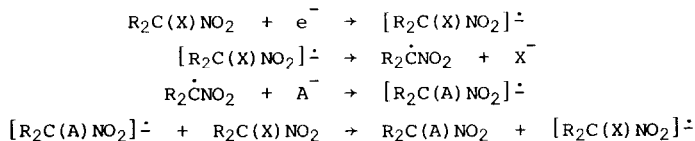ELECTRON SPIN RESONANCE STUDIES OF ELECTRON ADDITION TO 2-CHLORO- AND 2-BROMO-2-NITROPROPANE

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Summary: The products of electron addition to 2-chloro- and 2-bromo-2-nitropropane, which include
their radical anions, have been detected by electron spin resonance spectroscopy.
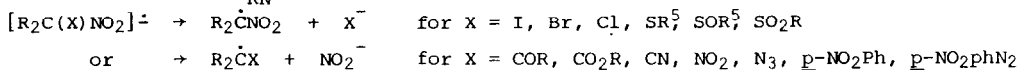
Radical anions of various aliphatic α-substituted nitro compounds have been proposed as
reactive intermediates in radical-anion chain substitution reactions ($S_{RN}1$) (Scheme 1) and other
related reactions.[1,2,3]

Scheme 1

$$R_2C(X)NO_2 + e^- \rightarrow [R_2C(X)NO_2]^{\cdot -}$$
$$[R_2C(X)NO_2]^{\cdot -} \rightarrow R_2\dot{C}NO_2 + X^-$$
$$R_2\dot{C}NO_2 + A^- \rightarrow [R_2C(A)NO_2]^{\cdot -}$$
$$[R_2C(A)NO_2]^{\cdot -} + R_2C(X)NO_2 \rightarrow R_2C(A)NO_2 + [R_2C(X)NO_2]^{\cdot -}$$

These radical-anion intermediates are so unstable that they cannot in general be detected by
ordinary e.s.r. techniques.[1,2,3] They are able to break down in two directions (Scheme 2)
depending on the nature of the α-substituent (X). The subsequent 2-nitropropyl radical and the
radical-anion of $R_2C(A)NO_2$ in the $S_{RN}1$ reaction have in some cases been detected by e.s.r.[4]

Scheme 2 $\quad [R_2C(X)NO_2]^{\cdot -} \rightarrow R_2\dot{C}NO_2 + X^- \quad$ for X = I, Br, Cl, SR,[5] SOR,[5] SO_2R

$\qquad\qquad$ or $\quad \rightarrow R_2\dot{C}X + NO_2^- \quad$ for X = COR, CO_2R, CN, NO_2, N_3, p-NO_2Ph, p-NO_2phN_2

Our studies are aimed at observing these intermediate radical-anions, where the electron adds,
and how they break down. Such information could be invaluable for the further understanding of
the $S_{RN}1$ mechanism, especially for predicting the nucleofugic group (X^- or NO_2^-).

Experimental: Degassed samples were irradiated either in the pure state, or as dilute solutions
(ca. 1% v.v) in methanol (CD_3OD was used to avoid overlap with solvent radical features) or methyl
tetrahydrofuran (MeTHF). They were frozen as small beads in liquid nitrogen and irradiated at 77K
in a Vickrad ^{60}Co γ-ray source to doses of up to 1 Mrad. E.s.r. spectra were measured on a Varian
E109 spectrometer calibrated with proton resonance. Samples were annealed to selected temperatures
or until significant changes occurred in the e.s.r. spectra, and recooled to 77K for study.

Identification of radicals: Both the chloro- and bromo-derivatives gave a species having an
asymmetric triplet spectrum when irradiated in the pure state (Fig. 1). This is undoubtedly due to
·NO_2 radicals rigidly trapped in the solid matrix.[6] The radical $Me_2\dot{C}Br$ is thought to be responsible
for two broad features outside those for ·NO_2 shown in Fig. 1. There are the $M_I = \pm \frac{3}{2}$ features
for coupling to ^{79}Br and ^{81}Br (both have $I = \frac{3}{2}$ and similar magnetic moments). The resulting value
for A_{max} is comparable with those observed for a range of $R_2\dot{C}Br$ radicals.[7] Unfortunately the
radical $Me_2\dot{C}Cl$, almost certainly formed together with ·NO_2 in the radiolysis of pure $Me_2C(Cl)NO_2$,
could not be detected with certainty. This is thought to be because the features are again very
broad (from unresolved coupling to the six protons and a large anisotropy in both g and A) and are
predicted to lie under the intense features due to ·NO_2 radicals.

Table 1. E.s.r. Parameters for radicals formed in the radiolysis of $Me_2(Cl)CNO_2$ and $Me_2(Br)CNO_2$

Compound	Solvent	Radical	Nucleus	A-Values/G [a]			g-Values [a]	
				$A_{//}$	$A_\perp$	A_{iso}	$g_{//}$	$g_\perp$
$Me_2(Cl)CNO_2$	Pure	NO_2	^{14}N	70.2	$\{^{50.6}_{49.7}$	56.8	2.002	$\{^{2.007}_{1.992}$
		$[Me_2\dot{C}NO_2]$	^{14}N	4.3	<4	<4		
			^1H	20.3	20.3	20.3	ca 2.003	ca 2.003
	CD_3OD	$Me_2\dot{C}NO_2$	"	"	"	"	"	"
		$[Me_2(Cl)\dot{C}NO_2^-]$	^{14}N	40	⩾14	⩾22.7	2.003	2.038
			^{35}Cl	11	0±3	0±3		
	MeTHF	$Me_2\dot{C}NO_2$	"	"	"	"	"	"
		$Me_2(Cl)\dot{C}NO_2^-$	^{14}N	40	⩾14	⩾22.7	2.003	2.038
			^{35}Cl	11	0±3	0±3		
$Me_2(Br)CNO_2$	Pure	NO_2	^{14}N	70.2	$\{^{50.6}_{49.7}$	56.8	2.002	$\{^{2.007}_{1.992}$
		$Me_2\dot{C}Br$	$^{79/81}Br$	110G	b	b	2.00	b
	CD_3OD	$Me_2\dot{C}NO_2$	"	"	"	"	"	"
	MeTHF	$Me_2\dot{C}NO_2$	"	"	"	"	"	"
		$Me_2(Br)\dot{C}NO_2^-$	^{14}N	ca 40	b	b	2.005	b
			$^{79/81}Br$	ca 38	b	b		

a $G = 10^{-4}T$ b   Not resolved or concealed by other features.

The major species detected in both MeTHF and CD_3OD glasses (the former after annealing to ca. 100K to remove solvent radicals) had an e.s.r. spectrum comprising a binomical septet of triplets (Fig. 2). This is undoubtedly the radical $Me_2\dot{C}NO_2$, whose e.s.r. parameters (Table 1) are comparable with other radicals of this type[8] The spectra are well defined despite the rigidity of the matrices because all six protons are equivalent and are β to the unpaired electron so that the anisotropic hyperfine coupling is small. To give sharp lines the methyl groups must be rotating rapidly at 77K. Also the ^{14}N coupling is small and fairly isotropic and there is no large variation in the g-values.

On further annealing, for both solvents, the Me_2CNO_2 features were lost irreversibly, revealing weaker features which we assign to the previously unknown radical-anions (Fig. 3). For the bromo-derivative, the outermost features were well removed from those due to $Me_2\dot{C}NO_2$ and other radicals, and we are certain that they were present directly after exposure. For the chloro-derivative the features were initially largely obscured by those for the other radicals, and we cannot be sure that they were present prior to annealing. Our identification of the radical $Me_2C(Cl)\dot{N}O_2^-$ (Fig. 3) rests on the fact that the overall form of the spectrum is very similar to those for simple alkyl nitro radical-anions $(R\dot{N}O_2^-)$[4] The 4 outer $(M_I = \pm 1)$ "parallel" features are clearly split into quartets through coupling to ^{35}Cl and ^{37}Cl nuclei. (They both have $I = \frac{3}{2}$ and similar magnetic moments, separate features are not resolved in our spectra).

Fig. 1 First derivative X-band e.s.r. spectrum for pure $Me_2C(Br)NO_2$ after exposure to ^{60}Co γ-rays at 77K, showing a triplet characteristic of stationary $\cdot NO_2$ radicals, and outer lines assigned to $Me_2\dot{C}Br$ radicals.
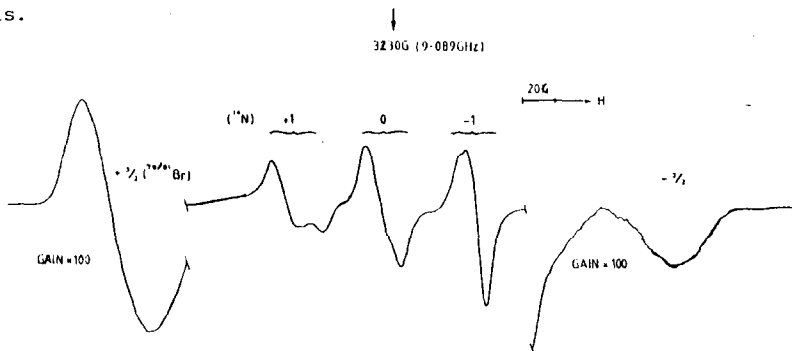

Fig. 2 First derivative X-band e.s.r. spectrum for $Me_2C(Cl)NO_2$ in CD_3OD after exposure to ^{60}Co γ-rays at 77K, showing feature assigned to $Me_2\dot{C}NO_2$ radicals.
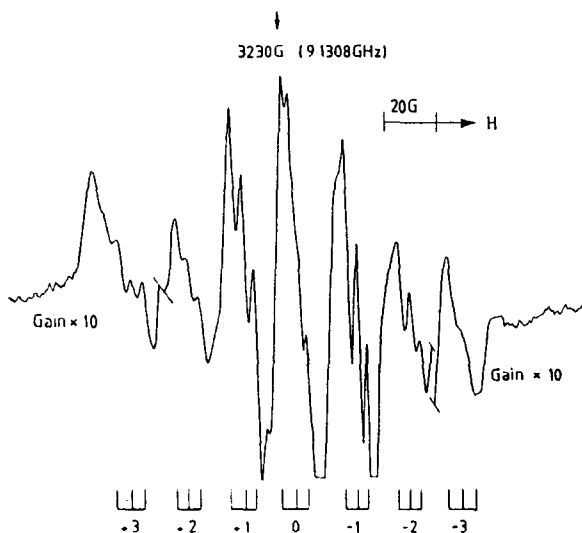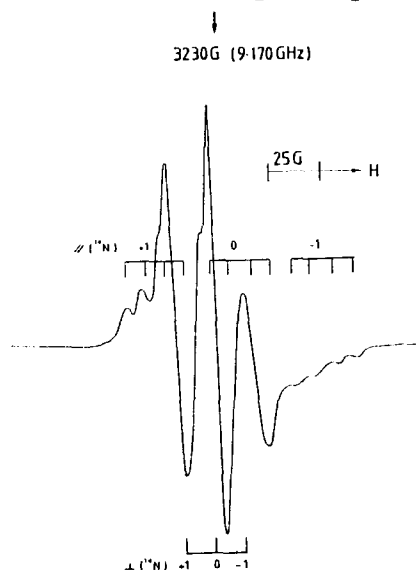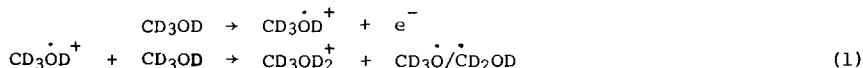
Fig. 3 First derivative X-band e.s.r. spectrum for irradiated $Me_2C(Cl)NO_2$ in MeTHF after annealing to remove solvent radicals and $Me_2\dot{C}NO_2$ radicals, showing features assigned to $Me_2C(Cl)\dot{N}O_2^-$ anions.
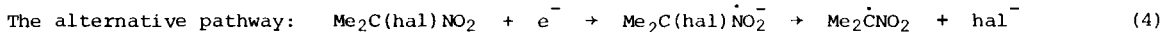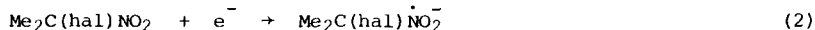

The "perpendicular" $M_I = \pm 1$ features show no resolved coupling to ^{35}Cl and ^{37}Cl. Our derived parameters are given in Table 1. The spectrum assigned to the bromo radical-anion was less well defined, and only the "parallel" or maximum values for the hyperfine coupling could be extracted. Again, coupling to ^{14}N is only slightly reduced from that for simple $R\dot{N}O_2^-$ anions (ca. 44G for $A_{//}$ and 18G for $A_\perp$), and the "parallel" coupling to bromine is similar to that of chlorine after allowing for the increased nuclear magnetic moments.

Radiation Mechanisms: Clearly the dominating reaction in the pure compounds differs completely from those for the solutions. Thus there is no sign of $\cdot NO_2$ in any of the irradiated solutions. For both solvents, it is probable that electron addition is the dominating act, electron loss being indiscriminate, and hence largely from solvent molecules, for example:

$$CD_3OD \rightarrow CD_3\overset{\cdot}{O}D^+ + e^-$$

$$CD_3\overset{\cdot}{O}D^+ + CD_3OD \rightarrow CD_3OD_2^+ + CD_3\overset{\cdot}{O}/\overset{\cdot}{C}D_2OD \tag{1}$$

The results show that two routes are followed on electron capture:

$$Me_2C(hal)NO_2 + e^- \rightarrow Me_2C(hal)\overset{\cdot}{NO_2^-} \tag{2}$$

$$\rightarrow Me_2\overset{\cdot}{C}NO_2 + hal^- \tag{3}$$

The alternative pathway: $Me_2C(hal)NO_2 + e^- \rightarrow Me_2C(hal)\overset{\cdot}{NO_2^-} \rightarrow Me_2\overset{\cdot}{C}NO_2 + hal^- \tag{4}$

is not responsible for the formation of $Me_2\overset{\cdot}{C}NO_2$ radicals at 77K since there is no evidence for interconversion (4) on annealing to the melting points of the two glasses. The dominating mechanism for the pure compounds is, in our view, electron return followed by homolysis[9]:

$$[Me_2C(hal)NO_2]^+ + e^- \rightarrow [Me_2C(hal)NO_2]^* + Me_2\overset{\cdot}{C}hal + \overset{\cdot}{N}O_2 \tag{5}$$
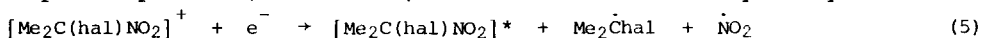
In both cases, broad outer features suggested some pairwise trapping of radicals, which is often observed for such homolyses[9] were observed; and for the bromo-derivative, both expected radical products were detected.

Significance to $S_{RN}{}^1$ Reactions: Our results confirm that halide ions are lost in preference to nitrite ions on dissociative electron capture. However, they pose an interesting question about the mechanism of this process, since they show that direct electron addition can give dissociation without going via the relaxed nitro radical-anion. Such dicotomy has been observed previously and one of us[9] has suggested that it is associated with the way in which the parent molecules change shape on electron-capture. In the present instance this is either a bending at nitrogen to give the pyramidal anion, or a stretching of the C-hal bond to give $Me_2\overset{\cdot}{C}NO_2$ and halide anion. Once the stable anions are formed they show no tendency to lose halide ions in our low-temperature systems, but previous inability to detect these anions by e.s.r. spectroscopy under conditions that give relatively stable nitro-alkane radical-anions in the liquid-phase[4] does suggest that they do dissociate at higher temperatures. These results, together with those for a range of other $Me_2C(X)NO_2$ compounds, will be reported fully in the near future.

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