Unstable Intermediates. Part 183.[1] An Electron Spin Resonance Study of Radicals formed in Irradiated Sodium and Potassium Nitrite

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Exposure of $K[NO_2]$ to ^{60}Co γ-rays at 77 K gives approximately equal yields of $NO_2^{\cdot}$ and $[NO_2^{\cdot}]^{2-}$ radicals, by simple electron transfer. On annealing at >77 K the e.s.r. features characteristic of these radicals are lost, largely by recombination to give $[NO_2]^-$ ions. However, relatively low yields of a two-nitrogen centre previously described as $[N_2O_4^-]$ are then detected. This is stable at room temperature, and is exclusively formed on exposure at this temperature. Similar results have been obtained from $Na[NO_2]$, except that the parallel features for $[NO_2]^{2-}$ are extremely broad and hence identification is tentative. These results are discussed in the light of previous conclusions. In particular, it is suggested that the two-nitrogen species is probably $[N_2O_4]^{3-}$. The structure of this novel radical is discussed qualitatively. When the nitrites are doped with nitrate ions in low concentration the behaviour at 77 K remains unchanged, but, on annealing, $[NO_3]^{2-}$ ions are formed in addition to the two-nitrogen centre. This result confirms the primary formation of $[NO_2]^{2-}$ in the sodium salt and shows that the electron affinity of $[NO_3]^-$ is greater than that of $[NO_2]^-$.

THE effect of high-energy radiation on nitrates and nitrites both in the crystalline state[2] and in solution[3] has been very widely studied. E.s.r. measurements have shown that, at low temperatures, the results for sodium and potassium nitrate are remarkably simple, involving only electron ejection followed by electron capture [equation (1)]. The radicals formed are trapped

$$2[NO_3]^- \longrightarrow NO_3^{\cdot} + [NO_3^{\cdot}]^{2-} \qquad (1)$$

at 77 K presumably by self-distortions. Thus, for example, $[NO_3^{\cdot}]^{2-}$ is pyramidal whereas $[NO_3]^-$ is planar.

Results for the nitrites are less clear cut. Zeldes and Livingston[4] irradiated $Na[NO_2]$ at 77 K, but detected only NO_2. Since no electron-gain centre was detected one must conclude either that its resonance was too broad to detect, or that some mechanism operates to selectively convert the electron-gain centres into diamagnetic products. Another, but less probable explanation is that these are converted by some mechanism into NO_2 radicals. These workers found that on annealing above 77 K the NO_2 radicals were lost irreversibly and were not replaced by other detectable paramagnetic species. In contrast, two groups studied the products of room-temperature radiolysis of $Na[NO_2]$ and observed two distinct products, one being identified as NO_2 and the other, which contained two equivalent ^{14}N nuclei, as $[N_2O_4]^-$.[5,6] These NO_2 radicals differed from those detected at 77 K in orientation: those at 77 K were nearly axially symmetric with respect to the *b* crystallographic axis, as expected for loss of an electron from $[NO_2]^-$ with no orientational change; however, those formed at room temperature had the *a* axis as the axis of near symmetry, implying a 90° rotation.[5,6] Identification of NO_2 was supported by the observation of a broad electronic transition in the 400 nm region,[5] since NO_2 in the gas phase absorbs strongly in this region.

I was prompted to re-examine these systems because of our results for irradiated N_2O_4.[7] In this study a centre containing two ^{14}N nuclei was well defined and was identified with some certainty as the anion, $[N_2O_4]^-$. The ^{14}N hyperfine coupling ($A_{max.}$ 56.4 G †) was far greater than that previously assigned to $[N_2O_4]^-$ (8 G),[5,6] and hence I felt that the previous identification was wrong. This conclusion is strongly supported by theory, which suggests that the lowest empty orbital for N_2O_4 is the $6b_{1u}$ σ^* orbital.[8] This assignment accords with our results,[7] but not at all with those previously assigned to $[N_2O_4]^-$.[5,6] Another aim of the present work was to endeavour to understand the apparent absence of paramagnetic electron-gain centres in the studies both at 77 K (ref. 4) and room temperature.[5,6]

EXPERIMENTAL

AnalaR grade $Na[NO_2]$ and $K[NO_2]$ were used as supplied, since recrystallised samples from purified water did not give different results. Freshly supplied salts were used to minimise the nitrate level. Aged samples gave $[NO_3]^{2-}$ on irradiation at room temperature, showing that nitrate was formed on storage. Samples doped with nitrate gave similar results.

Samples were irradiated as very fine powders at 77 K or room temperature in a Vickrad ^{60}Co γ-ray source at a dose rate of *ca.* 2 Mrad h^{-1} for between 0.1 and 2.0 h. E.s.r. spectra were recorded on a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar after decanting the nitrogen, and were re-cooled to 77 K whenever significant changes in the e.s.r. spectra were observed.

RESULTS AND DISCUSSION

Irradiation at 77 K.—Exposure of $K[NO_2]$ at 77 K gave the e.s.r. spectrum shown in Figure 1. This displays very narrow features assigned to stationary NO_2 radicals (Table) together with intense 'parallel' features separated by 2 × 36 G, clearly assignable to $[NO_2]^{2-}$ radicals. The 'perpendicular' features for this radical overlap with the $I = 0$ features for NO_2 and so no reliable parameters could be obtained. However, the parallel features are quite distinctive and the hyperfine coupling compares well with previous reliable estimates.[9] The concentrations of NO_2 and $[NO_2]^{2-}$ are, in fact, comparable: that for $[NO_2]^{2-}$ appears to be relatively low because of the far greater anisotropy in the hyperfine coupling which arises because $[NO_2]^{2-}$ is a π radical whilst NO_2 is a σ radical.[10] Thus in this case,

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

as with the nitrates, a simple electron transfer has occurred [equation (2)]. For Na[NO_2] the features for

$$2[NO_2]^- \longrightarrow NO_2^{\cdot} + [NO_2^{\cdot}]^{2-} \qquad (2)$$

NO_2 were also well defined (Figure 2) and the data are again in good agreement with expectation (Table). In this case, no well defined parallel features for $[NO_2]^{2-}$ can be seen. There is, however, distinct curvature in the spectral regions expected for the $I = \pm 1$ parallel lines which I feel fairly confidently are due to $[NO_2]^{2-}$. This ion is a powerful electron donor and, since it is adjacent to four Na^+ ions which occur in three magnetically inequivalent sites with respect to $[NO_2]^-$, I postulate that the spectrum should comprise sets of features from hyperfine coupling to two equivalent ^{23}Na nuclei (seven lines) and two other inequivalent nuclei (eight lines). These 56 lines could well overlap to give the very broad feature detected. The smaller magnetic moment for ^{39}K would account for the far narrower lines obtained with K[NO_2]. Thus I postulate that, for both salts, reaction (2) dominates at 77 K. This result ties in exactly with our studies of aqueous and methanolic glasses containing $[NO_2]^-$ ions, the primary products again being NO_2 and $[NO_2]^{2-}$.[11] However, these studies were complicated by the tendency for $[NO_2]^{2-}$ ions to protonate to give $[HNO_2]^-$ ions.

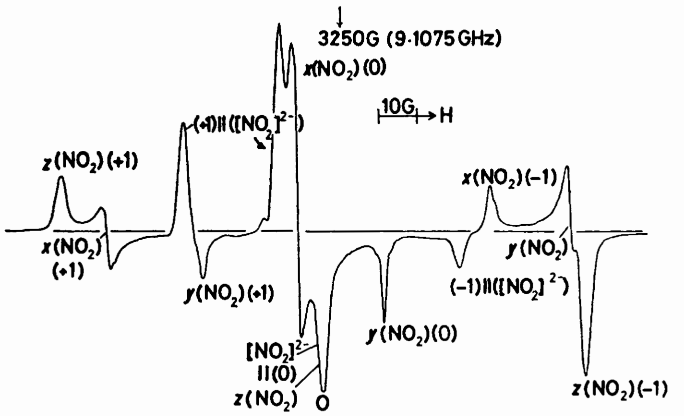


FIGURE 1 First-derivative *X*-band e.s.r. spectrum for K[NO_2] after exposure to ^{60}Co γ-rays at 77 K for 0.1 h, showing features assigned to $NO_2^{\cdot}$ and $[NO_2^{\cdot}]^{2-}$ radicals

One aspect of the spectrum for NO_2 in Na[NO_2] is noteworthy, namely that the outermost (z) features are far broader than the x and y features (Figure 2). A second-derivative spectrum was best analysed in terms of an extra triplet splitting, although the definition was poor [Figure 2(*b*)]. This seems to rule out the possibility of hyperfine coupling to ^{23}Na. Also, such interactions with neighbouring cations are usually almost isotropic because of the dominance of electron transfer into the outer *s* orbitals of the cations, whereas the present interaction is clearly extremely anisotropic. I tentatively suggest a very weak coupling to a neighbouring $[NO_2]^-$ ion. Because of the large difference in bond angle between NO_2 (*ca.* 134°) and $[NO_2]^-$ (*ca.* 120°), it seems reasonable to postulate that an $NO_2 \cdots [NO_2]^-$ pair could remain quite unsymmetrical on the e.s.r. time scale. (The relative orientations are wrong for the formation of $[N_2O_4]^-$.[7])

Annealing at >77 K.—On annealing, the spectra for both salts initially broadened reversibly, presumably because of the onset of significant librational or rotational motion. Later, there was a marked decrease in intensity, the loss of NO_2 being greater than that of $[NO_2]^{2-}$. However, as the features for NO_2 and $[NO_2]^{2-}$ were lost a new signal was detected (radical A) (Figure 3). These overlap with the $M_I = 0$ component for NO_2, but are much narrower and hence can be located with reasonable accuracy. The e.s.r. spectra obtained after exposure at room temperature were similar to those obtained on annealing. Samples containing nitrate ions gave radical B in addition to A, both sets of features appearing simultaneously (Figure 3). Features from $NO_2^{\cdot}$ were suppressed or hidden under these conditions.

E.s.r. data for radicals trapped in K[NO_2] and Na[NO_2]

Host	Radical	^{14}N Hyperfine coupling/G A_x	A_y	A_z	$A_{iso.}$	g_x	g_y	g_z
K[NO_2]	$NO_2^{\cdot}$	50.0	47.6	68.0	55.2	2.005 7	1.992	2.002 0
Na[NO_2]	$NO_2^{\cdot}$	49.0	46.4	67.5	54.3	2.005 7	1.992	2.002 0
K[NO_2]	$[NO_2]^{2-}$	36.0	*ca.* (−) 2	*ca.* (−) 2	*ca.* 11	2.002 0	*ca.* 2.007 3	*ca.* 2.007 3
K[N_3]–K[NO_3] [a]	$[NO_2]^{2-}$	37.2	(−) 4.3	(−) 4.3	9.5	2.002 9	2.007 1	2.007 8
K[NO_2]	$[N_2O_4]^{3-}$ (A)	8	6	2	5.3	2.005 0	2.007 5	2.006 2
Na[NO_2]	$[N_2O_4]^{3-}$ (A)	8	*b*	*b*		2.005 0	*b*	*b*
Na[NO_2] [c]	$[N_2O_4]^{3-}$	8	2	2	4	2.005 5	2.004 7	2.014 2
N_2O_4 [d]	$[N_2O_4]^-$	51.9	47.1	56.4	51.8	2.003 1	1.991 5	2.003 0
K[NO_2]	$[NO_3^{\cdot}]^{2-}$ (B)	64	30	30	41.3			
Na[NO_2]	$[NO_3^{\cdot}]^{2-}$ (B)	62	30	30	40.7			
e	$[NO_3^{\cdot}]^{2-}$	61.4	30.2	30.2	40.6	1.997 6	2.004 1	2.004 1

[a] A. Reuveni, R. Poupko, and Z. Luz, *J. Magnetic Resonance*, 1975, **18**, 358. [b] Unresolved. [c] Ref. 5: identified as $[N_2O_4]^-$ therein. [d] Ref. 8. [e] Ref. 12.

Radical B. Features for B were much broader for the sodium than for the potassium salt. This again suggests the presence of unresolved superhyperfine coupling to a group of ^{23}Na nuclei. For species A in the potassium salt quite accurate parameters could be derived from the outer features (Table). These agree reasonably with those reported for Na[NO_2] after exposure at room temperature,[5,6] if one allows for some libratory averaging of the room-temperature spectra. However, the data are not characteristic of $NO_2^{\cdot}$ radicals, and I am puzzled by the previous identification of the species as $NO_2^{\bullet}$.[5,6] In my view, the species is $[NO_3^{\bullet}]^{2-}$, as can be judged by comparison with data for this radical obtained from nitrate ions (Table). The fact that B was not obtained when fresh high-grade samples were used confirms this identification and suggests that impure samples were used previously; $[NO_3^{\bullet}]^{2-}$ radicals were presumably formed from $[NO_2^{\bullet}]^{2-}$ [equation (3)]. The fact that $[NO_3^{\bullet}]^{2-}$ ions were formed on annealing doped Na$[NO_2]$ samples strongly supports the initial formation of $[NO_2^{\bullet}]^{2-}$ ions. We have previously shown[11] that

$$[NO_3]^- + [NO_2^{\bullet}]^{2-} \longrightarrow [NO_3^{\bullet}]^{2-} + [NO_2]^- \quad (3)$$

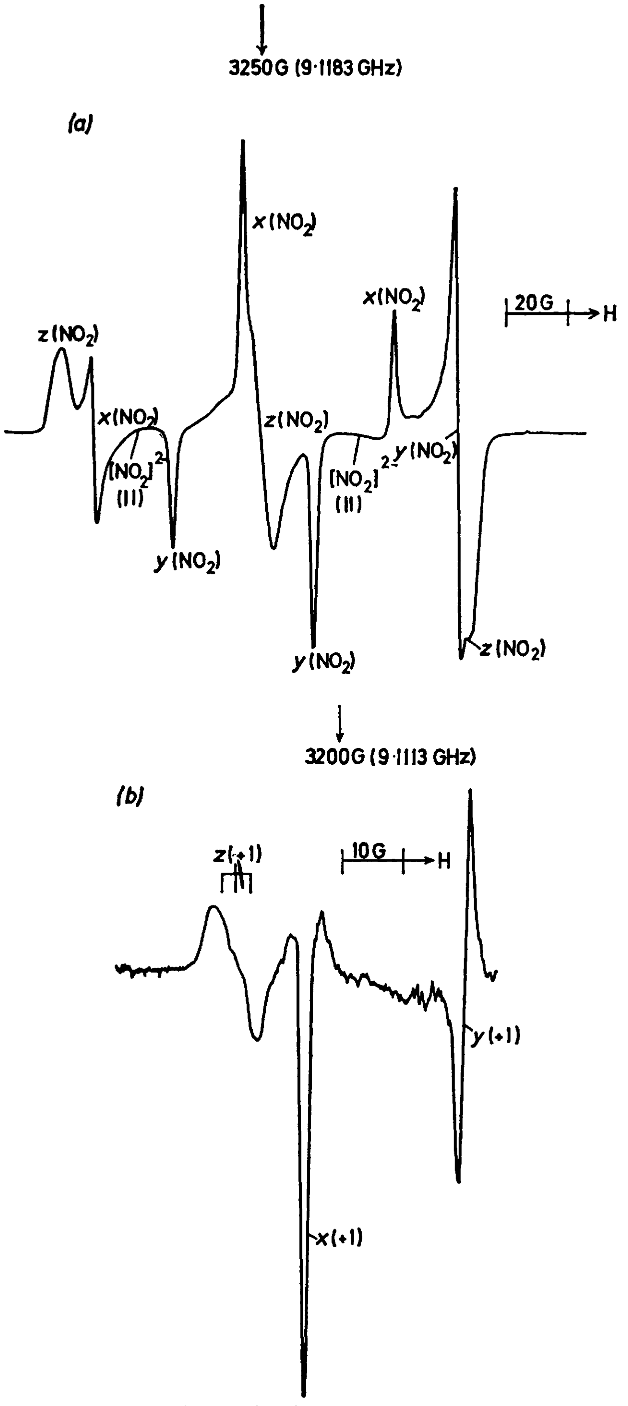


FIGURE 2 (*a*) First-derivative *X*-band e.s.r. spectrum for Na$[NO_2]$ after exposure to ^{60}Co γ-rays at 77 K for 0.5 h, showing features assigned to $NO_2^{\bullet}$ and, possibly, $[NO_2]^{2-}$ radicals. (*b*) A second-derivative spectrum of the (+1) NO_2 features showing possible splitting of the broad *z* component

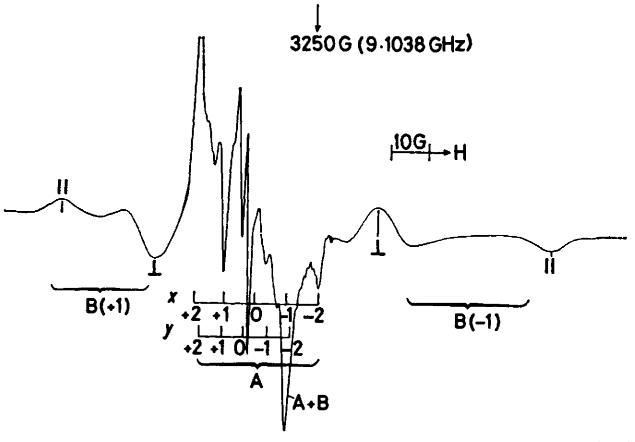


FIGURE 3 First-derivative *X*-band e.s.r. spectrum for K$[NO_2]$ after annealing to *ca.* 200 K and re-cooling to 77 K, showing outer features (B) assigned to $[NO_3^{\bullet}]^{2-}$ radicals and central features (A) assigned to $[N_2O_4]^{3-}$ radicals

$[NO_3^{\bullet}]^{2-}$ ions can be generated from nitrite ions in aqueous alkaline solutions [equation (4)], but clearly nitrate ions are responsible in the crystalline salts.

$$[NO_2]^- + O^{-\bullet} \longrightarrow [NO_3^{\bullet}]^{2-} \quad (4)$$

If $[NO_3^{\bullet}]^{2-}$ is formed from nitrate ions, the postulated movement of the radical thought to be NO_2 is unnecessary (see Figure 4). As stressed above, loss of an electron by nitrite gives $NO_2^{\bullet}$ radicals having their magnetic axes along *b*. However, gain of an extra electron by $[NO_3]^-$ in a nitrite site gives $[NO_3^{\bullet}]^{2-}$ whose magnetic axes are along *a*, as required by the single-crystal data.[5]

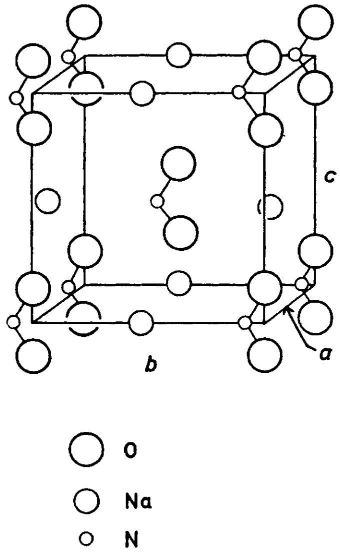
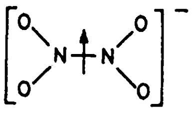


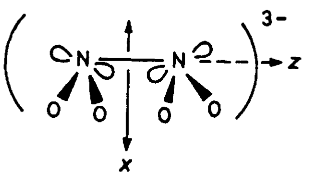
FIGURE 4 Crystal structure of Na$[NO_2]$ at room temperature

Centre A. This centre is clearly the same as that previously thought to be $[N_2O_4]^-$. The quintet at 8 G (z) is reasonably well defined for both salts, but the x and y features are very difficult to extract, almost certainly because the magnitude of the ^{14}N hyperfine coupling is small and significant quadrupole shifts are involved. Unfortunately, in the single-crystal studies, spectra near the x and y axes were so poorly defined that no data are reported, the parameters being derived by an extrapolation. The resulting hyperfine data (Table) must be viewed as being only approximate. The most striking difference between my results and those previously reported is in g_z. The crystal value was extrapolated, but the powder spectral analysis is unsatisfactory in some respects. Nevertheless, I am satisfied that the two species are the same.

If we have correctly identified $[N_2O_4]^-$ in irradiated N_2O_4, then centre A cannot be $[N_2O_4]^-$. Also, if this ion has the expected planar structure (1), the observed ^{14}N coupling constants for centre A are far too small. The only obvious alternative is the unknown radical $[N_2O_4]^{3-}$. The ion $[N_2O_4]^{2-}$ does not exist. However, the $[N_2O_4]^{3-}$ ion probably has structure (2) and, since the N–N bond is weak, electron loss will probably be from the σ orbital. If so, this ion is another example of the relatively rare class of σ^1 radicals. Other examples include $[Ag_2]^+$,[12] $[(MeO)_3B{\cdot}B(OMe)_3]^-$,[13] and $[N_2O_4]^+$.[8]



(1)



(2)

It might be supposed that the observed ^{14}N coupling constants for $[N_2O_4]^{3-}$ would be approximately half those for $[NO_2]^{2-}$ since the structures of $[NO_2]^{2-}$ and $[NO_2]^-$ are expected to be similar, and the unpaired electron is equally divided between the two NO_2 groups. In fact, $A_\parallel(^{14}N)$ for $[N_2O_4]^{3-}$ (centre A) is considerably less than $A_\parallel$ for $[NO_2]^{2-}$ (Table). The simplest explanation for this result is that the planes of the two NO_2 groups are tilted in the manner shown in (2). (This is expected by analogy with the structure of $[S_2O_4]^{2-}$ ions.[14]) If the $2p_\pi$ orbitals on nitrogen remain almost pure $2p$ in the dimer, then the experimental $A_\parallel$ values will be reduced because the parallel field is not along either p orbital. This would result in a concomitant increase in the ^{14}N coupling along the x axis. This is indeed suggested by my interpretation of the powder spectrum. The large positive g shift ($g_{obs.} - 2.002\,3$) obtained from the crystal studies [5] (probably associated with g_y for $[N_2O_4]^{3-}$) is unexpected, since it is apparently greater than that for the parent $[NO_2]^{2-}$ ions (Table). If my analysis of the powder spectrum is correct, the results are more reasonable as can be judged by comparing the data for $[N_2O_4]^{3-}$ and $[NO_2]^{2-}$ in the Table. In fact, $A_{iso.}$ is close to half the value for $[NO_2]^{2-}$ and the smaller, non-axial, anisotropic component is understandable in terms of the tilted structure (2). I am therefore confident that the $[N_2O_4]^{3-}$ postulate is consistent with the data.

If this is accepted, it would seem that the tendency for $[NO_2]^{2-}$ to form $[N_2O_4]^{3-}$ is greater than that for NO_2 to form $[N_2O_4]^-$. This is probably a function of the relative orientations of the parent $[NO_2]^-$ ions, which are ideally placed for $[N_2O_4]^{3-}$ formation (Figure 4) but for which a relative reorientation of 180° is required for $[N_2O_4]^-$ formation.

The fact that $[NO_3]^{2-}$ is formed from $[NO_2]^{2-}$ on annealing, and is then stable at room temperature, shows that electron transfer between $[NO_2]^{2-}$ and $[NO_2]^-$ is relatively easy, and that $[NO_3]^-$ has a greater electron affinity than $[NO_2]^-$. Had radical A been $[N_2O_4]^-$, doping with $[NO_3]^-$ should have increased its yield. In fact, the yield of A was not clearly changed on doping. This shows that it was not formed from $[NO_3]^-$ impurities, but sheds no light on the alternative $[N_2O_4]^-$ and $[N_2O_4]^{3-}$ formulations.

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