An Electron Spin Resonance Study of the Dinitrogen Tetroxide Radical Cation †

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Exposure of dilute solutions of dinitrogen tetroxide in $CFCl_3$ to ^{60}Co γ-rays at 77 K gave the radical cation $[N_2O_4]^+$. The e.s.r. spectrum of this cation closely resembles that for $NO_2^\cdot$, except that $A_{iso}(^{14}N)$ is slightly increased. Small extra splittings are discussed in terms of very weak hyperfine coupling to the second nitrogen. The structure can be thought of as being $NO_2^\cdot$ strongly perturbed by linear NO_2^+ cations. This conclusion is in agreement with recent *ab initio* calculations. The results are compared with previous studies of irradiated crystalline dinitrogen tetroxide.

In our study of radiolysis products in crystalline dinitrogen tetroxide at 77 K [1] we identified $NO_2^\cdot$ as a major product, together with $[N_2O_4]^-$ and a species tentatively identified as $[N_2O_4]^+$. Our major concern was with the radical anion, whose e.s.r. spectrum showed two strongly coupled ^{14}N nuclei. This was interpreted in terms of the σ^* structure (I), the excess electron being accepted into the weak, long N–N bond. Such σ^* radicals are now well established.[2] They are often precursors to dissociative electron capture, and it was suggested that one source of $NO_2^\cdot$ was the dissociation (1).

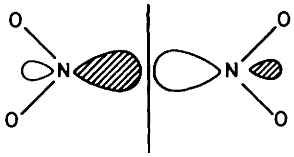
$$N_2O_4 + e^- \longrightarrow [N_2O_4]^- \longrightarrow NO_2^\cdot + NO_2^- \quad (1)$$

The species thought to be $[N_2O_4]^+$ was very poorly defined, the e.s.r. features being largely obscured by intense lines assigned to $NO_2^\cdot$ and $[N_2O_4]^-$ radicals. However, there appeared to be two equivalent ^{14}N nuclei and it was tentatively suggested that the structure was σ, the semi-occupied molecular orbital (s.o.m.o.) being the N–N σ orbital (II). This species was also thought to decompose by reaction (2); the

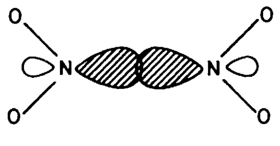
$$[N_2O_4]^+ \longrightarrow NO_2^\cdot + NO_2^+ \quad (2)$$

NO_2^+ cation perturbing the $NO_2^\cdot$ radical sufficiently to make it differ significantly from that formed from $[N_2O_4]^-$. However, even with two different types of $NO_2^\cdot$ radicals, we were unable to explain the appearance of doublet splittings for certain crystal orientations for the species formed initially at 77 K. On annealing the spectra of $NO_2^\cdot$ were greatly simplified, and the data given relate to these modified species.[1]

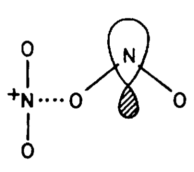
Although there has been considerable controversy regarding the correct interpretation of the photoelectron spectra for dinitrogen tetroxide,[3-6] all workers agree that the first ionization potential (11.4 eV) corresponds to electron loss from the $6a_g$ orbital,[7,8] which is the σ orbital crudely represented in (II). However, Yoshioka and Jordan [9] have recently shown that *ab initio* calculations do not place this as the s.o.m.o for relaxed $[N_2O_4]^+$ radicals. Their calculations suggest that there is a major structural rearrangement to give the low-symmetry species (III), which resembles an $NO_2^\cdot$ radical associated with a linear NO_2^+ cation.[9] The charge density contour diagram for the highest occupied molecular orbital (h.o.m.o.), calculated by Yoshioka and Jordan, is given in Figure 1. Their calculations suggest that the initially formed D_{2h} structure, (II), is 1.56 eV above that of the cation–radical complex, (III), the dissociation energy for the D_{2h} structure being only 0.54 eV to give $NO_2^\cdot + NO_2^+$. The bond angles and bond lengths for the $NO_2^\cdot$ and NO_2^+ portions of the stable structure, (III), closely resemble those of the separate species, and it seems that the weak bonding between them is dominated by charge-quadrupole and charge-induced dipole interactions.[9]



(I)



(II)



(III)

In view of these calculations it seemed probable that at least one of the $NO_2^\cdot$-like species detected in irradiated dinitrogen tetroxide might have been $[N_2O_4]^+$ in the ion–radical structure, (III). We therefore decided to prepare the cation separately from all the other species formed in the pure compound. This was accomplished by irradiating very dilute solutions of the tetroxide in trichlorofluoromethane at 77 K. It is now well established that this solvent reacts efficiently with electrons ejected in the radiation process, but that the hole centres are mobile *via* electron transfer, and will react with any substrate whose ionization potential is less than *ca.* 11.8 eV. This technique has been used in the production of alkane cations,[10,11] ether cations,[12,13] aldehyde and ketone cations,[14] and many other novel organic and organometallic radical cations, but has not previously been used to form inorganic cations.

Experimental

Solutions were prepared by passing nitrogen dioxide gas into trichlorofluoromethane. Samples were frozen to 77 K to obtain N_2O_4 and they were exposed to ^{60}Co γ-rays at this temperature in a Vickrad source to doses of *ca.* 1 Mrad.

E.s.r. spectra were recorded on a Varian E 109 *X*-band spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker BH 12E field probe, which were standardized with a sample of diphenylpicrylhydrazyl (dpph). Samples were annealed using a Varian variable-temperature accessory or simply by decanting the liquid nitrogen from the

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† *Non-S.I. units employed:* 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T; 1 eV $\approx 1.60 \times 10^{-19}$ J.

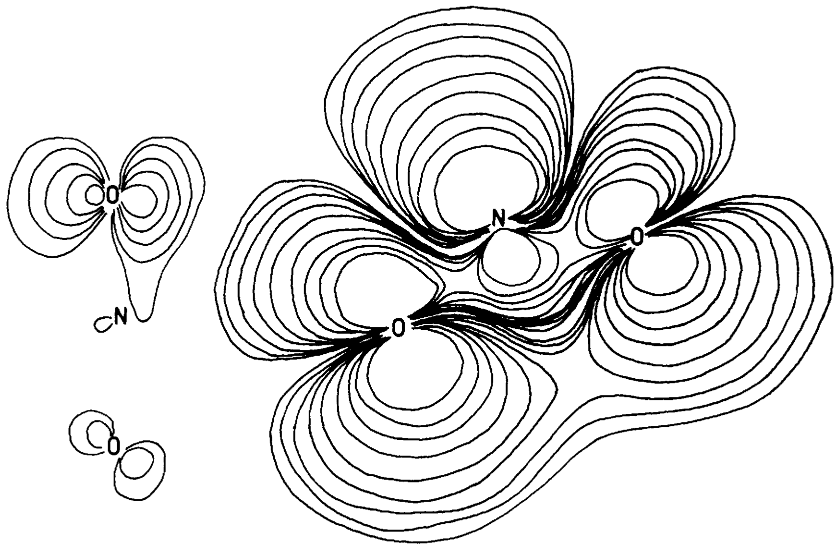

Figure 1. The charge density contour diagram for the s.o.m.o. of the $[N_2O_4]^+$ cation (reproduced from ref. 9)

insert dewar and recooling to 77 K wherever significant spectral changes were observed.

Results and Discussion

In our experience, any e.s.r. signals derived from the solute in experiments of this type must either be due to the parent cations or to unimolecular breakdown products thereof. The form of the e.s.r. spectrum obtained from the tetroxide is remarkably similar to that for $NO_2^{\bullet}$ radicals (Figure 2). The derived e.s.r. parameters given in the Table show that, relative to the gas-phase $NO_2^{\bullet}$ radical, the *g*-tensor components are closely similar but there is a clear increase of *ca.* 6 G in $A_{iso.}$ corresponding to an increase in estimated 2*s* character[15] from *ca.* 9.56 to *ca.* 10.7%. However, there is a fall in the anisotropic coupling (2*B*) which corresponds to a reduction from *ca.* 45.4% $2p_z$ character to *ca.* 31.2%. Thus there is a fall in total spin density of *ca.* 13%. Unfortunately we cannot judge if this corresponds to an increase in density on the two oxygen atoms of the $NO_2^{\bullet}$ group or to a transference of spin density on to the NO_2^+ unit. Probably both changes are involved. The reduction in estimated *p*/*s* ratio suggests a small decrease in the ONO angle relative to $NO_2^{\bullet}$ radicals. The calculations do not indicate such a reduction.

One curious aspect of the e.s.r. spectra (Figure 2) is that most of the features appear as doublets with splitting in the range 2—5 G. We have previously suggested that a small extra doublet splitting observed in a spectrum assigned to $[C_2F_4]^+$ cations may be due to an intermolecular interaction with a fluorine atom in a neighbouring $CFCl_3$ molecule.[16] To check on this possibility we prepared $[N_2O_4]^+$ in tetrachloromethane, but unfortunately the features were so broad that the small doublet splitting was not resolved. However, the linewidths did suggest that this splitting was still present. We therefore adopted the alternative approach of generating genuine $NO_2^{\bullet}$ radicals in $CFCl_3$. This was accomplished by photolysing dilute solutions of nitromethane in this solvent. The resulting e.s.r. spectra for $NO_2^{\bullet}$ were completely normal (Table), being almost identical to those for $NO_2^{\bullet}$ in alkali-metal halide crystals. The features are quite narrow (Figure 3) and, in particular, there are no extra doublet splittings. Note that $A_{iso.}$ has increased relative to the gas-phase value, but remains significantly less than that assigned to $[N_2O_4]^+$.

We therefore favour the alternative possibility that the

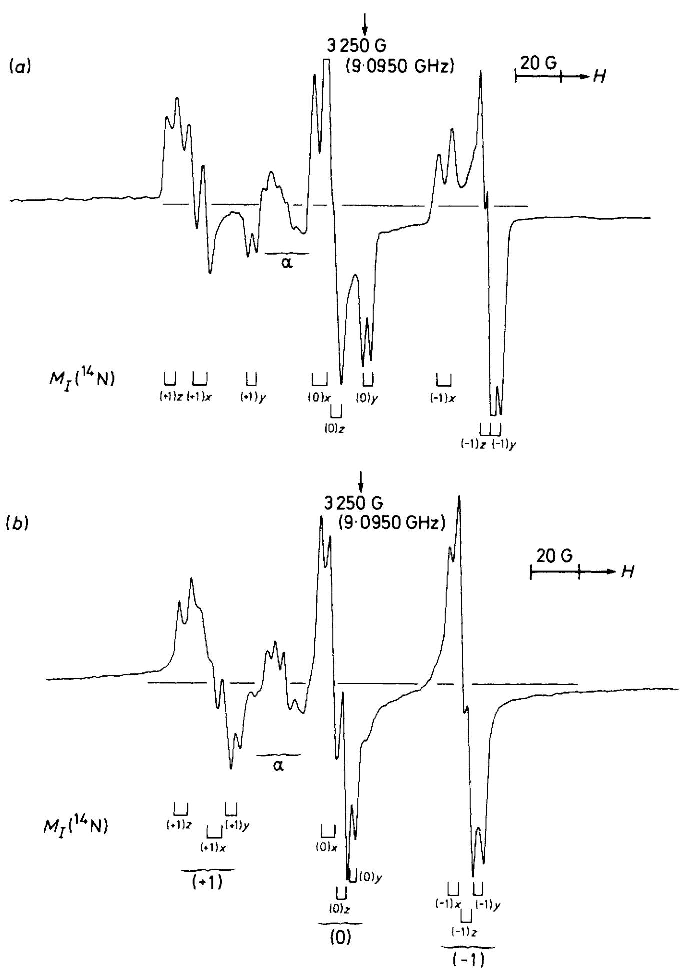

Figure 2. First derivative *X*-band e.s.r. spectrum for a dilute solution of dinitrogen tetroxide in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K: (*a*) showing features assigned to the dinitrogen tetroxide cation radical, and (*b*) after annealing to 162 K and recooling to 77 K, showing features assigned to the rearranged cation. The features marked α are due to an impurity in the solvent which is very difficult to remove

Table.

Radical	Matrix (77 K)	^{14}N hyperfine coupling (G)				g Values[a]		
		A_x	A_y	A_z	$A_{iso.}$	g_x	g_y	g_z
$[N_2O_4]^+$	$CFCl_3$	54	53	69	58.7	2.0066	2.0017	1.9914
$[N_2O_4]^+$	$CFCl_3$[b]	54	54	63	57.0	2.0060	2.0017	1.9980
$NO_2^{\cdot}$[c]	Gas phase	46.13	44.88	66.76	52.59	2.0062	2.0020	1.9910
$NO_2^{\cdot}$[d]	N_2O_4	47.8	45.9	64.7	52.8	2.0050	2.0021	1.9920
$NO_2^{\cdot}$[e]	$CFCl_3$	51.1	48.7	70.9	56.9	2.0055	2.0020	1.9920

[a] Since $[N_2O_4]^+$ has only C_s symmetry the g- and A-tensor components do not necessarily share common axes. However, the similarity of the derived values to those for $NO_2^{\cdot}$ radicals suggests that they must be close if not equal. [b] After annealing. [c] R. M. Lees, R. F. Curl, jun., and J. G. Baker, *J. Chem. Phys.*, 1966, **45**, 2037. [d] Ref. 1. [e] From $MeNO_2$ (Figure 3).

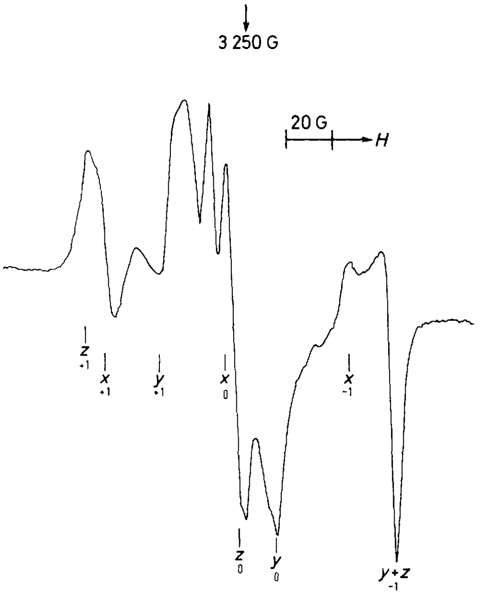

Figure 3. First derivative X-band e.s.r. spectrum of $NO_2^{\cdot}$ radicals in $CFCl_3$

splitting is due to coupling to the ^{14}N nucleus of the NO_2^+ unit. This splitting would normally be a 1 : 1 : 1 triplet but three factors could lead to doublets in the present case. One is that there is a very strong linear electric field for NO_2^+ which will exert a strong aligning effect on the quadrupolar ^{14}N nucleus. Another is that the directions for the turning points observed in the powder spectrum correspond to those for the g- and A-tensors for the $NO_2^{\cdot}$ unit which are not expected to be near the principal values for the ^{14}N coupling for the NO_2^+ unit. Hence the splitting observed will be for directions well removed from the principal directions. The third factor is that when the hyperfine coupling energy is small, as must be the case for this radical, the quadrupole effect may dominate and in off-axis directions a doublet is then often observed rather than a triplet. We suggest that this is the reason why doublets appear in the present case. It is important to note that doublets with similar splittings were frequently seen for one of the ' $NO_2^{\cdot}$ ' centres in N_2O_4 crystals.[1]

The decrease in spin density and increase in $A_{iso.}(^{14}N)$ for the $NO_2^{\cdot}$ unit strongly suggests that this centre is not $NO_2^{\cdot}$ formed according to reaction (2). In our extensive studies of environmental effects on $NO_2^{\cdot}$ in various matrices,[17] we observed that strongly interacting matrices do give rise to a small increase in $A_{iso.}$, the maximum value being 60.6 G for $NO_2^{\cdot}$ in $La_2[Mg_3(NO_3)_{12}]\cdot 24H_2O$.[18] However there is no major loss in total spin density for non-liberating radicals. It is possible, but unlikely, that the large fall in $2B$ for the $[N_2O_4]^+$ cation is due to libratory motion. This is unlikely since the range of g values is actually greater than that for $NO_2^{\cdot}$ radicals. Furthermore, heating did not cause any immediate further reduction in the $2B$ term. There was however, an irreversible change in the spectrum after annealing to *ca.* 162 K and recooling to 77 K, as shown in Figure 2(*b*). Clearly the overall anisotropies in both g and A have been reduced and there seems to have been a small decrease in $A_{iso.}$. Remarkably, the small doublet splittings remain almost unchanged, suggesting that NO_2^+ is still present. We suggest that some rearrangement of structure has occurred but that the $NO_2^{\cdot}$ and NO_2^+ units have not been separated.

Radicals in Dinitrogen Tetroxide.—It seems probable that at least one of the species originally described as $NO_2^{\cdot}$ in irradiated dinitrogen tetroxide[1] was, in fact, the radical cation, $[N_2O_4]^+$. Unfortunately, the initial spectra at 77 K were too complicated for unambiguous interpretation but several of the single-crystal spectra revealed the presence of closely spaced doublets similar to those obtained herein, which we suggest are due to the NO_2^+ unit in $[N_2O_4]^+$. The species formed on annealing is clearly $NO_2^{\cdot}$ separated from the NO_2^+ ion, as can be judged from the data given in the Table.

If this is correct, then the species described as $[N_2O_4]^+$ with D_{2h} symmetry must have been the precursor to the C_s species. Our results for $[N_2O_4]^+$ in $CFCl_3$ suggest that the barrier to the conversion $D_{2h} \longrightarrow C_s$ is low in this matrix, since there was no sign of the σ radical, (II). It is possible that the initially formed cation is more stable in the crystalline N_2O_4 matrix since it retains the shape of the parent molecules. Thus we suggest that in the radiolysis some D_{2h} cations were able to rearrange to the stable C_s structure, whilst others were trapped as such in the crystal lattice.

Acknowledgements

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