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ELECTRON ADDITION TO 5-BROMO-5-NITRO-1,3-DIOXANES

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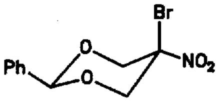
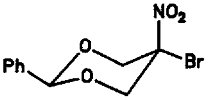
Summary: Studies using e.s.r. spectroscopy show a remarkable range of possible modes of electron capture by 5-bromo-5-nitro-1,3-dioxanes; capture in C-Br bonds, capture at nitro groups, dissociative capture with loss of bromide anions, and dissociative capture with loss of nitrite anions.

Electron spin resonance spectroscopy has been used in this study to indicate a remarkable range of possible modes of electron addition to the 5-bromo-5-nitro-1,3-dioxanes, (1), (2), and (3). These studies were prompted by the unusual electron transfer reactions of 5-bromo-5-nitro-1,3-dioxanes.[1]

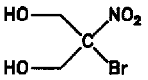
(1)



(2)



(3)



(4)

In these studies we have used a low temperature matrix method in which electrons are generated by ionising radiation and add efficiently to substrate molecules. Methanol (CD_3OD) and methyltetrahydrofuran (MeTHF) are good matrices for uniquely observing electron addition.[2,3] This 'temperature resolved' procedure[2] has the advantage over time resolved methods in that highly reactive species, expected to have very short lifetimes in fluid solution, are trapped in the rigid matrices and can be studied at leisure.

In our studies[4] of α-substituted nitroalkanes [$R_2C(X)NO_2$] we have been able to characterise the electron addition adducts, $R\text{-}\dot{N}O_2^{-}$, (equation 1) and with suitable leaving groups (X), loss of of X^- (equation 2) could often be detected. We have argued that a necessary stage in loss of X^- is insertion of the excess electrons in the (stretched) C-X bond, but such intermediates have not been detected.[4] In fact, it is normally found that electron addition to R-hal derivatives (hal = I,Br,Cl) results in direct loss of hal^- (equation 3).

$$R_2C(X)NO_2 + e^- \longrightarrow R_2C(X)\dot{N}O_2^{-} \qquad (1)$$

$$R_2C(X)\dot{N}O_2^{-} \longrightarrow R_2\dot{C}\text{-}NO_2 + X^- \qquad (2)$$

$$R\text{-}hal + e^- \longrightarrow R^{\cdot} + X^- \qquad (3)$$

However, one of us has proposed[2] that on electron addition (equation 3) as the radical species flattens and hybridisation changes from *sp*^{3} to pure 2*p* on carbon is prevented, σ^* radical anions result. Examples include $[CF_3C\overset{\cdot}{-}I]^-$, $[C_6F_5\overset{\cdot}{-}I]^-$, $[RC{\equiv}C\overset{\cdot}{-}I]^-$, [uracil$\overset{\cdot}{-}$I(Br)]$^-$, and [imidazole$\overset{\cdot}{-}$I(Br)]$^-$.[3] The other controlling factor is the influence of the groups (R) in $R_3C^{\cdot}$ on the energy of the unpaired electron. Groups with high electron affinity such as CF_3 increase that of carbon so much that σ^* bonding is clearly observed.[2]

Results

Formation of C-Br σ^* Radical Anions.

Surprisingly, σ^* radical anions are apparently formed in MeTHF by electron capture in the C-Br bond by (1) (Figure 1), (2), and (3) (see Table). The spectra have all the expected characteristics of σ^* radicals. $A_{max.}$(Br) is far greater than for $R_2\dot{C}$-Br radicals, and the $A_{/\!/}$, $A_{\perp}$, $g_{/\!/}$, and $g_{\perp}$ values fit well with those for other such σ^* radical anions.[2,3]

In contrast, these radical anions were not observed for the analogous open chain, 2-bromo-2-nitropropan-1,3-diol (4). The stability of the dioxane radical anions can be explained by a combination of factors which include the -I effect of the two oxygen substituents and of the nitro group, but also some restraining effect of the ring since the electronic factors do not seem to be sufficient. We suggest that the flattening process normally occurs concurrently with bond breaking and encounters a barrier for the cyclic compounds that is sufficient to stabilise the σ^* intermediates.

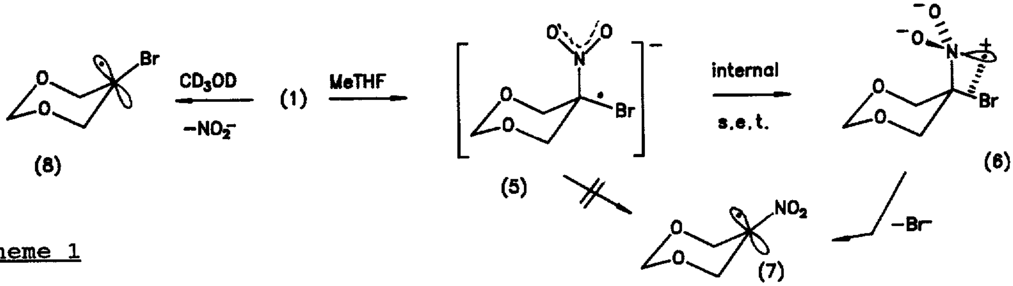
Formation of Nitro π^* Radical Anions.

Whereas π^* nitro radical anions were formed directly[4] from $Me_2C(Br)NO_2$ and (4) at 77 K, they were also formed when MeTHF glasses containing the σ^* radical anions were annealed to *ca*. 130 K. Their formation occurred concurrently with loss of σ^* radical features, so we postulate internal electron transfer as their mode of formation. These nitro radical anions were identified by their characteristic ^{14}N coupling constants [$A_{/\!/}(^{14}N)$ = 42 G, $A_{\perp}$ =19 G; $A_{/\!/}(^{79/81}Br)$ = 51 G, $A_{\perp}$ = 0 G; $g_{/\!/}$ *ca*. 2.01, $g_{\perp}$ *ca*. 2.002] and by the extra splitting of bromine, similar to that observed[4] for $[Me_2C(Br)\dot{N}O_2^-]$ [*cf*. $A_{/\!/}(^{14}N)$ *ca*. 40 G, $(^{79/81}Br)$ *ca*. 38 G].

It is surprising that the σ^* species undergo electron transfer rather than dissociation. The relatively large bromine splitting suggests some admixture with the C-Br σ/σ^* orbitals with those of the SOMO on the nitro group [e.g. (6)],[4] in which case it is even more surprising that this is not the first formed species. A possible explanation (Scheme 1) is that when the electron is trapped in the localised C-Br σ^* orbital the C-Br bond stretches considerably whilst the nitro group remains planar. This tends to confine the SOMO to the C-Br region. The lack of overlap between C-Br σ^* and nitro π^* orbitals suggests that the orientation of the nitro plane is initially orthogonal to the C-Br bond [e.g. (5)]. For electron transfer, the nitro group must become pyramidal and the C-Br bond shorten to its normal length.

Formation of the $R_2\dot{C}\text{-}NO_2$ Radicals in MeTHF.

These radicals were formed on annealing samples of the nitro radical anions of (1)-(4) to *ca*. 150 K. The e.s.r. spectra (2 H = 28 G, ^{14}N *ca*.4 G) of the radicals derived from (1)-(3)[e.g. (7)] show large hyperfine coupling to two axial protons and weak coupling to two equatorial protons.



Scheme 1

TABLE 1 E.s.r. data for C-Br σ^* radical anions

	^{81}Br hyperfine coupling/G^a				
	$A_{/\!/}$	$A_\perp$	A_{iso}	$g_{/\!/}$	$g_\perp$
(1)	300	79	153	2.000	2.023
(2)	255	73	134	2.000	2.020
(3)	300	79	153	2.000	2.023

a G = 10^{-4}: Data taken for best simulations using corrections to second order.

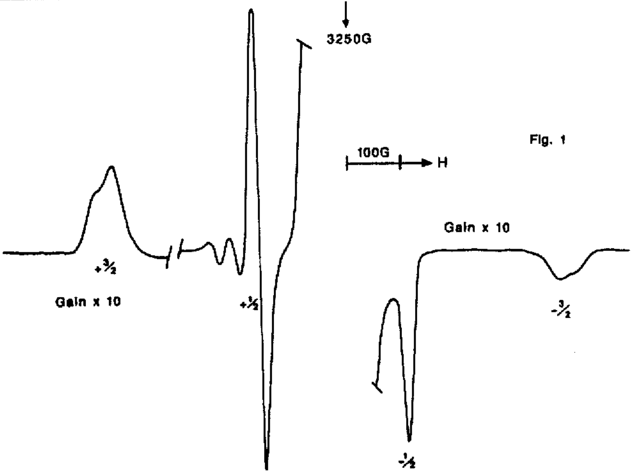


Figure 1
First derivative X-band e.s.r. spectra for dilute solutions of (1) in MeTHF after irradiation to ^{60}Co γ-rays at 77 K showing features characteristic of a large hyperfine coupling to ^{81}Br and ^{79}Br, assigned to the σ^* radical anions.

Dissociation with Loss of Nitrite Anions.

Generally the same adducts are formed in MeTHF as in CD_3OD[2,3,4] and the absence of the above species in CD_3OD is again surprising. It appears that rapid nitrite loss is favoured on electron addition to (1)-(3). The major radicals detected were $R_2\dot{C}$-Br radicals, e.g. (8) [$A_{\parallel}(^{79/81}Br) = 100$ G, $A_{\perp}$ *ca*. 30(±10) G, 2 H *ca*. 47 G (to axial hydrogens)]. These exhibit a characteristic $M_I = +1/2$ feature and a very weak $M_I = -3/2$ lines with a maximum bromine splitting of 100 G. These data are similar to those for the 5-radical of 5-bromo-6(H)-uracil.[6] We suggest that there is weak H-bonding to the oxygen atoms of the nitro group of the parent molecules which tips electron addition in favour of the nitro group. Subsequent strengthening of these H-bonds decreases electron density on bromine making dissociation by loss of bromide less likely and results in nitrite loss. Evidence for this effect has been reported for fluid solution studies of $R_2C(X)NO_2$ radical anion reactions.[7]

$S_{RN}1$ reactions,[7] which proceed *via* intermediate radical anions $[R_2C(X)\dot{N}O_2^{-}]$ were slower[1] for 5-bromo-5-nitro-1,3-dioxanes than for 2-chloro-2-nitropropane. These results[1] contradict the relative rates observed for dissociation for halogenonitro radical anions (i.e. X = I > Br > Cl > F)[1,7] Therefore, some factor other than relative nucleofugicity must account for this anomaly. The results from e.s.r. spectroscopy show that the dioxane radical anions, [e.g.(6)], are more stable than $Me_2C(Cl)NO_2^{-}$ (largely dissociated at 77 K in MeTHF[4]). A combination of conformational restraints imposed by the ring and the -I effects of the two ß-oxygens probably account for the relative stability of the dioxane radical anions.

The two diastereoisomers (2) and (3) were chosen in order to test whether the radical anions of (1)-(3), or the resulting $R_2\dot{C}$-NO_2 radicals, were stabilised by overlap of the SOMO's with the MO's of the ß-oxygens. No such stabilisation was observed.

These results provide further evidence[1,3,4] that e.s.r. spectroscopy at low temperature can be used to explain results of reactions carried out in fluid solution which proceed *via* intermediate radicals and radical anions, and that temperature, solvent, and subtle changes in structure yield remarkably different modes of electron addition.

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