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RADICAL CATIONS OF ORGANIC NITRO-DERIVATIVES

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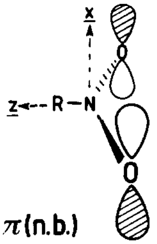
Summary: Attempts to generate the radical cations of nitroalkanes using the standard procedure of exposing dilute solutions in fluorotrichloromethane at 77 K to ionizing radiation gave low yields of the expected products, having a SOMO confined to oxygen as judged by their e.s.r. spectra, together with a species whose e.s.r. spectra closely resembles that of NO_2 radicals. It is suggested that these are rearranged cations, $(O\dot{N}OR)^+$. Similar treatment of nitrobenzene and a range of its ring-substituted derivatives gave initial electron loss from benzene π orbitals, but on annealing these rearranged into radicals similar to those for the nitroalkanes.

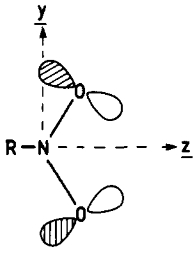
Although nitroalkane and nitroarane radical anions have been extensively studied by e.s.r. spectroscopy, we know of no reports concerning the e.s.r. spectra of the corresponding radical cations. According to theory, and to the results of photoelectron spectroscopy,[1,2] the SOMO for the nitroalkanes is expected to be confined to the two oxygen atoms. There are three possible orbitals [π(n.b.), n and n*] which should be close in energy, as indicated in I, II and III.

I



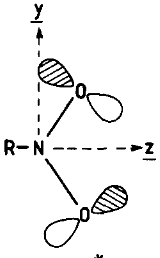
π(n.b.)

II



n

III



n*

The expected situation is thus similar to that found for nitrates, where electron addition to give $\cdot NO_3^{2-}$ results in conversion from a planar to a pyramidal structure, the excess electron being primarily on nitrogen, whilst electron-loss gives $NO_3\cdot$, the electron being in a combination of in-plane oxygen orbitals.[3,4]

It was therefore a surprise to find that the e.s.r. spectra for a range of nitroalkanes which had been treated by a procedure which has proven to be ideal for the generation of radical-cations from neutral molecules, gave the expected cations only in low yields at 77 K, the dominant species detected by e.s.r. spectroscopy being species with spectra closely resembling that of $\cdot NO_2$.

The preparative procedure comprises exposing very dilute solutions of the nitro-derivatives in solvents such as fluorotrichloromethane to ^{60}Co γ-rays at 77 K. Electrons, ejected from $FCCl_3$ molecules are efficiently trapped by the solvent, thus prohibiting electron-capture by solute molecules, whereas the $(FCCl_3)^+$ cations are mobile via electron transfer and will react with solute molecules provided their electron affinities are less than ca. 11.8 eV.[5-8] In most cases, primary cations are detected. However, we have found that proton, or hydrogen-atom transfer is common, even at 77 K, if the SOMO is localised and C-H groups are in sterically favourable sites.

Structure of the Primary Cations of Nitroalkanes: Typical e.s.r. spectra assigned to RNO_2^+ ions are shown in Figure 1, and the parameters derived therefrom are given in the Table. As expected for structures I, II or III, the ^{14}N hyperfine coupling is small, since it is due, primarily, to spin-polarisation of the O-N σ electrons.[4] For all these structures, two g-components are expected to be greater than 2.0023 since the half-filled SOMO is coupled to one or other of the filled orbitals by field in the radial plane. For III, the orbital thought to be favoured for the SOMO of the cation,[1,2] or for II, g_{min} should be along x and slightly greater than 2.0023, and considerably less than g_x or g_y. For I, g_{min} should be along x but should be equal to

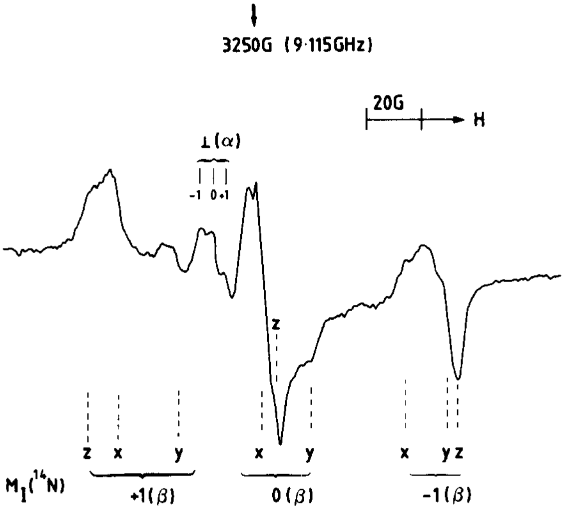


Figure 1

First derivative X band e.s.r. spectrum for a dilute solution of nitromethane in $FCCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features (α) assigned to $(R\text{-}NO_2\cdot)^+$ cations and (β) assigned to the re-arranged cations $(O\text{-}\dot{N}OR)^+$.

TABLE: ESR Parameters for Radical-Cations of Nitroalkanes and NO_2

Radical	^{14}N Hyperfine Coupling Constants[a]				g-values		
	A_x	A_y	A_z	A_{iso}	g_x	g_y	g_z
NO_2[b]	46.13	44.8	66.76	52.56	2.0062	1.9910	2.0020
$MeONO^+$[c]	52.5	44.9	66.2	54.5	2.005	1.994	2.002
$EtONO^+$[c]	52.0	44.7	66.8	54.5	2.0050	1.9935	2.0020
$MeNO_2^+$	3.0	3.0	d	-	2.016	2.016	ca. 2.002

(a) G = 10^{-4} T; (b) NO_2 in gas phase;
(c) Not precisely equal to principal values since symmetry does not require that the g- and A- tensors will share principal axes;
(d) Features hidden under $M_I = 0$ component for $MeONO^+$.

2.0023. Unfortunately, this species was always a minor component at 77 K and we have only been able to detect the low-field features, so no clear distinction between these structures can be drawn on the basis of the e.s.r. data.

Structure of the NO_2-type species: Although the ^{14}N hyperfine coupling components and g-tensor components derived approximately from the powder spectra are remarkably close to those for $\cdot NO_2$ radicals (Table), we consider that formation of NO_2 radicals is highly unlikely in these experiments. For example, for $(MeNO_2)^+$ ions to give $\cdot NO_2$ radicals would require the formation of CH_3^+ ions, which is energetically most improbable:

$$(MeNO_2)^+ \longrightarrow Me^+ + \cdot NO_2 \, . \qquad .... \; [1]$$

We recall that the isoelectronic radicals $RCO_2\cdot$ decompose readily, usually at temperatures well below 77 K:

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \, , \qquad .... \; [2]$$

a major part of the driving force being the high stability of linear CO_2 molecules. A similar reaction for $(RNO_2)^+$ cations would give $R\cdot + NO_2^+$, but alkyl radicals, $R\cdot$, were not detected. We suggest that instead of giving separate fragments, incipient C-N bond fission is followed by rearrangement to give $(O\dot{N}OR)^+$ cations. Although these cations have not previously been detected, their $A(^{14}N)$ and g-tensor components are expected to be close to those for $\cdot NO_2$, except that $A_{iso}(^{14}N)$ should be somewhat enhanced for $(O\dot{N}OR)^+$ radicals for the same reason that small, highly charged cations enhance the ^{13}C coupling for $\cdot CO_2^-$ ions,[9] as, indeed, does alkyl substitution on oxygen.[10] In fact, data now assigned to $(O\dot{N}OR)^+$ cations do show slightly enhanced isotropic coupling constants. Unfortunately, there is no sign of proton hyperfine coupling, so delocalisation onto the alkyl groups must be small, if this assignment is correct.

In particular, we note that the spectrum for irradiated solutions of $(CH_3)_3CNO_2$ differed from the remainder, but this difference can be understood in terms of rotation or libration of the $-O\dot{N}O$ unit. For the ethyl derivative, despite all attempts to remove impurities, another radical was detected in yields comparable with that for the $(O\dot{N}OR)^+$ radicals. Although the spectra were well defined, we have not been able to identify this species, but we hope to by using ^2H and ^{13}C labelled starting material. These results will be reported later.

Aryl derivatives: The e.s.r. spectrum assigned to $(PhNO_2)^+$ at 77 K was poorly defined, but was undoubtedly due to major electron-loss from the benzene ring. That for the *para*-methyl derivative was better defined, showing a well-resolved 1:3:3:1 quartet due to coupling to the methyl protons (Figure 2). Thus the SOMO must be similar to that for the toluene cation, since the methyl proton coupling (20 G) is close to that for toluene cations (18 G).[11] However, features characteristic of $RNO_2\cdot^+$ cations, having a SOMO confined to oxygen were also detected, and these grew in intensity on warming. NO_2-like features appeared (Figure 2*b*).

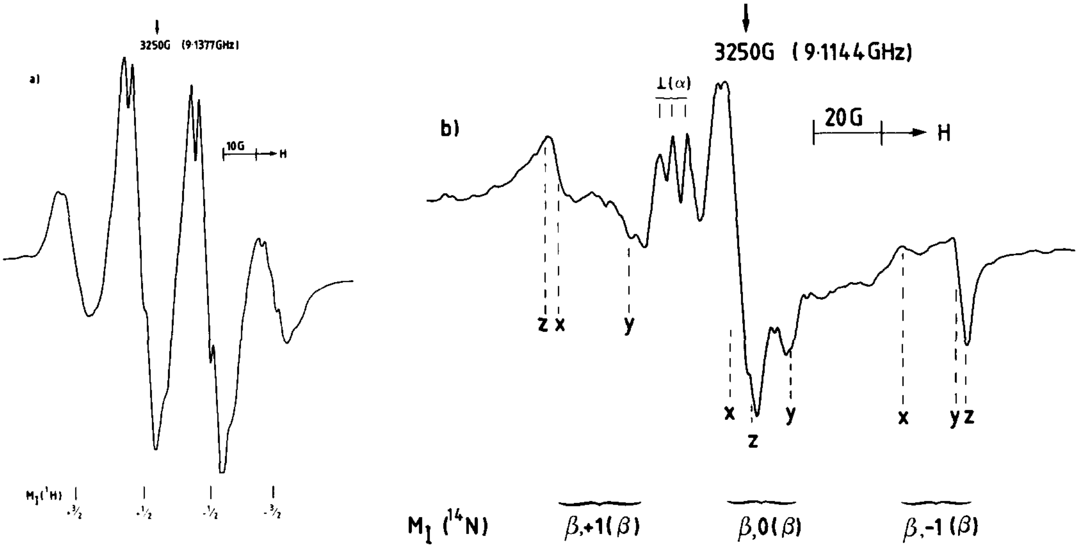


Figure 2

E.s.r. spectrum for (*a*) *p*-nitrotoluene and (*b*) nitrobenzene in $FCCl_3$ after exposure to ^{60}Co γ-rays at 77 K, (*a*) showing features assigned to the parent cations. The major quartet splitting (20 G) is due to hyperfine coupling to the methyl protons. In (*b*) the primary cations have been converted on annealing into cations in which the SOMO is confined to oxygen (α) and rearranged cations $(O\dot{N}OAr)^+$ (β).

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