Unstable Intermediates. Part 174.[1] Electron Spin Resonance Spectrum of Tetraoxodinitrate(1—) formed by Radiolysis of Dinitrogen Tetraoxide

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Exposure of crystalline N_2O_4 to ^{60}Co γ-rays at 77 K gives three distinct paramagnetic centres, A, B, and C. The e.s.r. spectrum for A is characteristic of $NO_2^{\cdot}$ in a variety of subtly different sites, and that for B, which shows the presence of two equivalent nitrogen atoms, is assigned to the species $[N_2O_4]^-$. The third centre, C, which is poorly defined, also contains two equivalent nitrogen atoms and is tentatively identified as $[N_2O_4]^+$. Solutions of N_2O_4 in methanol (CD_3OD) give centres A and B′. The e.s.r. parameters for B are related to those for B′, and it is suggested that they are the same species, with centre B undergoing a minor libratory motion. The unpaired electron in centre B ($[N_2O_4]^-$) is in a σ^* orbital having a smaller $2p:2s$ ratio and a higher spin density on nitrogen than in the corresponding orbital of NO_2 from which it is derived. It is concluded that the electron is strongly confined to the two nitrogen atoms in $[N_2O_4]^-$ and probably in $[N_2O_4]^+$, which also appears to have a σ structure.

THE N–N bond in dinitrogen tetraoxide is long, and lengthens unusually rapidly when the solid is heated.[2] The tetraoxide is thermally unstable and has been the source of $NO_2^{\cdot}$ in a variety of e.s.r. studies of this radical.[3-5] However, $NO_2^{\cdot}$ is also conveniently formed by the action of ionizing radiation on nitrites and nitrates.[6] Although this small radical may undergo hindered rotations or librations in the solid state, its parameters are not otherwise appreciably dependent on the medium.[7]

It is frequently observed that electron-loss centres formed in the presence of the parent molecules form 'dimers',[8-10] which are often σ^* radicals, an example being reaction (1).[9] Although exposure of sodium nitrite

$$[PR_3]^+ + PR_3 \longrightarrow [R_3PPR_3]^+ \tag{1}$$

to γ-rays at 77 K gives only NO_2 and $[NO_2]^{2-}$ radicals,[11] exposure at ambient temperatures gives NO_2 and a dinitrogen centre identified as $[N_2O_4]^-$,[12,13] presumed to be formed by a comparable dimerisation (2). Similar σ^*

$$NO_2 + [NO_2]^- \rightleftharpoons [N_2O_4]^- \tag{2}$$

radicals can often be prepared by electron addition to corresponding diamagnetic dimers, typical examples being (3)—(5).

$$F_2 + e^- \longrightarrow [F_2]^- \tag{3}$$

$$RSSR + e^- \longrightarrow [RSSR]^- \tag{4}$$

$$R_3P{-}PR_3 + e^- \longrightarrow [R_3P{-}PR_3]^- \tag{5}$$

We therefore hoped that $[N_2O_4]^-$ could be formed from N_2O_4 by electron addition, using the radiolysis technique to achieve this. Electron loss would give $[N_2O_4]^+$, whose e.s.r. spectrum might well resemble that for $[N_2O_4]^-$, and hence it was necessary to distinguish between these two species. The aim of this work was therefore to prepare both these centres, and to learn more about their electronic structure *via* their e.s.r. spectra.

EXPERIMENTAL

Amorphous solid N_2O_4 was obtained from the liquid by pipetting small droplets directly into liquid nitrogen. Single crystals were grown in capillary tubes having extremely fine-bore tips, filled *in vacuo* with liquid N_2O_4. These were lowered slowly into a Dewar flask containing partially solidified ethanol. The beads and capillary tubes were exposed to ^{60}Co γ-rays in a Vickrad source at 77 K at a dose rate of 2.7 Mrad h^{-1} for up to 1 h.†

E.s.r. spectra were recorded on a Varian E3 spectrometer at 77 K. Samples were annealed in the empty insert Dewar with continuous monitoring of the e.s.r. spectra. They were re-frozen to 77 K whenever significant spectral changes were observed.

RESULTS AND DISCUSSION

Irradiation of the amorphous solid gave centres A, B, and C (Figure 1). The groups of features labelled A suggest that there are two or more different sites for this species, and this is confirmed by the single-crystal results. Centre B comprises a set of five asymmetric features, assigned to hyperfine coupling to two equivalent ^{14}N nuclei. The ± 1 components of the powder spectra overlap with those for centre A, but the single-crystal spectra leave no doubt that there are five lines rather than three, and even reveal the Breit–Rabi splitting of the inner features (Figure 2). A second set of features, labelled B′, were sometimes detected after irradiation of the amorphous material. This centre was only a minor component, and was not detected in the irradiated single crystals. However, irradiation of a solution of N_2O_4 in a CD_3OD glass gave B′ rather than B, together with features assigned to centre A. Features for CD_3OD radicals were also clearly defined, but the absence of a violet colour showed that e_t^- formation was largely suppressed.

A third set of lines was also obtained from the pow-

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† Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

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dered or crystalline substrate. These, labelled C in Figures 1 and 2, are considerably broader and are partially hidden by the more intense features for A and B. Nevertheless, there are clearly five components, and we have been able to extract tentative hyperfine parameters therefrom. We conclude firmly that the overall hyperfine interaction with ^{14}N is considerably less than that for centre B.

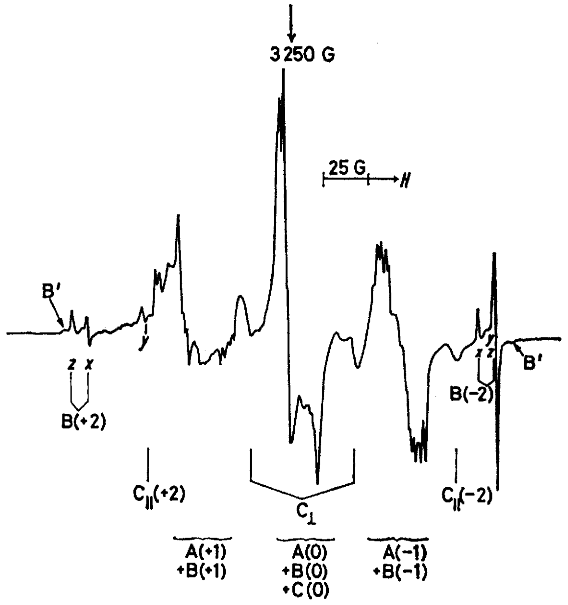

FIGURE 1 First-derivative X-band e.s.r. spectrum for amorphous N_2O_4 after exposure to ^{60}Co γ-rays at 77 K showing features for centres A, B, and C

Identification.—Centre A is clearly $NO_2^{\bullet}$. Parameters derived from this group of centres are compared with those derived from gaseous $NO_2^{\bullet}$ in the Table. The reduced value for $2B$ is typical of librating $NO_2^{\bullet}$ molecules and the differences within the group arise because the extent of libration differs. This centre is reasonably formulated as a product both of electron loss and of electron gain [equations (6)—(9)]. We stress that the primary cations and anions $[N_2O_4]^+$ and $[N_2O_4]^-$ are not necessarily the ground states of these species. Indeed, we have frequently found that steps such as (7) and (9) are in competition with the distortions that yield stable primary ions. Reactions (7) and (9) are expected to give $NO_2^{\bullet}$ radicals that have different librational properties since $[NO_2]^+$ is linear whilst $[NO_2]^-$ has a bond angle of *ca.* 120°. The single-crystal spectra show, in general, six sets of lines for $NO_2^{\bullet}$ and three sets for centre B. Since there are three magnetically distinct radicals per unit cell this suggests that there are two distinct types of NO_2 formed by (7) and (9) respectively. Thus NO_2 adjacent to $[NO_2]^+$ has slightly different properties from

$$N_2O_4 \longrightarrow [N_2O_4]^+ + e^- \qquad (6)$$

$$[N_2O_4]^+ \longrightarrow [NO_2]^+ + NO_2 \qquad (7)$$

$$N_2O_4 + e^- \longrightarrow [N_2O_4]^- \qquad (8)$$

$$[N_2O_4]^- \longrightarrow [NO_2]^- + NO_2 \qquad (9)$$

those adjacent to $[NO_2]^-$. This also provides an acceptable interpretation of the powder spectra.

Centre B could either be $[N_2O_4]^+$ or $[N_2O_4]^-$. The

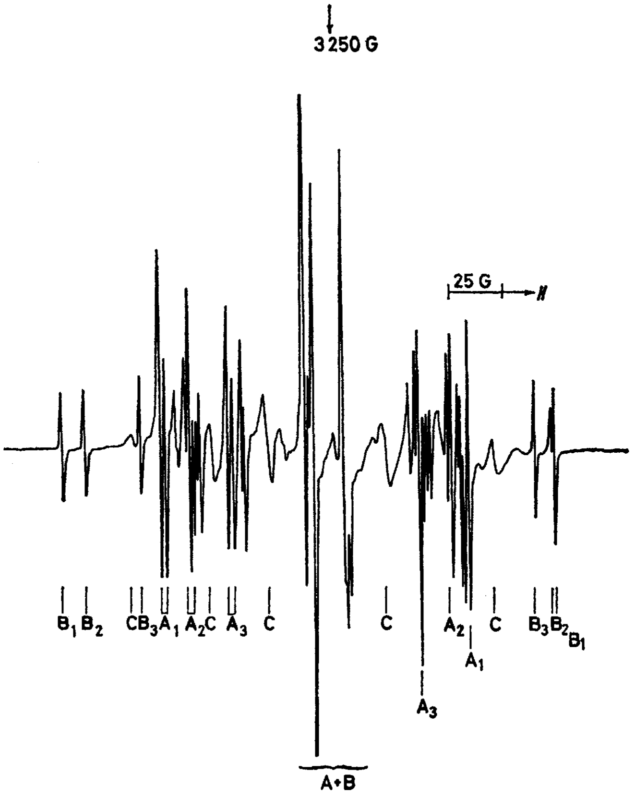

FIGURE 2 First-derivative X-band e.s.r. spectrum for a single crystal of N_2O_4 in an arbitrary orientation, that shows three sets of lines close to the x, y, and z positions for centres A and B

E.s.r. parameters of NO_2, $[N_2O_4]^-$, and $[N_2O_4]^+$ in a solid N_2O_4 matrix

	g_x	g_y	g_z	$g_{av.}$	$A_{iso.}$/G	B_x	B_y	B_z	a_s^2	a_p^2	λ^2
$[N_2O_4]^-$ (B) [a]	2.003 1	1.991 5	2.0030	1.999 2	51.8	+0.1	−4.7	+4.6			
$[N_2O_4]^-$ (B′) [a]	2.005 5	1.991 3	2.000 9	1.999 2	51.5	−3.7	−5.1	+8.8	9.4	29.0	3.1
$[N_2O_4]^+$ (C)	2.00	2.00	1.98	1.993	*ca.* 30	*ca.* −5	−5	+10	5.5	31.0	5.6
NO_2 (A) [b]	2.002 1	2.005 6	1.992 0	1.999 9	52.8	+11.9	−5.0	−6.9			
NO_2 (ice matrix) [c]	2.002 2	2.006 6	1.992 0	2.000 3	56.9	+13.33	−6.28	−7.24			
NO_2 (Pb[NO_3]$_2$) [d]	2.002 9	1.991 0	1.998 2	1.999 4	53.7	−5.2	−7.7	+12.9			
NO_2 (Na[NO_2]) [e]	2.005 7	1.991 0	2.001 5	1.999 4	54.7	−5.27	−7.95	+13.22			
NO_2 (g) [f]	2.006 2	1.991 0	2.002 0	1.999 7	52.59	−6.46	−7.71	+14.17	9.56	45.4	4.75

[a] Libration in xz plane reduced on going from B to B′. [b] Parameters taken from unique species left after annealing of low γ-dose samples. [c] Ref. 4. [d] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1974, 2247. [e] H. Zeldes and R. Livingstone, *J. Chem. Phys.*, 1961, **35**, 563. [f] Ref. 3.

parameters for B′ derived from methanolic solutions clearly relate to B, since $A_{\text{iso.}}$ and $g_{\text{av.}}$ and A_y and g_y are almost identical. This means that the centre in N_2O_4 is librating about y, giving partial averaging of the x and z parameters. Since formation of e_t^- is suppressed in CD_3OD together with centre C, it seems probable that B and B′ are electron-gain centres. Also, as outlined below, we expect parameters similar to those for B (B′) for $[N_2O_4]^-$, whereas those for centre C are closer to expectation for $[N_2O_4]^+$. These identifications are accepted in the following discussion.

Structures for $[N_2O_4]^-$ *and* $[N_2O_4]^+$.—Our results assigned to $[N_2O_4]^-$ show that the unpaired electron is in a σ^* orbital having relatively more total $2s$ character than for NO_2 (Table) and slightly greater $2p_z$ character. Thus the $p:s$ ratio (λ^2) has fallen, and the total spin density on nitrogen has increased. Qualitatively, this reflects the expected decrease in θ, the O–N–O angle, and seems to show that there is an increased tendency for the electron to become localized in the σ^* orbital of the dimer.

For $[N_2O_4]^+$ (centre C), the total $2s$ character is almost unchanged relative to NO_2, but the $2p_z$ character is increased. Thus λ^2 has increased, suggesting an increase in θ, as expected, since $[NO_2]^+$ is linear, but again the total spin density on nitrogen has increased and, by inference, that on oxygen has decreased, relative to NO_2, implying a greater localization in the σ orbital.

Structure of N_2O_4.—The N_2O_4 molecule is unusual in having a long N–N bond and being planar in the gaseous and solid states, with a relatively high barrier to rotation. There have been three recent calculations, two of which give the uppermost filled orbital as $6a_g$[14,15] and the other as $6b_{1u}$.[16] If our qualitative conclusions relating to $[N_2O_4]^-$ and $[N_2O_4]^+$ are correct, the last of these,[16] which is the most unsatisfactory anyway since it predicts dissociation, can be ruled out. The other two agree, at least in a qualitative sense, but we will call on the calculations of Howell and Van Wazer[15] as being the most useful for our purposes.

According to this analysis[16] the uppermost filled orbital for N_2O_4 is of $6a_g$ symmetry, and is pictured as comprising primarily an antibonding combination of oxygen $2p_z$ orbitals. The results we assign to $[N_2O_4]^+$ certainly do not relate to a species with an unpaired electron in this orbital. Rather, the spin appears to be in the $4a_g$ σ-bonding orbital comprising largely s–p hybrids on nitrogen. This could be raised above the $6a_g$ by N–N bond stretching and an increase in θ, which reduces the $2s$ content of the orbital.

The lowest empty orbital is given as $6b_{1u}$ σ^*, involving $2s$ and $2p_z$ nitrogen orbitals. This agrees most satisfactorily with our results for $[N_2O_4]^-$ and in this case there is no need to postulate any change in orbital levels on relaxation to the equilibrium configuration.

Comparison with the Centre in Sodium Nitrate.—Our results differ markedly from those assigned to $[N_2O_4]^-$ by Tateno and Gesi[12] in sodium nitrite irradiated at room temperature. Their results, confirmed by Atherton *et al.*,[13] show two equivalent nitrogen atoms with $A_{\parallel}(^{14}N) = 8$ G and $A_{\perp}$ $(^{14}N) = 2$ G. There is considerable uncertainty in $A_{\perp}$, but it is clearly small, and hence the radical is probably π in character. These workers suggest that the unpaired electron has moved from the N–N σ orbital into the π^* orbital as a result of bonding, and this is certainly reasonable. It is conceivable that the different environments promote different structures for $[N_2O_4]^-$. However, it is also quite possible that their centre is really $[N_2O_4]^{3-}$, formed from $[NO_2]^{2-}$ and $[NO_2]^-$. Absence of any electron-excess centres seems to support this suggestion.

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