Resolved ^{14}N Hyperfine Coupling for Surface Electrons on Magnesium Oxide in the Presence of Ammonia and Amines

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Summary Surface electrons on magnesium oxide react with ammonia and primary amines to give two centres whose e.s.r. spectra show ^{14}N hyperfine coupling indicative of interaction with either two or three equivalent nitrogen atoms together with other properties expected for solvated or trapped electrons.

SOLUTIONS of alkali metals in ammonia and primary amines are characterised by very narrow e.s.r. singlets with g-values just below 2·0023 (see Table) which are assigned to solvated electrons.[1] Hyperfine coupling to ^{14}N and ^{1}H is not detected because of very rapid exchange narrowing, and unfortunately is still not resolved on freezing to glassy solids, only broad singlets (ΔH_{MS} *ca.* 35 G) being obtained.[1] Knight-shift n.m.r. studies show that there is a large positive hyperfine coupling to ^{14}N and a very small negative coupling to ^{1}H, but the individual coupling constants are not revealed. A recent suggested distribution of the total coupling gave 12 G for $A_{iso}(^{14}N)$ for six primary ammonia molecules and 3 G for twelve secondary molecules.[1] If this is at all reasonable, it will be necessary to remove interaction with the secondary molecules before resolution into hyperfine components can be expected. One way of doing this might be for solvent molecules dilutely to react with electrons trapped on surfaces.

TABLE. E.s.r. data for electron centres formed on magnesium oxide doped with ammonia and various amines.

Centre	g_{av}	$A(^{14}N)/G$[a]	No. of equivalent nitrogen atoms
F_s-centre (MgO)	2·0007	—	—
Metal–NH_3	2·0015	b	b
K–$EtNH_2$	2·00194	b	b
MgO–NH_3[d]	2·0010[c]	11·0 ± 0·5	3
MgO–NH_3[e]	2·0010	16·5 ± 1·0	2
MgO–$MeNH_2$[d]	2·0017	9·0 ± 0·3	3
MgO–$MeNH_2$[e]	2·0010	10·0 ± 1·0	2
MgO–$EtNH_2$[d]	2·0012	7·6 ± 0·3	3
MgO–Pr^nNH_2[d]	2·0014	8·5 ± 0·4	3
MgO–Pr^iNH_2[d]	2·0014	7·2 ± 0·5	3

[a] G = 10^{-4}T. [b] Unknown. [c] ±0·005 (relative uncertainty is considerably reduced). [d] High coverage (10^{-4} mol g^{-1}). [e] Low coverage (2×10^{-5} mol g^{-1}). (Spectra were too weak at lower coverage to give reliable data.)

Surface electrons on magnesium oxide powders have been well characterised[2] (Table). We now report that exposure of such centres to ammonia and primary amines gives new centres whose e.s.r. spectra indicate the presence of either two or three equivalent nitrogen atoms dependent on the degree of surface coverage. Details are given in the Table and a typical spectrum is shown in the Figure. Replacing NH_3 by ND_3 and CH_3NH_2 by CD_3ND_2 or CD_3NH_2 gave no significant spectral changes. However substitution of ^{14}N by ^{15}N in NH_3 and CH_3NH_2 gave the predicted changes, thus proving that the hyperfine splitting arises entirely from nitrogen nuclei.

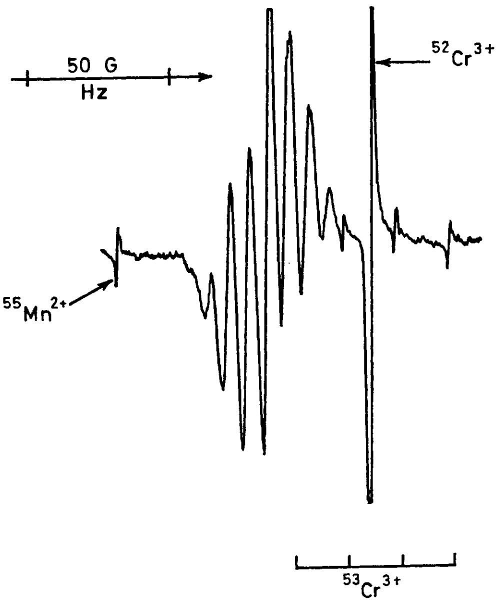

FIGURE. First derivative e.s.r. spectrum from $(CH_3)_2CHND_2$ adsorbed on MgO powder (10^{-4} mol g^{-1}) after exposure to ^{60}Co γ-rays at 77 K. Features from $^{52}Cr^{3+}$, $^{53}Cr^{3+}$, and $^{55}Mn^{2+}$ are from impurities in the MgO sample. Identical spectra were obtained when surface electrons were generated using γ-rays and hydrogen to suppress V_K centre formation, followed by exposure to ammonia or amine vapour prior to e.s.r. measurement

We postulate that these centres are intermediate between F_s-centres and solvated electrons. In support of this are the low g-values, which fall between that for F_s-centres and those for the corresponding solvated electrons (Table), the ready microwave power saturation, and the absence of any ^{1}H hyperfine coupling. Also, excess of ammonia gave a broad (ΔH_{MS} *ca.* 30 G) singlet, similar to that for frozen metal–ammonia solutions.[1] If this is accepted, the results give a good measure of $A_{iso}(^{14}N)$, which is likely to be somewhat reduced for the fully solvated electron. They also show that the anisotropic proton coupling is small which suggests that the mean electron-proton separation is large, *i.e.* that the N–H protons are not directed into the cavity. Finally they indicate that the $2p$ (N) character in the wavefunction is small.

Although we favour this 'solvation' model, we should consider an alternative in which the ammonia or amine molecules are co-ordinated to surface Mg^{2+} ions and the hyperfine interaction occurs *via* electron delocalisation on to these cations. This model is related to the lithium centre in ethylamine.[2] The main objection to this mode of interaction is that there is strong i.r. evidence against the co-ordination of ammonia molecules to surface Mg^{2+} ions.[3] It seems that ammonia molecules are very weakly adsorbed, the interaction being primarily *via* hydrogen-bonding to surface oxide ions.[3]

We thank Drs. A. J. Tench and R. Catterall for helpful advice.

(*Received, 5th September* 1977; *Com.* 921.)

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[2] R. Catterall, I. Hurley, and M. C. R. Symons, *J.C.S. Dalton*, 1972, 139.

[3] A. J. Tench and D. Giles, *J.C.S. Faraday I*, 1972, **68**, 193.