Radical Cations of Nitroso Derivatives

A Radiation-chemical and Electron Spin Resonance Study

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Exposure of dilute solutions containing nitrosobenzene in trichlorofluoromethane to ⁶⁰Co γ -rays at 77 K gave the corresponding radical cation, characterised by e.s.r. spectroscopy. The results confirm the interpretation of liquid-phase data assigned to this cation, which showed that loss is from an in-plane σ -orbital localised on nitrogen and oxygen, rather than from the aromatic π -system. However, solutions containing the t-butyl derivative in equilibrium with its dimer,(Me₃CNO)₂, gave primarily the dimer cation, (Me₃CNO)[±]₂, with possible traces of the monomer cation. The e.s.r. data for the latter resemble those for the nitrosobenzene cation, whereas results for the dimer cation suggest that loss is from a π -type orbital with very low spin density on the two equivalent nitrogen atoms.

Some years ago Cauquis *et al.*¹ studied liquid-phase e.s.r. spectra assigned to nitrosobenzene cations and various derivatives thereof, and suggested that the SOMO lies in the plane of the benzene ring as in (I), rather than being a π -SOMO as is found



for the corresponding radical anions.² Thus the SOMO closely resembles those of ${}^{*}NO_{2}$ and of the iminoxy radicals (II).^{3,4} No solid-state spectra for this interesting class of radical has been reported to our knowledge, and we therefore thought it of interest to use the new 'freon' solution method for preparing these cations unambiguously.⁵ This technique involves exposing very dilute solutions of the substrate in solvents such as CFCl₃ to ionizing radiation at low temperatures. The solid-state reactions involved are summarised in reactions (1)–(4), which are self-explanatory, X being any substrate with an ionization potential less than that for the solvent (*ca.* 11.8 eV in this case):

$$CFCl_3 \rightarrow CFCl_3^{+} + e^- \tag{1}$$

$$e^{-} + CFCl_{3} \rightarrow (CFCl_{3})^{-} \rightarrow \dot{C}FCl_{2} + Cl^{-}$$
⁽²⁾

$$CFCl_3^{*+} + CFCl_3 \to CFCl_3 + CFCl_3^{*+}$$
(3)

$$CFCl_3^{*+} + X \to CFCl_3 + X^{*+}$$
(4)

We also attempted to prepare an alkyl derivative, and selected $(CH_3)_3C$ —NO as being the most likely candidate. The problem with nitrosoalkanes is that they readily dimerise, even in dilute solution. For Me₃C—NO, dimerisation is sterically inhibited, but, even so, at low temperatures we have found it impossible to avoid some dimer formation. Hence, perforce, we have also studied the radical cation of $(Me_3CNO)_2$, the e.s.r. results making an interesting contrast with those for the monomer cations.

Experimental

Nitrosobenzene (Aldrich) and 2,2'-dimethyl-2-nitrosopropane (Me₃CNO, Aldrich) were dissolved in purified, degassed CFCl₃ (Fluka) and frozen as small beads in liquid nitrogen. A range of concentrations in the region of 0.01 mole fraction were used, and the Me₃CNO beads were blue, indicating the presence of a considerable proportion of the monomer at 77 K.

Samples were exposed to ⁶⁰CO γ -rays at 77 K in a Vickrad source with doses up to *ca*. 2 Mrad. E.s.r. spectra were measured using an X-band Varian E-109 spectrometer at 77 K. Samples were annealed by decanting the coolant and monitoring the e.s.r. spectra as the sample temperature increased. Samples were recooled to 77 K when significant spectral changes occurred.

Q-Band spectra were measured using a Bruker ER-200 spectrometer with a specially adapted gas-flow cryostat which enabled us to obtain spectra at ca. 90 K without annealing the irradiated samples above this temperature during transfer.

Results and Discussion

Nitrosobenzene

The Q-band spectrum (fig. 1) was far better defined than that at X-band, although there was reasonable agreement in the extracted data. It is not obvious why this should be the case, but it may be connected with the lack of symmetry of the cation, such that the g and (¹⁴N) A tensors only share one common axis. This may be responsible for the unusual strength of the features marked +1(x) and -1(x, y) in fig. 1. The ¹⁴N isotropic coupling extracted from these spectra (ca. 34 G) is close to the liquid-phase value (37 G), but significantly reduced, and we were not able to fit the spectra using 37 G. It seems probable that A_{iso} is temperature dependent, reflecting a small increase in the average C—N—O angle on cooling. However, it is clear from the results that structure (I) is correct, the SOMO being in the benzene plane with relatively high 2s-character on nitrogen.

2,2'-Dimethyl-2-nitrosopropane Dimers

Although the very dilute solutions used contained largely monomer units at room temperature and, judging from the colour, also in the frozen state, nevertheless the major cation formed was always the dimer, $(Me_3CNO)_2^{++}$. This can be judged from fig. 2(*a*) and (*b*), which show that coupling to ¹⁴N is very small, in marked contrast with the results for PhNO⁺, and that there are two equivalent nitrogen atoms, giving rise to the quintet splitting of the *x* feature. This preference reflects the smaller ionisation potential for the dimer, as revealed by photoelectron spectroscopy of the methyl derivative [MeNO, 9.68 eV; (MeNO)₂, 8.63 eV]. We expect the t-butyl derivative to follow the same trend. In unpublished work we have established that when two substrates are present, that with lower ionisation potential preferentially forms the cation under our conditions, even when it is the minor constituent. However, these studies also suggest that the other cation should be present in low, but detectable concentration.

We therefore increased the gain in the regions in which the $M_1(^{14}N) = \pm 1$ features were expected, and invariably obtained features identical with those shown in fig. 2(c). Exposure to visible light decreased the concentration of the dimer cation, but with little significant gain in the outer features. The resulting data (table 1) are sufficiently close to those for PhNO⁺ cations that we have some confidence therein.



Fig. 1. First-derivative Q-band e.s.r. spectrum for nitrosobenzene in CFCl₃ after exposure to ⁶⁰Co *y*-rays at 77 K, showing features assigned to the radical cation, PhNO⁺,

Aspects of Structure

If the results assigned to Me_3CNO^+ radicals are correct, there is a clear shift of spin density from nitrogen, presumably to oxygen. This may reflect the change in carbon orbital hybridisation (*ca. sp*² for PhNO⁺ and *ca. sp*³ for Me_3C-NO^+). This will alter the effective energy of the nitrogen $2p(\pi)$ orbital, and, given that the SOMO has antibonding character, the shift in spin density should be as observed. In fact, the form of the HOMO suggested by Kuhn *et al.* for MeNO has the required antibonding character.⁶

The SOMO for the dimer cation is clearly quite different. The structure of the methyl analogue $(trans-azomethanedioxide, (MeNO)_2]$ has been discussed by Kuhn *et al.*,⁶ as well as by Frost *et al.*⁷ It is suggested that the HOMO is as shown in (III), which indicates the upper lobes of the $2p(\pi)$ orbitals involved. Clearly, the major spin density is on oxygen, but there is real π -spin density on nitrogen as well. Our results are in good accord for a SOMO of this form for the dimer cation. The estimated spin density on each nitrogen is *ca.* 10%, leaving 40% on each oxygen, in good accord with structure (III). The very low 2*s*-character on nitrogen establishes the π -character of this orbital. Since

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Fig. 2(a) and (b). For legend see facing page.





Fig. 2. First-derivative e.s.r. spectra for Me_3NO^+ (Me_3NO_2 in CFCl₃ after exposure to ${}^{60}Co \gamma$ -rays at 77 K (a) at X-band at 77 K, showing features assigned to the dimer cation, $(Me_3CNO)_2^{++}$, (b) at Q-band showing increased resolution for the spectrum assigned to $(Me_3CNO)_2^{++}$ cations and (c) at X-band at high gain, after partial photolysis, showing features tentatively assigned to the cation Me_3CNO^+ . The central region contains dimer features.

it is bonding between the two nitrogen atoms, the weak N—N bond of the parent should be strengthened in the cation, which shows no tendency to decompose on annealing to ca. 160 K.



These results show that an orbital switch must occur as dimerisation proceeds, since the SOMO of the parent cation is potentially part of the N–N σ -bond:



For sufficiently long N—N bonds the σ -structure is presumably the more stable. A similar structural dilemma was considered for the dimer cation of 'NO₂, *i.e.* N₂O₄^{++,8,9}. In this case some evidence for the σ -structure was obtained from irradiated N₂O₄ crystals,⁸ but irradiation of N₂O₄ in CFCl₃ gave a rearranged species best represented as (IV).⁹ Furthermore, in the case of MeNO₂⁺⁺ the first-formed species was not the expected cation with major spin density on oxygen, but was the σ -cation (V).¹⁰ This readily rearranged to (VI) on annealing above 77 K. The e.s.r. parameters for the cations (IV) and (VI) closely resembled those for 'NO₂ itself, as expected for these structures.

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			g values	(I4N h	yperfine	e couplir	ng const	ants ^b					
matrix	(<i>T</i> /K)	g,	g	82	A_x	A	Az	$A_{ m iso}$	2B	$a_{s}^{2}(%)$	$a_{p}^{2}(%)$	p/s	(%)(d+s)	ref.
MeNO ₂	(room ature)	2.0()7 (aver:	age)		I	ł	37	I	6.7	I	ļ		q
CFCI ₃ (7	(1)	2.0033	2.002	2.002	25	54	22	34	20	6.1	62	10.1	68.1	с
CFCI ₃ (7	(Ľ	2.004	2.002	2.002	24	4	24	30.7	13.3	5.6	42	7.5	49.5	c, d
gas		2.0062	1.9910	2.002	46.13	4 .8	66.76	52.6	15.4	9.6	45.4	4.75	55	в
CFCI ₃ (7	(1	2.0021	2.0058	2.0113	5.0	0	0	1.7	3.3	0.3 (2N)	10 (2N)	33	20	b, f

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Fig. 3. As for fig. 2, after annealing to ca. 150 K, showing isotropic features assigned to spintrapped $CFCl_2$ radicals.



Clearly, the preferred structures for these species vary widely, but there can be no doubt that for $(RNO)_2^{++}$ dimer cations the basic structure of the parent is retained, the SOMO being the weakly bonding π -orbital (III).

$$(\mathbf{IV}) \cdot \mathbf{N} \stackrel{\mathsf{O}}{\longrightarrow} \stackrel{(\mathbf{V})}{\longrightarrow} H_3 C \overset{\mathsf{O}}{\mathsf{NO}}_2^+ \qquad (\mathbf{VI}) \cdot \mathbf{N} \stackrel{\mathsf{O}}{\longrightarrow} \stackrel{\mathsf{O}}{\overset{\mathsf{O}}{\mathsf{CH}}_3}$$

We also draw attention to the similarity between the $R_3C-\dot{N}O^+$ cations and $R_2N-\dot{N}O$ cations derived from *N*-nitrosodialkylamines.^{11,12} The isotropic hyperfine coupling to the (NO) nitrogen of *ca*. 45 G is significantly increased, suggesting a smaller N-N-O bond angle than the C-N-O angles for the carbon derivatives. This is expected on simple electronegativity arguments on going from carbon to nitrogen substituents.¹³ However, the situation is complicated by the possibility of conjugative π -delocalisation onto the second nitrogen. Nevertheless, the trend in $A_{iso}(^{14}N)$ on going from $R_3C\dot{N}O^+$ to $R_2N-\dot{N}O^+$ and $\dot{N}O_2$ (*ca*. 31 to 45 to 52.6 G) nicely follows the increase in electronegativity of the variable ligand.

Spin Trapping

The monomer, Me_3C —NO, is important as a spin trap in radical chemistry, since it will add a wide range of radicals, X', to give nitroxide radicals, (X) (Me_3C)NO, having characteristic e.s.r spectra. For example, 'CCl₃ radicals add to give (CCl₃) (Me₃C)NO, having A_{iso} (¹⁴N) = 12.7 G and A_{iso} (³⁵Cl) = 2.46 G.¹³ We would not expect (CFCl₃)⁻⁻

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radicals or $(RNO)_2^{++}$ radicals to be able to add in this manner, but $\dot{C}FCl_2$ radicals formed from the parent solvent anions should add readily. This indeed occurred on annealing, with good isotropic spectra appearing just below the softening point of the solids (*ca.* 160 K), as can be seen in fig. 3.

The data $A(^{14}N) = 12.2$ G and $A(^{35}Cl) = 2.2$ G (2Cl) accord well with those for the $-CCl_3$ adduct, and clearly establish the presence of two equivalent chlorine atoms. Thus dissociative electron capture must occur at some stage in this system.

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