Unstable Intermediates. Part 175.[1] Effect of Ionizing Radiation on *N*-Nitrosodimethylamine: an Electron Spin Resonance Study

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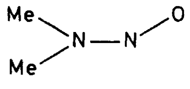
Exposure of *N*-nitrosodimethylamine to ^{60}Co γ-rays at 77 K gave two paramagnetic centres detected by e.s.r. spectroscopy. One had hyperfine coupling to two non-equivalent nitrogen atoms whose estimated isotropic coupling constants agreed with those for the anions R_2NNO^- in fluid solution. These anions, formed in methanol at 77 K, became protonated on annealing. The other centre had a large isotropic coupling (*ca.* 40 G) indicative of a σ-radical, and we suggest that it is the species $Me_2N{=}\dot{N}O^+$, which is isoelectronic with the well known iminoxyl radicals, $R_2C{=}\dot{N}O$. The results indicate an increased spin-density on nitrogen on going from $R_2C{=}\dot{N}O$ to $R_2N{=}\dot{N}O^+$.

THE organic nitrosamines (R_2NNO) are powerful carcinogens that may be formed in the stomach from nitrites used in food preservatives.[2] Stevenson and his co-workers [3,4] have shown that for R = ethyl or higher homologues, radical anions, $R_2N{=}NO^-$ can be formed by interaction with alkali metals in ethers. Their results [$A_{iso}(^{14}N\text{-}1) \approx 12.6$ G,† $(^{14}N\text{-}2) \approx 2.4$ G] suggest that these anions are planar π-radicals with the unpaired electron strongly localised on the nitroso nitrogen (N^{-1}). The parent molecules are known to have the planar bent structure (1).[5-7] Photoelectron spectroscopic results have been interpreted to show that the highest filled MO is π, with a low density on the amino-nitrogen atom, the next highest level being non-bonding on oxygen.[8] These conclusions were supported by CNDO/2 and CNDO/S MO calculations.[8]



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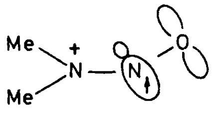

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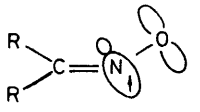

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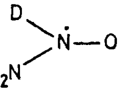

(4)

We have studied the effect of ^{60}Co γ-rays on *N*-nitrosodimethylamine in the expectation that, at 77 K, the primary cation and anion would be formed. The solid-state e.s.r. spectrum for the anion would enable us to verify the conclusion that it is a π^*-radical,[4] and e.s.r. data for the cation would make possible an interesting comparison with the inferences from p.e. spectroscopy and MO calculations.

EXPERIMENTAL

N-Nitrosodimethylamine was the highest grade available, and was used as such, or in solution in [$^2H_4$]methanol or [$^2H_3$]methyl cyanide. Samples were rapidly frozen to 77 K and exposed to ^{60}Co γ-rays in a Vickrad cell at 77 K for between 0.1 and 2.0 h at a dose rate of 2.7 Mrad h^{-1}.

E.s.r. spectra of the samples still at 77 K were measured with a Varian E3 X-band spectrometer. Samples were annealed in the otherwise empty insert Dewar flask with continuous monitoring of the spectra, and quickly recooled to 77 K whenever significant spectral changes were observed.

RESULTS AND DISCUSSION

Two main paramagnetic centres have been detected, both being formed in the pure material (Figure 1). Centre A with the larger hyperfine coupling constants seems to be formed preferentially in [$^2H_4$]methanol (Figure 2), whereas centre B is formed preferentially in [$^2H_3$]methyl cyanide.

Centre A. Data for this radical are given in Table 1. The parallel values are unambiguous, but there is room for error on the perpendicular features because these overlap with the parallel features for centre B. Unfortunately the *g* values are all similar and the *Q*-band spectra gave no better resolution. However, we are confident that the values listed are close to the correct ones. The values for N-1 are expected to be close to the principal values, but this may not be true for N-2 if the radical has the σ-structure suggested by the data.

From the value for A_{iso}, we can obtain a rough estimate of the atomic 2*s* character of the orbital on N-1, by dividing by the estimated A° value of 550 G.[9] This gives 7.3%. Similarly the 2*B* value (the principal component of the dipolar coupling) can be divided by the calculated $2B^\circ$ value of 34 G[9] to give a 2*p* character of *ca.* 60% (Table 2). These results show that this is a

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† 1 G = 10^{-4} T.

[1] Part 174, D. R. Brown and M. C. R. Symons, *J.C.S. Dalton*, 1977, 1389.

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[3] G. R. Stevenson and C. J. Colon, *J. Phys. Chem.*, 1971, **75**, 2704.

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[8] D. R. Battiste, L. P. Davis, and R. V. Nauman, *J. Amer. Chem. Soc.*, 1975, **97**, 5071.

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σ-radical with the spin strongly localised on the nitrosyl nitrogen (N-1). In our view, the radical is most probably the parent cation, having structure (2). This is iso-electronic with the well established iminoxyl radicals (3),[10,11] which have similar e.s.r. properties. Thus, typically, $A_{\text{iso}}(^{14}\text{N}) \approx 30$ and $2B \approx 13$, giving $a_s^2 \approx 0.059$ and $a_p^2 \approx 0.40$.[11] We cannot conclude much about the hyperfine coupling to N-2 except to say that it is relatively small, as expected. However, the results confirm the presence of a second weakly coupled nitrogen atom, thus supporting structure (2). We conclude that this is the correct structure for centre A.

TABLE 1

E.s.r. data for centre A (assigned to Me_2NNO^+), centre B (assigned to Me_2NNO^-), and centre C [probably $Me_2N\dot{N}(D)O$]

		^{14}N Hyperfine coupling (G) [a,b]					
		N-1			N-2		
Medium	Centre (radical)	$A_\parallel$	$A_\perp$	A_{iso}	$A_\parallel$	$A_\perp$	A_{iso}
Me_2NNO	A (Me_2NNO^+)	61 ± 1			14 ± 1		
CD_3OD	A	61 ± 1	30 ± 1	40.3	14 ± 1	*ca.* 0	*ca.* 4.7
Me_2NNO	B (Me_2NNO^-)	36 ± 1	*ca.* 0	*ca.* 12	6 ± 1	*ca.* 0	*ca.* 2
THF [c]	Me_2NNO^-			12.6			2.4

[a] 1 G = 10^{-4} T. [b] g Values close to 2.002 3 unless otherwise stated. [c] From ref. 4 (THF = tetrahydrofuran).

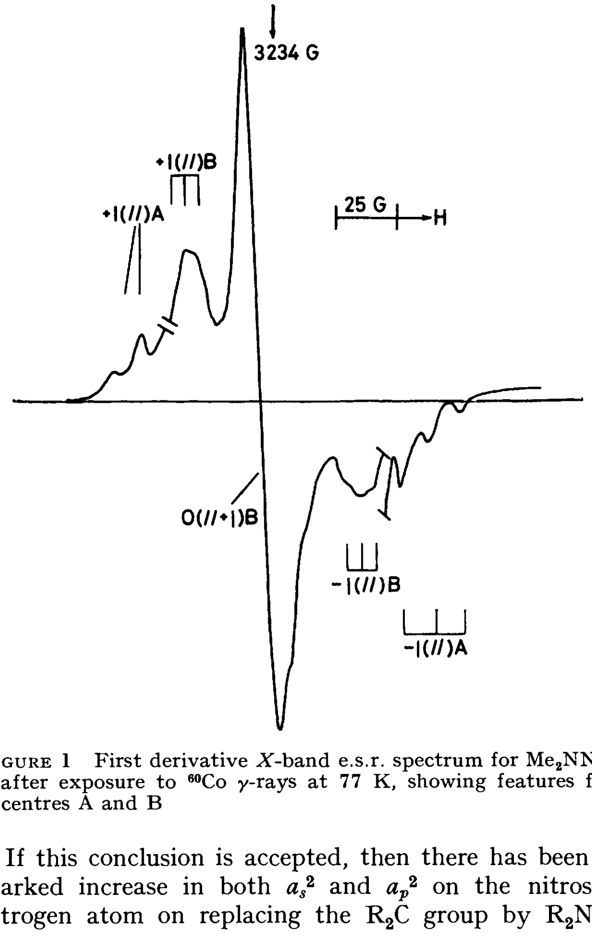

FIGURE 1 First derivative X-band e.s.r. spectrum for Me_2NNO after exposure to ^{60}Co γ-rays at 77 K, showing features for centres A and B

If this conclusion is accepted, then there has been a marked increase in both a_s^2 and a_p^2 on the nitrosyl nitrogen atom on replacing the R_2C group by R_2N^+. This is expected on the basis of our usual arguments relating to the effect of increasing the electronegativity of the ligands B in AB_2 radicals.[9] However, we had expected the $p : s$ ratio, reflecting the bond angle at N-1, to fall, indicating an increased bending, whereas it appears to have increased slightly. Nevertheless, in view of the uncertainty in the value for $A_\perp(^{14}\text{N})$ we do not wish to put weight on this apparent anomaly.

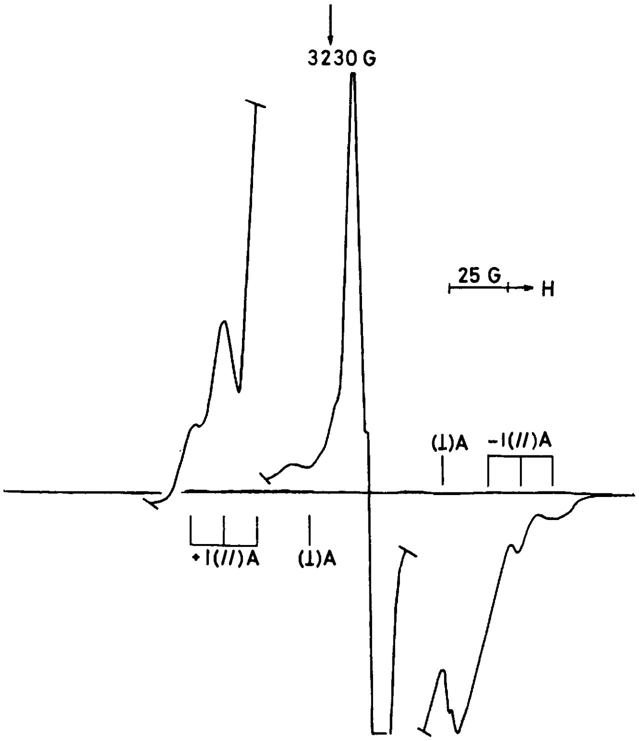

FIGURE 2 First derivative X-band e.s.r. spectrum for Me_2NNO in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to centre A

TABLE 2

Calculated atomic orbital populations, a_{2s}^2 and a_{2p}^2, for the nitrogen atoms of centres A and B

Centre	Radical	a_s^2	a_p^2	$a_s^2 + a_p^2$	a_p^2/a_s^2
A	Me_2NNO^+	N-1, 0.073	0.60	0.67	8.3
B	Me_2NNO^-	N-1, 0.022	0.71	0.732	35
		N-2, 0.003	0.12	0.123	40

[10] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86.

[11] W. M. Fox and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 1503.

Centre B. Unfortunately, as with the powder spectra for nitroxide radicals,[12] it is difficult to estimate a value for $A_\perp$, and all we can say is that it is small for both N-1 and N-2. However, taking $A_\perp \approx 0$ gives A_{iso} values for N-1 and N-2 close to the liquid-phase values reported[4] for the radical anions. This supports an assignment to the parent anions, which are expected to be the electron excess centres from Me_2NNO molecules.

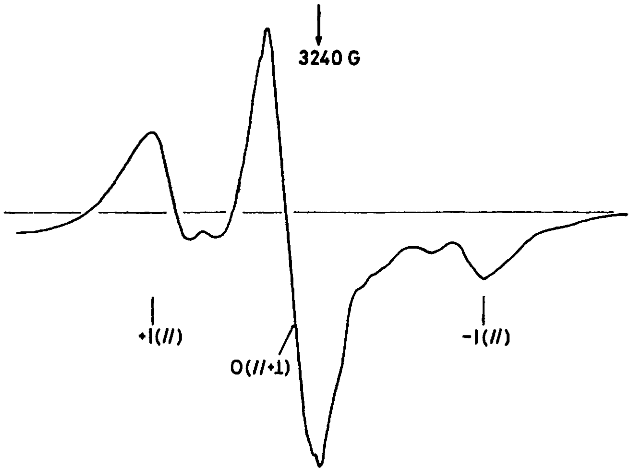

FIGURE 3 First derivative X-band e.s.r. spectrum for Me_2NNO in CD_3OD after exposure to ^{60}Co γ-rays at 77 K and annealing until centres A and B were lost, and recooling to 77 K, showing features assigned to $Me_2N\dot{N}(D)O$ radicals

Thus the effect of ionizing radiation in this instance appears to follow the simplest possible course at 77 K:

$$Me_2NNO + \gamma \longrightarrow Me_2NNO^+ + e^- \qquad \text{(i)}$$

$$Me_2NNO + e^- \longrightarrow Me_2NNO^-. \qquad \text{(ii)}$$

This is a common result for many inorganic materials, but relatively unusual in the organic field.

On annealing the pure material both centres were lost simultaneously, suggesting a simple reversal of steps (i) and (ii). However, in methanolic glasses, centre A was lost relatively rapidly, leaving B, which on further warming changed irreversibly to a new, but similar centre, C (Figure 3).

Centre C. We suggest that this is the nitroxide species (4), formed by deuteriation of the anion by solvent. This was supported by replacing CD_3OD by CH_3OH, which gave, after annealing to remove the signals for $H_2\dot{C}OH$ and $H\dot{C}O$ radicals, a poorly defined pair of doublets in the expected regions for the $M_I = \pm 1$ parallel features. The value of *ca.* 30 G for $A_\parallel(N^{-1})$ is reasonable for this centre (4), but the features are too poorly defined for us to obtain $A_\perp(^{14}N)$ or any data for N-2. However, the fact that the parallel $M_I = +1$ line is far stronger than the $M_I = -1$ line shows that '$g_\perp$' is $> g_\parallel$, to much the same extent as found for the simple nitroxides, $R_2\dot{N}O$.

It is interesting to compare these conclusions for the cationic centre with the p.e. spectroscopy results.[8] They are apparently contradictory in that our structure corresponds to neither the highest or next highest filled MO as deduced from p.e. spectroscopy and from CNDO-type calculations. This result is not unusual, however, because p.e. spectroscopy is concerned with the cation under Franck-Condon conditions, that is with the nuclear configurations of the parent molecule. We, however, are studying the ground state of the radical cations. Thus we suggest that the π-level is the highest for the molecular configuration, but that when the $N\dot{N}O$ angle increases, the level that we detect rises above the π-level, because of the loss of $2s$-character on N-1.[9,13] Thus we suggest that the ground-state of the radical cation is less bent than the parent molecule. That this is probable can be gauged by comparing the bond angles for NO_2^- (*ca.* 120°) and NO_2 (*ca.* 134°).

Jakubowski and Wan[14] have recently shown that *N*-nitrosodimethylamines in a water–isopentane–ethanol glass at 77 K gave $Me_2N\cdot$ radicals on exposure to u.v. light of $\lambda > 300$ nm. The other product, presumably NO, was not detected by e.s.r. spectroscopy. We did not detect $Me_2\dot{N}$ radicals in the present experiments, so optical excitation, either direct or as a result of electron return, does not seem to play an important role in the radiolysis process.

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