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ELECTRON SPIN RESONANCE STUDIES OF THE EFFECTS OF IONIZING RADIATION ON CYANAMIDE AND DIMETHYL CYANAMIDE

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A range of radicals have been obtained from pure H_2NCN and Me_2NCN and from solid solutions favouring electron capture or electron loss. Those well characterized by ESR spectroscopy include $H_2N(H)C{=}\dot{N}$, $Me_2\dot{N}CN^+$ and $Me_2N\cdot$.

1. Introduction

We know of no previous ESR studies of radicals formed from H_2NCN or Me_2NCN. The former is an important compound since it is formed under "primordial" conditions – that is, it is formed by the action of ionizing radiation on primitive atmospheres [1]. It is thought to be a precursor in the formation of amino acids and hence has considerable evolutionary significance [2]. It is also an important interstellar molecule [3], and has extensive industrial usage.

Its radiation chemistry has, nevertheless, been neglected, with the exception of a pulse radiolysis study of its solution in water [4,5]. In this work, conditions were controlled to give attack by solvated electrons, H· atoms, or ·OH radicals, selectively. Electrons were said to add, to give $H_2N\dot{C}N^-$, on the basis of increased absorption in the 220 nm region, but all that can really be claimed is that reaction with electrons is efficient. Similarly, H_2NCN reacted rapidly with H· and ·OH, but the structures of the resulting intermediates remain a matter of speculation.

We have undertaken an extensive study of the effect of ionizing radiation on H_2NCN, and included Me_2NCN also, since it was anticipated that the results for this compound would be easier to interpret and would give some useful clues in the task of spectral interpretation for H_2NCN.

Here we report those results which seem to be unambiguous; the remainder will be reported in full elsewhere.

2. Experimental

Cyanamide (Fluka) purified by recrystallization, had a melting point of 43–44°C. Its deuterated form, having the same melting point, was obtained by crystallization from D_2O. Samples were used directly after preparation because of the marked tendency for H_2NCN to dimerize. Tetramethyl cyanamide was used as supplied (Aldrich).

Samples, in the form of fine powders or dilute solutions in CD_3OD or $CFCl_3$ were exposed to ^{60}Co γ-rays at 77 K in a Vickrad source for up to 2 Mrad. ESR spectra were measured on a Varian E-109 spectrometer at 77 K. Samples were annealed either using a Varian variable temperature insert, or by decanting the liquid nitrogen from the insert Dewar and recooling to 77 K at given temperature intervals, or when significant changes were observed in the ESR spectra.

3. Results and discussion

3.1. Pure H_2NCN and D_2NCN

The major species detected by ESR spectroscopy gave well-defined spectra at ≈ 110 K (fig. 1). Below this temperature these features broadened, and were partially obscured by broad features from a second radical which were lost reversibly above ≈ 100 K.

The well-defined spectrum is assigned to the hydrogen adduct I.

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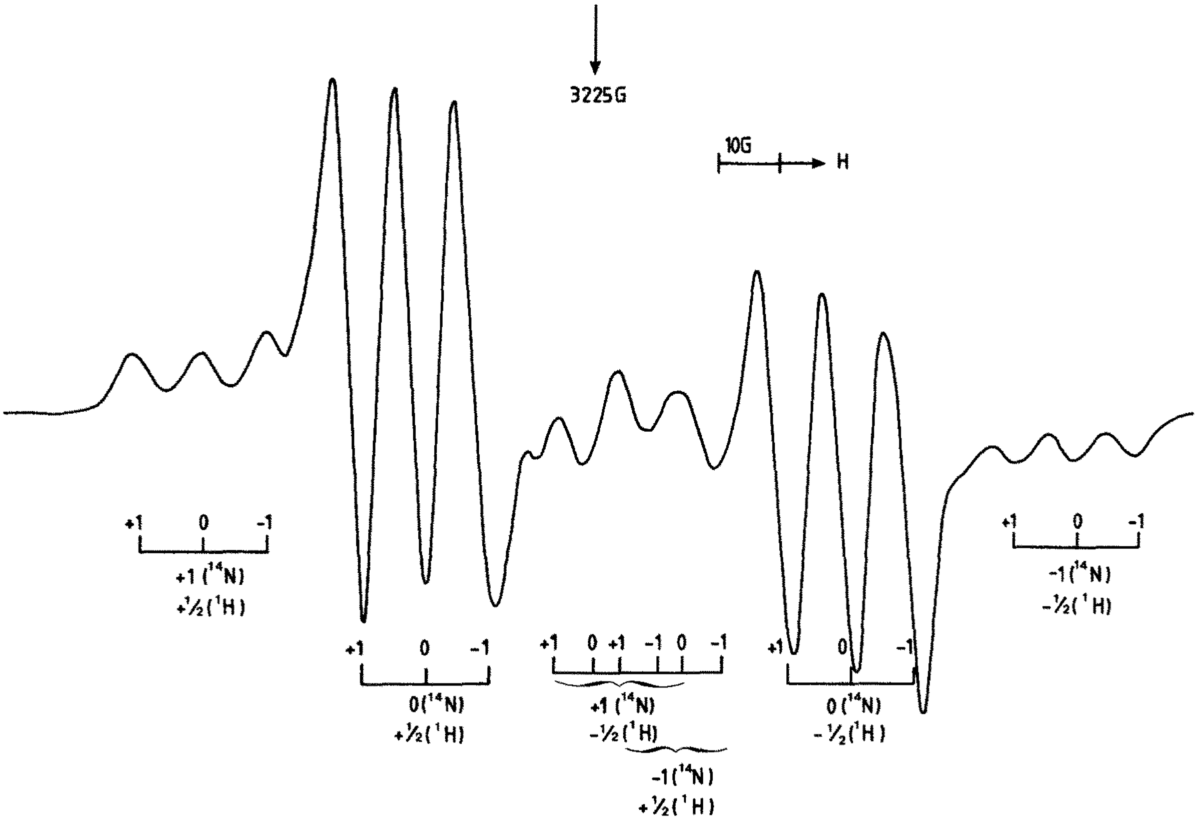


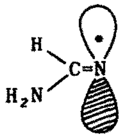
Fig. 1. First-derivative X-band ESR spectrum for H_2NCN after exposure to ^{60}Co γ-rays at 77 K and annealing to ≈110 K, showing features assigned to ${}^{H}_{H_2N}\!>\!C{=}\dot{N}$ radicals.

Table 1
Hyperfine coupling parameters for radicals derived from H_2NCN and Me_2NCN together with those for related radicals

Radical	Source/solvent	$A(^1H)$ (G)	$A(^{14}N)$ (G)
${}^{H}_{H_2N}\!>\!C{=}\dot{N}$	H_2NCN/H_2NCN	70 (^{2}H:11)	38 ($N_1\parallel$); ≈0 ($N_1\perp$) 10 ($N_2\parallel$); ≈10 ($N_2\perp$) [a]
${}^{H}_{H_3C}\!>\!C{=}\dot{N}$	CH_3CN/CH_3CN	85 (^{2}H:13)	33 (∥); ≈0 (⊥) [b]
Me_2N	Me_2NCN/CD_3OD	26	42 (∥); ≈0 (⊥)
Me_2N			
$Me_2\dot{N}CN^+$	$Me_2NCN/CFCl_3$	22	22 ($N_1\parallel$); ≈0 ($N_1\perp$) 8 ($N_2\parallel$); ≈0 ($N_2\perp$)

[a] This datum (10 G) is not a principle value, but it is probable that the anisotropy for N_2 is small.
[b] Ref. [6].

I



Data for this radical are compared with those for similar species in table 1, and there can be little doubt about the identity and structure. The singly occupied molecular orbital is formally confined to the in-plane 2p orbital on nitrogen, but there is extensive σ–π delocalisation, especially into the N–H orbital of the added hydrogen atom, the estimated spin density on hydrogen being ≈0.14. D_2NCN gave the deuterated adduct with the correct spectral modifications.

There are two reasonable routes to this product, the most probable being shown in the reactions:

$$H_2NCN \rightarrow (H_2\dot{N}CH)^+ + e^-, \quad (1)$$

$$H_2NCN + e^- \rightarrow H_2N\dot{C}N^-, \quad (2)$$

$$H_2N\dot{C}N^- + H_2NCN \rightarrow H_2NC(H)\dot{N} + HNCN^-. \quad (3)$$

Step (3) is expected since H_2NCN is relatively acidic. If this is correct, we conclude that the species with broad lines is either $H_2\dot{N}CN^+$ or $H\dot{N}CN$ formed by proton loss, and that the dissociation reaction

$$H_2N\dot{C}N^- \rightarrow H_2\dot{N} + CN^- \quad (4)$$

is slower than the protonation reaction (3), since $\cdot NH_2$ radicals were not detected.

3.2. Pure Me_2NCN

The best defined product on exposure at 77 K was

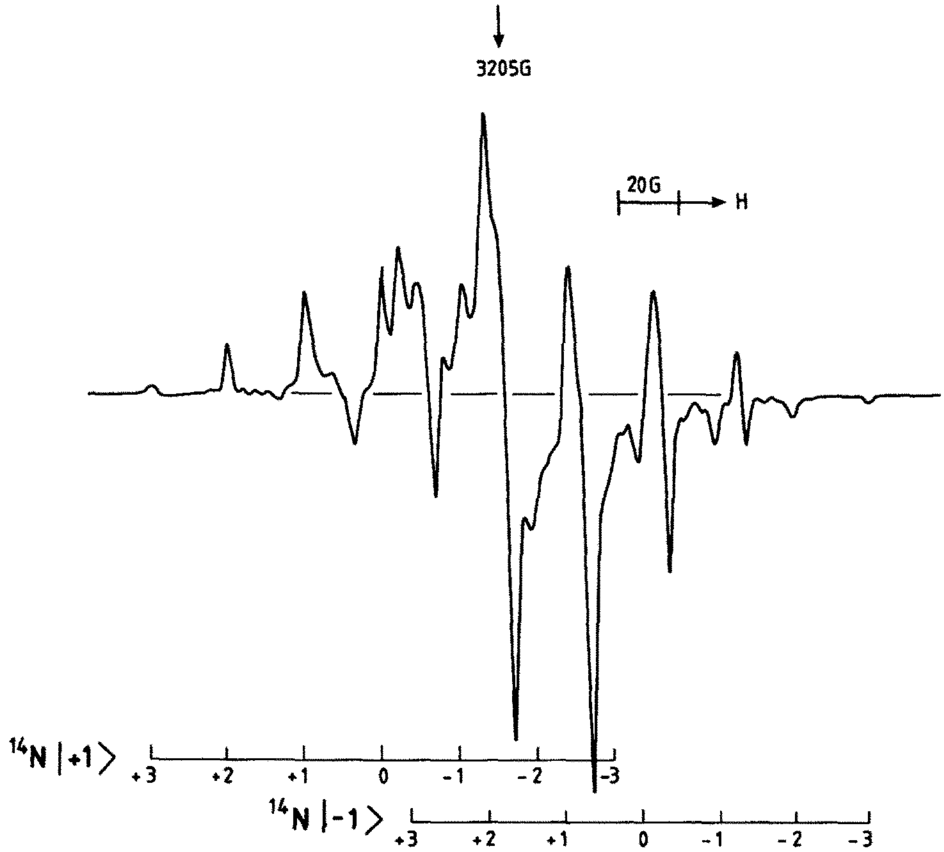


Fig. 2. First-derivative X-band ESR spectrum for Me_2NCN in CD_3OD after exposure to ^{60}Co γ-rays at 77 K and annealing to ≈110 K, showing features assigned to $Me_2N\cdot$ radicals. (Only the parallel features are labelled in the stick diagram.)

the $Me_2N\cdot$ radical. The ESR spectrum for this species was well defined, and the derived parameters are identical with those previously assigned to $Me_2N\cdot$ radicals in the solid state [7–9]. Again, other less defined features were present, which remain unassigned at present. These radicals are clearly the result of dissociative electron capture:

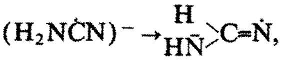
$$Me_2NCN + e^- \rightarrow Me_2N\cdot + CN^- . \tag{5}$$

In this case the protonation route followed by H_2NCN is not available, and the radical anion is unstable.

3.3. Solutions in CD_3OD

The same species were obtained from dilute solutions in CD_3OD, thus confirming reactions (2), (3) and (5), since electron capture is the only major reaction expected to occur under these circumstances [10]. We conclude that the radical anion $(H_2N\text{–}CN)^-$ is relatively stable, and acts as a base in CD_3OD, whereas that of Me_2NCN dissociates before protonation can occur. The latter is clearly favoured by the greater stability of the $Me_2N\cdot$ radical relative to $\cdot NH_2$.

So far, our attempts to identify the parent anion, $(H_2N\dot{C}N)^-$, claimed to be an important intermediate in pulse-radiolysis studies [4,5] have failed, despite the low temperatures at which we work. It is possible that the anion undergoes the unimolecular rearrangement



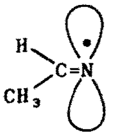
$$(H_2N\dot{C}N)^- \rightarrow {}^{H}_{H\bar{N}}\!\!>\!C{=}\dot{N}, \tag{6}$$

since the resulting radical anion might have an ESR spectrum similar to that assigned to radical I.

These results contrast interestingly with those for radicals derived from the structurally similar compound CH_3CN [11,12]. This gives a stable radical anion $Me\dot{C}N^-$, which shows no tendency to dissociate. However, photolysis ($\lambda > 640$ nm) at 77 K gave $\cdot CH_3 + CN^-$. Remarkably, this reaction was reversed on standing in the dark, for $CD_3 + CN^-$ ($\cdot CH_3$ radicals react preferably with the matrix).

In protic media at low temperatures these anions were protonated, giving II

II



with a large proton hyperfine coupling, comparable with that found for radical I (table 1).

3.4. Solutions in $CFCl_3$

This solvent was chosen because dilute solutions of neutral compounds (A) commonly give the corresponding radical cations, A^+, which are readily detected by ESR spectroscopy [13]. We were unable to study cyanamide because it is insoluble in this and related solvents, so attention was centred on Me_2NCN. There is little doubt that the resulting highly complicated ESR spectrum is due to Me_2NCN^+ radicals. A good fit for the major features was obtained using $A(^1H) = 22$ G, $A_\parallel(^{14}N_1) = 22$ G and $A_\parallel(N_2) = 8$ G, with $g_\parallel = 2.002$. The fact that the low-field features are more intense than those at high field implies that at least one of the other g-values is > 2.002, but we have not been able to extract further data from the spectra. There may be some tendency for Me_2NCN molecules to associate since a central triplet probably due to $H_2\dot{C}N{<}$ units were observed even in very dilute systems. This species might be $H_2\dot{C}N(Me)CNH^+$ formed by internal proton transfer, but this seems improbable to us.

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