side, and a shoulder at 12,500 cm.$^{-1}$. The concentration was estimated to be about 10^{-4}M using the extinction coefficient [4] for solutions of potassium in ethylenediamine.

(2) Dilution with pure solvent resulted in a change in the relative intensities of the electron spin resonance signals which was most marked in the region 10^{-5}—10^{-6}M (see Figure). No change in the g-factors, ΔH_{ms}, or A_{iso} were detected, and the original spectra were restored by removal of solvent. We identify the singlet with $e^{-}_{\text{solv.}}$. The shoulder at 12,500 cm.$^{-1}$ disappeared on dilution, and the optical spectra consisted solely of the 15,800 cm.$^{-1}$ band for solutions 2×10^{-5}—10^{-6}M. Electron spin resonance measurements indicate a maximum optical density of about 0·02 for $e^{-}_{\text{solv.}}$ at 10^{-6}M; thus, it was not possible to detect the expected band in the 7000 cm.$^{-1}$ region.

(3) Freshly prepared solutions saturated at $-78°$ were a deeper blue and the central electron spin resonance line was absent at room temperature. The optical spectrum consisted of two bands of approximately equal intensity at 15,800 and 12,500 cm.$^{-1}$, corresponding to a concentration not less than 10^{-3}M.

(4) The effect of decomposition products ($K^{+}EtNH^{-}$) was to broaden the electron spin resonance hyperfine lines (but not the singlet), whilst suppressing the singlet. The difficulty in obtaining spectra which showed further enhancement of the singlet (solutions $<10^{-6}$M) probably arose from the presence of traces of decomposition products. No changes in optical spectra were observed except those attributable to ethylamide ion.

These observations are consistent with the following scheme:

(a) $M_{\text{exp.}}$ ($\nu_{\text{max.}} = 15{,}800$ cm.$^{-1}$) is in equilibrium with $e^{-}_{\text{solv.}}$ ($\nu_{\text{max.}} \sim 7800$ cm.$^{-1}$) according to eqn. (1) which is readily constrained to favour $M_{\text{exp.}}$ by excess potassium cations. These reactions are slow compared with the inverse of the observed hyperfine splitting (*i.e.*, $\tau > 3{\cdot}6 \times 10^{-8}$ sec.).

(b) The broadening of the electron spin resonance lines from $M_{\text{exp.}}$ on addition of potassium cations arises from rapid electron exchange ($\tau \sim 3{\cdot}6 \times 10^{-8}$ sec.) between $M_{\text{exp.}}$ and normal solvated cations having different nuclear spin configurations

$$K^{*}_{\text{exp.}} + K^{+}_{\text{solv.}} \rightleftharpoons K_{\text{exp.}} + K^{+*}_{\text{solv.}} \qquad (2)$$

(c) A species absorbing at 12,500 cm.$^{-1}$ which is favoured by high metal concentration has no associated electron spin resonance spectrum. Others [5] have identified this band with the " dimer," a spin-paired species involving two metal nuclei, and in equilibrium with the monomer:

$$2\ K_{\text{exp.}} \rightleftharpoons \text{Dimer} \qquad (3)$$

This equilibrium is also attained slowly compared with the inverse of the hyperfine coupling ($\tau > 3{\cdot}6 \times 10^{-8}$ sec.).

No attempt has been made to estimate an equilibrium constant for eqn. (1) in view of the competing equilibria outlined above. In conclusion, we note that the difference in g-factors emphasises the different environments for the two species, and also that the g-factor of $e^{-}_{\text{solv.}}$ is closer to the free spin value in ethylamine than in ammonia.[6]

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[5] R. R. Dewald and J. L. Dye, *J. Phys. Chem.*, 1964, **68**, 121; M. Ottolenghi, K. Bar-Eli, H. Linschitz, and T. R. Tuttle, jun., *J. Chem. Phys.*, 1964, **40**, 3729.

[6] R. Catterall and M. C. R. Symons, *J.*, 1965, 3763.