Formation of the Radical Cation $N_2H_6^{\cdot+}$ in Irradiated Hydrazinium Sulphate ($N_2H_6^{2+}SO_4^{2-}$): an Electron Spin Resonance Study

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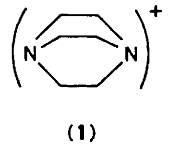
Exposure of [$N_2H_6^{2+}SO_4^{2-}$] at 77 K to ^{60}Co γ-rays gave $SO_4^{\cdot-}$ radicals and a novel species with two equivalent nitrogen nuclei and six equivalent protons, thought to be $N_2H_6^{\cdot+}$ formed by electron capture; these species readily gave $NH_3^{\cdot+}$ radicals on annealing.

Radicals commonly labelled 'σ*' after the nature of their SOMOs[1] are of great importance in the chemistry of second and subsequent row elements such as P, As, S, Se, Cl, Br, and I. For example, $P_2R_6^{\cdot+}$ 'dimers' are formed when $PR_3^{\cdot+}$ cations react with PR_3,[2,3] but they can also be formed by electron addition to compounds containing P–P bonds. Their structures are crudely represented as $(\sigma)^2$, $(\sigma^*)^1$ and they are often remarkably stable.

In marked contrast, most attempts to prepare first row analogues have failed. For example, $R_3N^{\cdot+}$ cations do not react according to (1)[4] and $R_2O^{\cdot+}$ cations do not give

$$R_3N^{\cdot+} + R_3N \rightarrow R_3N\overset{\cdot}{-}NR_3^+ \qquad (1)$$

$R_2O\overset{\cdot}{-}OR_2^+$ cations,[5] in marked contrast with the behaviour of $R_2S^{\cdot+}$ cations.[6—8] In fact, the only N–N σ* radicals that we know of are those with structures that are restrained by ring systems, the best known being the cation (**1**).[9,10] These species formed by electron loss from the neutral molecules are not strictly σ* radicals since the N ··· N separation is large, and the question of direct bonding is ambiguous.



(**1**)

Following our failure to detect reaction (1),[4] we turned to electron addition as a possible route, and selected the di-cation $N_2H_6^{2+}$ as a potential reactant.

Exposure of the powdered solid, $N_2H_6^{2+}SO_4^{2-}$ to ^{60}Co γ-rays at 77 K resulted in an intense e.s.r. spectrum comprising well known features for $SO_4^{\cdot-}$ radicals, together with a novel set of features assigned to an electron-gain centre (α). The spectrum for (α) can be analysed in terms of two equivalent nitrogen nuclei and six equivalent protons with the expected marked anisotropy. The complex spectrum was simplified by using $N_2D_6^{2+}SO_4^{2-}$, as shown in Figure 1. This suggests that it is the $N_2H_6^+$ σ* cation. Strongly supporting this assignment is the fact that, since $SO_4^{\cdot-}$ radicals are present in relatively high concentration, (α) is almost certainly an electron-gain centre. Also, on annealing, (α) decomposes irreversibly to give $NH_3^{\cdot+}$ radicals, reaction (2). Reaction (2), which is the reverse of (1), is expected to occur thermally, since reaction (1) appears not to occur. The e.s.r. spectra for $NH_3^{\cdot+}$ were

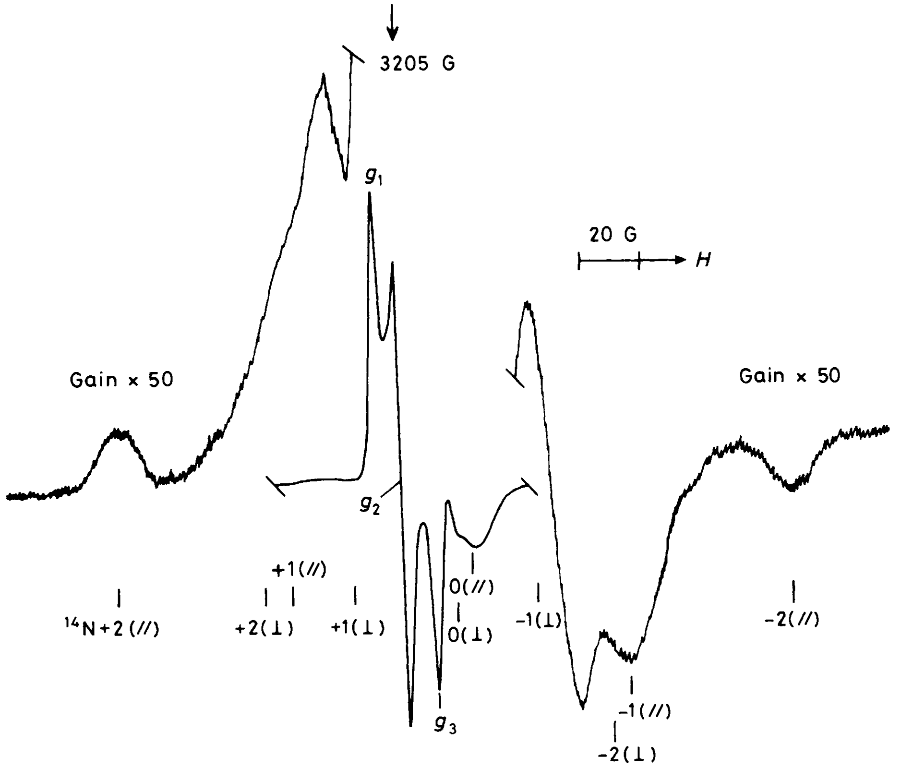


Figure 1. First derivative X-band e.s.r. spectrum for $N_2D_6^{2+}SO_4^{2-}$ after exposure of the powder to ^{60}Co γ-rays at 77 K, showing central features (g_1,g_2,g_3) assigned to $SO_4^{\cdot-}$ radicals, together with features assigned to $N_2D_6^{\cdot+}$ cations. A good computer simulation was obtained for this spectrum using the parameters given in the text. (1 G = 10^{-4} T.)

$$N_2H_6^{\cdot +} \rightarrow NH_3 + NH_3^{\cdot +} \qquad (2)$$

quite characteristic of this well known radical, and its identification is assumed to be correct.

If (α) is $N_2H_6^{\cdot +}$, then analysis of the e.s.r. data in the usual way gives $A_{\parallel}(^{14}N) = 56$, $A_{\perp}(^{14}N) = 30$ G, whence $A_{iso} \approx 39$ and $2B \approx 17$, assuming positive signs. These give *ca.* 7% 2s-character and 52% 2p-character on each nitrogen. The high total spin-density suggests that $A(^1H)$ is negative (≈ -14 G). [$A(^2H)$ was poorly resolved, giving ≈ 2.2 G.] The p : s ratio of *ca.* 7.5 shows that the two $-NH_3$ units must be nearly planar, and this accords with the relatively large magnitude of the (negative) proton coupling. The structure accords with the ease of dissociation (2), and with the reluctance of reaction (1) to occur, and the contrast with $P_2H_6^{\cdot +}$ and $P_2R_6^{\cdot +}$ cations is marked, since here, the normal pyramidal character is retained at the two $-PR_3$ units.

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