Radical-nucleophilic ($S_{RN}1$) Reactions: Electron Spin Resonance Studies of Electron-capture Processes. Part 5.[1] *p*-Nitrobenzyl and *p*-Nitrocumyl Systems

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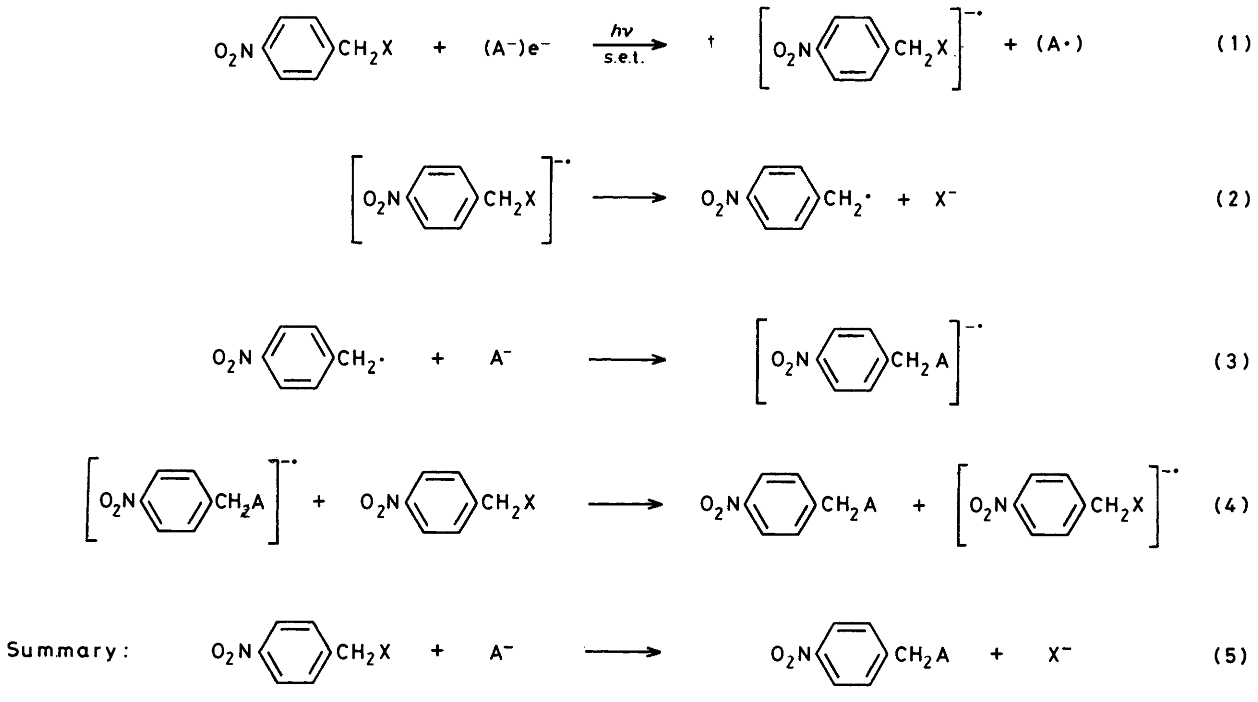
Electron spin resonance spectroscopy has been used to probe two of the steps postulated for the radical-nucleophilic substitution ($S_{RN}1$) mechanism for *p*-nitrobenzyl and *p*-nitrocumyl systems. These two steps are electron-capture by *p*-nitrobenzyl and *p*-nitrocumyl derivatives to form radical-anions and their dissociation to yield radicals and anions [equations (1) and (2) in Scheme 1]. A range of radical-anions (p-$NO_2C_6H_4CH_2X)^{-•}$, with X = I, Br, Cl, and SCN and (p-$NO_2C_6H_4CMe_2X)^{-•}$, with X = Br and NO_2 have been unambiguously identified by e.s.r. spectroscopy and shown to be infinitely long-lived at low temperature. Our results indicate that the *p*-nitrobenzyl radical-anions do not dissociate to give *p*-nitrobenzyl radicals at the temperatures used (77 K to *ca.* 160 K). However, dissociation of the *p*-nitrocumyl radical-anions (p-$NO_2C_6H_4CMe_2X)^{-•}$, with X = Br and NO_2, to *p*-nitrocumyl radicals (p-$NO_2C_6H_4\dot{C}Me_2$) and bromide and nitrite anions respectively was clearly observed. The results are compared with those obtained for solution $S_{RN}1$ reactions for which these radical-anions and radicals are postulated as intermediates.

The radical-anions of *p*-nitrobenzyl halides and *p*-nitrobenzyl radicals were postulated as intermediates in the radical-nucleophilic ($S_{RN}1$) substitution reactions between anions and *p*-nitrobenzyl halides (Scheme 1) in the first publications[2,3] in which the $S_{RN}1$ mechanism was proposed. The $S_{RN}1$ mechanism was also proposed for 2-halogeno-2-nitropropanes in one of these publications.[3] However, the term $S_{RN}1$ (substitution, radical-nucleophilic, unimolecular) was suggested some years later by Bunnett[4] in his studies of substitution reactions of halogenoarenes. Bunnett derived the term $S_{RN}1$ from the obvious similarity of steps 2 and 3 [equations (2) and (3)] with the S_N1 mechanism as illustrated in Scheme 2.

The $S_{RN}1$ mechanism for *p*-nitrobenzyl halides is shown in Scheme 1. Initiation of the chain reaction [equation (1)] requires electron-capture by the *p*-nitrobenzyl halide to form its radical-anion. The propagation steps of the chain reaction are shown in equations (2)—(4) and are summarised by equation (5). A considerable array of evidence[5–8] has been presented to support $S_{RN}1$ mechanisms for reactions involving various different types of substrates, especially *p*-nitrobenzyl, and the analogous *p*-nitrocumyl, halides.

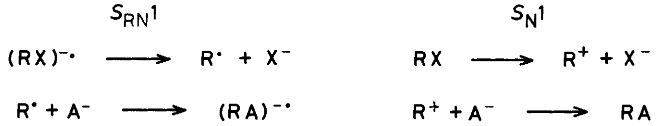
A wide range of nitro compounds, analogues of *p*-nitrobenzyl halides, have also been reported to undergo $S_{RN}1$ reactions. Examples of this range of compounds are shown in Scheme 3,



Scheme 1. † s.e.t. = single-electron-transfer

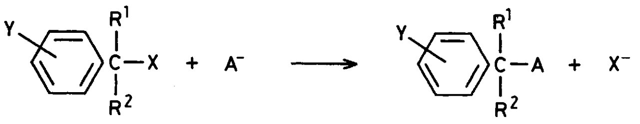
which indicates some of the possible anions, nucleofuges, and arene substitution patterns which allow $S_{RN}1$ reactions.

$S_{RN}1$ reactions have also been reported for analogous 'benzylic' systems which have the nitrobenzene moiety replaced by a heterocyclic moiety. These heterocyclic ring systems include 2- and 4-pyridine,[5] 2-methyl-5-nitrofuran,[1,19] 2-(1-methyl-1-nitroethyl)-5-nitrothiophene,[6,10] and 2-(chloromethyl)-N-methyl-5-nitroimidazole.[11]



Scheme 2.

From the viewpoint of e.s.r. spectroscopy, evidence for electron-capture by p-nitrobenzyl halides to yield the corresponding radical-anions, and their dissociation to p-nitrobenzyl radicals, has proved difficult to obtain.[12,13] However, radical-anions of p-nitrobenzyl systems which do not readily dissociate have been observed by various researchers using e.s.r. spectroscopy[13–15] (a number of these radical-anions are detailed in Table 1). The e.s.r. spectrum of the stable radical-anions of m-nitrobenzyl chloride has also been observed.[14] In our pre-



R^1, R^2 = H, H; Me, Me;
H, various R including Me, Et, Pr^i, Bu^t, cyclohexyl

X = Cl, Br, NO_2, N_3, SO_2Ph, $\overset{+}{N}Me_3$

Y = o, p-NO_2, (fast), m-NO_2, (slow), o, p-CN, 3,5-di-CF_3

A = Me_2CNO_2, NO_2, PhS, $PhSO_2$, malonates, N_3

Scheme 3.

Table 1. ^{14}N Hyperfine coupling constants for various nitrobenzyl and nitrocumyl radical-anions with approximate orbital populations on nitrogen

		^{14}N Hyperfine coupling/G[a]			Orbital populations for N/%[b]		
Radical-anion	Solvent	$A_{\parallel}$	$A_{\perp}$	A_{iso}	2s	2p	(2s and 2p)
$(PhNO_2)^{-\bullet c}$	CD_3OD	27.6	6.5	13.5	2.4	43	45.4
$(pNO_2C_6H_4CH_2F]^{-\bullet d}$	MeCN (238 K)	—	—	9.65	1.8	—	—
$(pNO_2C_6H_4CH_2Cl)^{-\bullet e}$	CD_3OD	29.5	*ca.* 6	*ca.* 13.8	2.5	47.5	50.0
	MeTHF	28.5	*ca.* 5	*ca.* 12.8	2.3	47	49.3
$(pNO_2C_6H_4CH_2Br)^{-\bullet f}$	CD_3OD	28	*ca.* 6	*ca.* 13.3	2.4	44	46.4
	MeTHF	26.5	*ca.* 5	*ca.* 12.1	2.2	44	46.2
$(pNO_2C_6H_4CH_2I)^{-\bullet g}$	CD_3OD	26	*ca.* 5[h]	*ca.* 12[i]	2.2	42	44.2
	MeTHF	24	—[j]	—	—	—	—
$(pNO_2C_6H_4CH_2SCN)^{-\bullet}$	CD_3OD	30	*ca.* 7	*ca.* 14.7	2.7	46	48.7
	MeTHF	29	*ca.* 6	*ca.* 13.7	2.5	46	48.5
$(pNO_2C_6H_4CH_2SPh)^{-\bullet k}$	EtOH (0 °C)	—	—	12.50	2.3	—	—
$(pNO_2C_6H_4CH_2SMe)^{-\bullet l}$	EtOH (0 °C)	—	—	12.60	2.3		—
$(pNO_2C_6H_4CH_2\overset{+}{N}Me_3)^{-\bullet m}$	EtOH (25 °C)	—	—	11.42	2.1	—	—
$[pNO_2C_6H_4CH_2C(NO_2)Me_2]^{-\bullet n}$	EtOH (25 °C)	—	—	12.73	2.3	—	—
$(pNO_2C_6H_4CMe_2Br)^{-\bullet}$	CD_3OD[o]	*ca.* 27	*ca.* 6	*ca.* 13	2.4	42	44.4
	MeTHF[o]	*ca.* 27	*ca.* 6	*ca.* 13	2.4	42	44.4
$(pNO_2C_6H_4CMe_2NO_2)^{-\bullet}$	CD_3OD	30	7	*ca.* 14	2.7	46	48.7
	(N_2)	4	0 + 2	*ca.* 12.7		48	
	MeTHF	28.5	*ca.* 5	*ca.* 12.7	2.3	—	50.3
$(3,5\text{-Di-}NO_2C_6H_3CH_2Cl)^{-\bullet}$	CD_3OD	29	0 ± 5	*ca.* 10	*ca.* 2		—
		[$^1H(3)$ *ca.* 3.5, only one ^{14}N]					
$(m\text{-}NO_2C_6H_4CH_2Cl)^{-\bullet p}$	EtOH (25 °C)	—	—	12.93	2.4	—	—
$(m\text{-Di-}NO_2C_6H_4)^{-\bullet q}$	CD_3OD	30	0 ± 5	*ca.* 10	*ca.* 2	—	—
		[$^1H(3)$ *ca.* 3.5, only one ^{14}N]					

[a] G = 10^{-4} T. [b] Estimated from the isotropic (2s) and anisotropic (2p) hyperfine coupling constants using $A° = 550$ G and $2B° = 33$ G, M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance,' Van Nostrand Reinhold, New York, 1978. [c] Ref. 22. [d] Ref. 15 $A_{max.}(F) = 25.73$ G, $a_{2,6}H = 3.35$ G, $a_{3,5}H = 1.02$ G, $a_{CH_2}H = 1.75$ G. [e] Cl Hyperfine coupling not resolved. [f] $A(^{81}Br)_{max.} = 26.5$ G. [g] $A_{max.}(^{127}I) = 22$ G. [h] Estimated from low-field component. [i] $A_{max.}(^{127}I) = ca.$ 20 G, $A_{x,y}$, g not clearly defined. [j] Only certain of the z-components. [k] Ref. 13; $a_{3,5}H = 3.48$ G, $a_{2,4}H = 2.25$ G, $a_{CH_2}H = 0.9$ G. $a_{3,5}H = 3.5$. [l] Ref. 13; $a_{3,5}H = 3.5$ G, $a_{2,4}H = 2.2$, $a_{CH_2}H = 1.0$ G. [m] Ref. 14; $a_{2,6}H = 3.25$ G, $a_{3,5}H = 1.01$ G, $a_{CH_2}H = 1.40$ G. [n] Ref. 14; $a_{2,6}H = 3.30$ G, $a_{3,5}H = 1.12$ G, $a_{CH_2}H = 1.84$ G. [o] At 77 K $A_{max.}(^{81}Br) = 25.7$ G. Inner lines hidden by p-$NO_2C_6H_4CMe_2$ derivative. New anion detected in CD_3OD on annealing to *ca.* 150 K; no detectable extra coupling. [p] Ref. 14; $a_{2,6}H = 3.42$ G, $a_4H = 3.58$ G, $a_5H = a_{CH_2} = a_{Cl} = 0.57$ G.

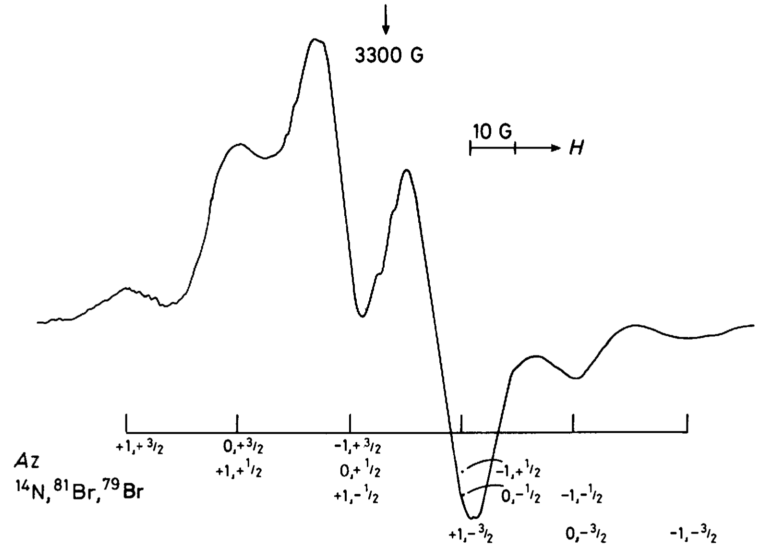


Figure 1. First-derivative X-band e.s.r. spectrum of *p*-nitrobenzyl bromide in dilute solution in MeTHF after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent radical-anions

liminary communication[16] we reported the e.s.r. spectra of the radical-anions of *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide; in this paper we report the full details of our studies using e.s.r. spectroscopy of *p*-nitrobenzyl and *p*-nitrocumyl radical-anions, and radicals.

E.s.r. spectroscopy at low temperature has been successfully used to identify radical-anions and radicals which are postulated as intermediates in $S_{RN}1$ reactions, and provide evidence for various steps in the mechanistic sequence, for various different substrates. Electron-capture to form stable radical-anions [step 1 in the $S_{RN}1$ mechanism, as illustrated for *p*-nitrobenzyl halides in equation (1)], has been observed using e.s.r. spectroscopy for aryl halides,[17] 2-substituted-2-nitropropanes,[18] and α-substituted 2-methyl-5-nitrofurans.[1] Dissociation of these radical-anions, step 2 in the $S_{RN}1$ mechanism to the corresponding radicals (phenyl, 2-nitropropan-2-yl, and 5-nitrofurfuryl respectively) and anions, has also been successfully observed using e.s.r. spectroscopy.[1,17,18] The 2-nitropropan-2-yl radical ($Me_2\dot{C}NO_2$) was also observed to undergo reaction with new anions to form new radical-anions[19] (step 3 in the $S_{RN}1$ mechanism). The use of e.s.r. spectroscopy at low temperature to observe matrix-isolated radical-anions and radicals is well documented.[17-21]

Results and Discussion

Identification of Radical-anions and Radicals.—The advantage of the use of e.s.r. spectroscopy at low temperature of matrix-isolated species is that the first formed intermediates are often detectable, and for strongly coupled nuclei anisotropic coupling constants are obtained which lead to good estimates of spin densities. The disadvantage is that lines are broad and smaller hyperfine splittings are not resolved. By using certain solvents such as CD_3OD and methyltetrahydrofuran (MeTHF), it has been established that the major reaction exhibited by dilute solutes is electron-capture.[20]

(a) *Identification of* p-*nitrobenzyl radical-anions*. The e.s.r. spectra obtained from dilute solutions of all the *p*-nitrobenzyl analogues (p-$NO_2C_6H_4CH_2X$ with X = I, Br, Cl, and SCN) studied showed features which could be assigned to the parent radical-anions (Table 1 and Figures 1—3). All the parent radical-anions display outer parallel features which provide unambiguous identification, the form of interaction with ^{14}N being very similar to that obtained for nitrobenzene radical-anions (Table 1) in rigid media.[22]

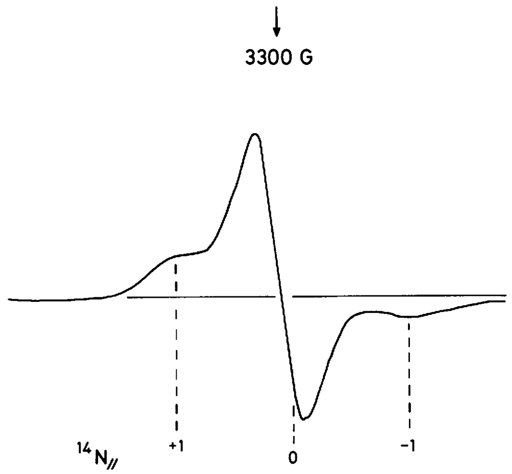


Figure 2. First-derivative X-band e.s.r. spectrum of *p*-nitrobenzyl chloride in dilute solution in MeTHF after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent radical-anions

The e.s.r. spectrum (Figure 1) obtained from the radical-anion of *p*-nitrobenzyl bromide in MeTHF comprised a set of parallel features exhibiting hyperfine coupling to ^{14}N and (^{81}Br + ^{79}Br) $A(^{81}Br)_{max.}$ = 26.5 G. For the chloride (Figure 2) only the nitrogen coupling was observed, but the lines were unusually broad, presumably as a result of weak coupling to chlorine. No dissociation of the radical-anions of *p*-nitrobenzyl bromide, chloride, or thiocyanate was observed to the softening point on annealing in either MeTHF or CD_3OD, indicating that they are infinitely long-lived in solid matrices at the temperature range used for the study.

The e.s.r. spectrum of the radical-anion of *p*-nitrobenzyl iodide (Figure 3) also showed hyperfine coupling to ^{14}N and ^{127}I $A(^{127}I)_{max.}$ = *ca.* 20 G. On annealing in CD_3OD the features assigned to (p-$NO_2C_6H_4CH_2I)^{-\bullet}$ were lost close to the softening point but features due to the corresponding *p*-nitrobenzyl radical (p-$NO_2C_6H_4\dot{C}H_2$) were not detected. As far as we can determine the e.s.r. spectrum of p-$NO_2C_6H_4\dot{C}H_2$ has

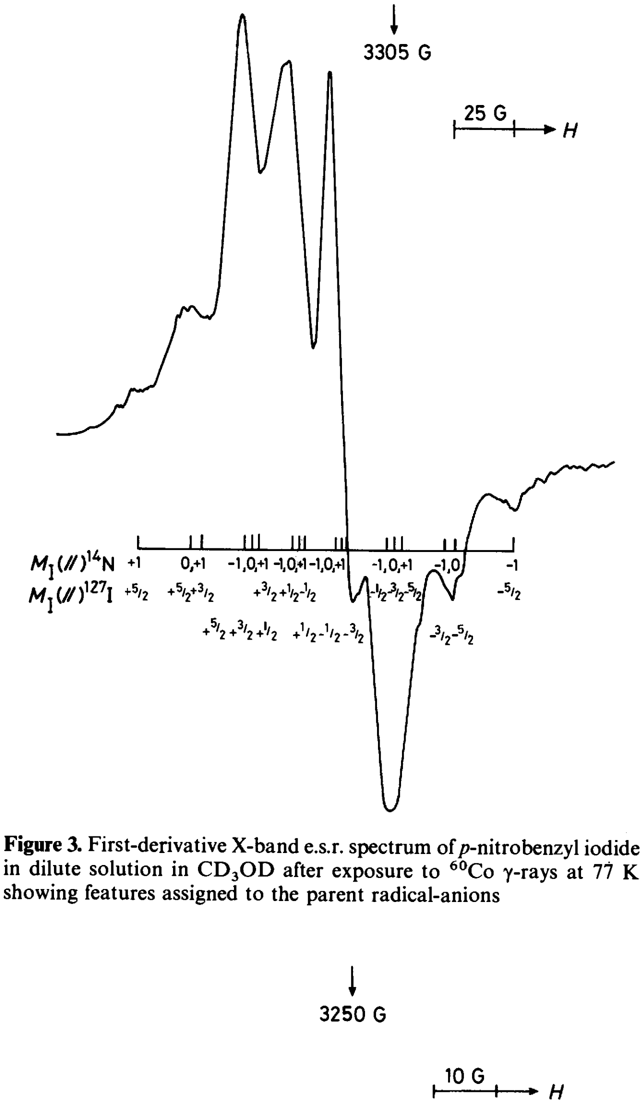


Figure 3. First-derivative X-band e.s.r. spectrum of *p*-nitrobenzyl iodide in dilute solution in CD_3OD after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the parent radical-anions

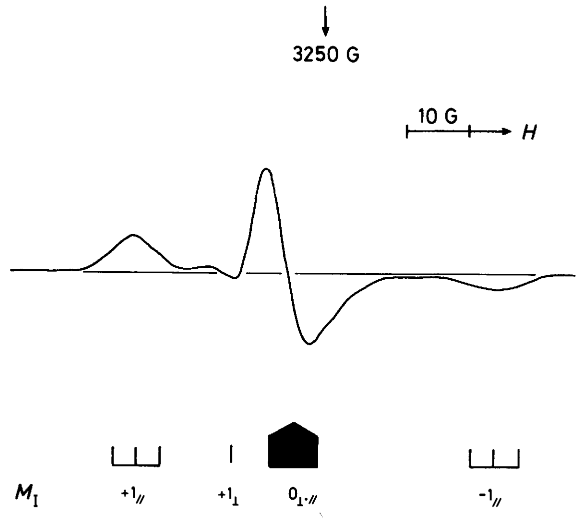


Figure 4. First-derivative X-band e.s.r. spectrum of *p*-$NO_2C_6H_4$-CMe_2NO_2 in dilute solution in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, and annealing to *ca.* 150 K, showing features assigned to the radical-anions, with extra-weak hyperfine coupling to the second nitro group

not been reported, but it should be characteristic and readily detectable in CD_3OD matrix.

(b) *Identification of* p-*nitrocumyl radical-anions and radicals.* Figure 4 shows the e.s.r. spectrum of $(p\text{-}NO_2C_6H_4CMe_2NO_2)^{-\bullet}$ radical-anions in CD_3OD with the normally observed features for these radical-anions as well as extra weak hyperfine coupling

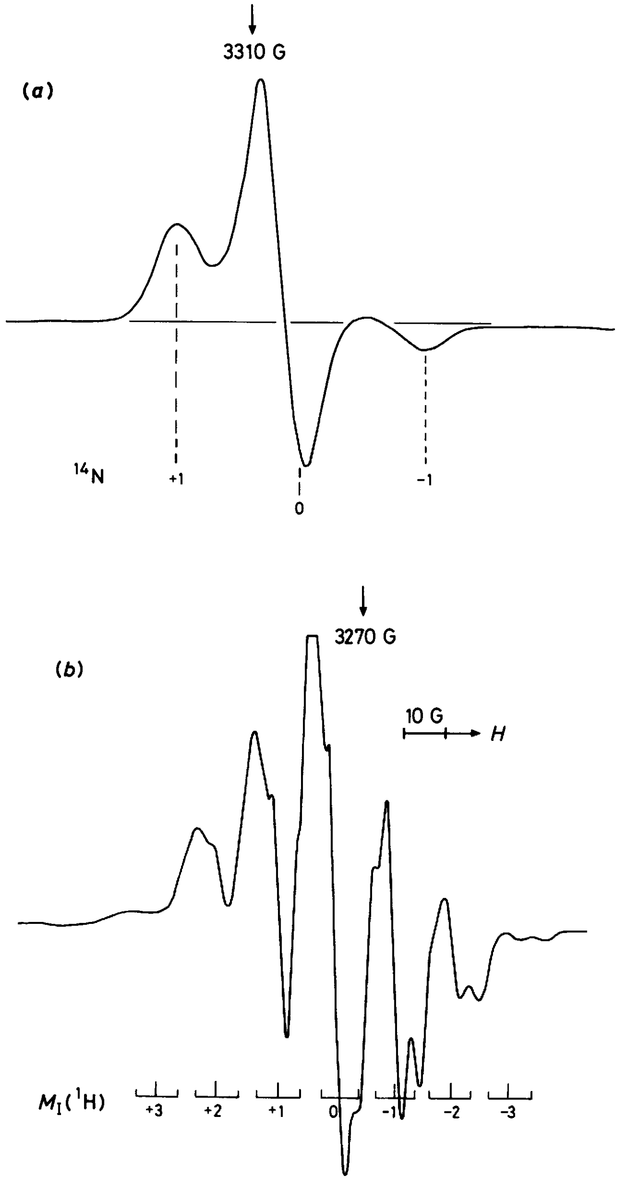


Figure 5. First-derivative X-band e.s.r. spectrum of *p*-$NO_2C_6H_4$-CMe_2Br in dilute solution in CD_3OD after exposure to ^{60}Co γ-rays; (*a*) at 77 K, showing features assigned to the radical-anions, and (*b*) after annealing to *ca.* 150 K, showing features assigned to *p*-NO_2-$C_6H_4\dot{C}Me_2$ radicals

which may be due to the second nitro group ($A_{\parallel}$ = *ca.* 4 G) indicating that the side-chain nitro group is close to the 'perpendicular' site giving large σ–π overlap. In CD_3OD, but not MeTHF, some traces of dissociation to *p*-nitrocumyl radicals (p-$NO_2C_6H_4\dot{C}Me_2$) was observed on further annealing.

The e.s.r. spectra obtained for $(p\text{-}NO_2C_6H_4CMe_2Br)^{-\bullet}$ in CD_3OD [Figure 5(*a*)] and MeTHF show a set of parallel features exhibiting hyperfine coupling to ^{14}N and (^{79}Br + ^{81}Br), $A_{max.}(Br)$ = 26 G. After annealing to *ca.* 150 K [Figure 5(*b*)] features which are assigned to *p*-$NO_2C_6H_4\dot{C}Me_2$ appeared in both e.s.r. spectra (Table 2). The hyperfine coupling constants [$A(^1H)$] assigned to the methyl protons (13.5 G) and the *ortho*-hydrogens (*ca.* 5 G) compare closely with those reported[23] for the corresponding cumyl radicals ($Ph\dot{C}Me_2$) (16.5 and 5.2 G respectively). The fall in spin density for the *p*-nitro derivative is probably due to slight delocalisation in the NO_2 group, but no clear ^{14}N coupling was resolved. The signals in the spectrum

Table 2. Hyperfine coupling for substituted benzyl radicals

Radical	Solvent	$A(^1H)/G^a$
p-$NO_2C_6H_4\dot{C}Me_2$	CD_3OD } MeTHF }	6 H = 13.5 2 H(*o*) = *ca.* 5
$Ph\dot{C}Me_2{}^b$	Cumene (203 K)	6 H = 16.5 2 H(*o*) = 5.2 2 H(*m*) = 1.7 1 H(*p*) = 6.0
p-$MeC_6H_4\dot{C}H_2$ (*ex* *p*-$MeC_6H_4CH_2Br$)	CD_3OD	2 H = 16 3 H = 6.7 2 H(*o*) = 5.0
	p-Xylene^c	2 H = 16.1 3 H = 6.7 2 H(*o*) = 5.13 2 H(*m*) = 1.7
(*p*-$MeC_6H_4CH_2Br)^{-\bullet}$	CD_3OD	*d*
	MeTHF	4 H ≈ 4.5 (3,6 and 3,5)

^{a} G = 10^{-4} T. ^{b} Ref. 23. ^{c} Ref. 24. ^{d} The radical-anion must be present at 77 K otherwise the dissociation product, *p*-$MeC_6H_4\dot{C}H_2$ would not grow in on annealing. Either the features are hidden under the intense solvent features ($\cdot CD_3$ + $\cdot CD_2OD$) or outer lines discussed in the text are due to the parent radical-anions.

for *p*-$NO_2C_6H_4\dot{C}Me_2$ grew on annealing, but for CD_3OD solutions, features due to a new radical-anion appeared, exhibiting normal hyperfine coupling for 14N and no extra splittings. This new radical, which was apparently found from *p*-$NO_2C_6H_6\dot{C}Me_2$ radicals, is unlikely to be due to bromide 'return' [*i.e.* (*p*-$NO_2C_6H_4CMe_2Br)^{-\bullet}$ is reformed] because of the absence of hyperfine coupling with Br. A possibility is the addition of CD_3OD to *p*-$NO_2C_6H_4\dot{C}Me_2$ radicals to form (*p*-$NO_2C_6H_4CMe_2OCD_3)^{-\bullet}$ after deuteron loss. This radical-anion should be particularly stable and is unlikely to dissociate under these conditions. If this conclusion is correct, and we can think of no alternative explanation, it is somewhat unprecedented. It represents a solvolysis occurring *via* a radical mechanism. It would be interesting to discover liquid-phase conditions that might promote this reaction.

(c) *Identification of other radicals and radical-anions.* Our results for the radical-anion of 3,5-dinitrobenzyl chloride show clearly that the spin density is largely confined to one NO_2 group, that on the other being very small. Thus, probably because of asymmetric solvation, an asymmetric SOMO has been selected.

The only non-nitro derivative studied was *p*-methylbenzyl bromide. This was selected as a typical molecule for comparative studies. The parent radical-anions were not clearly detected, but well defined features for the dissociation product, *p*-$MeC_6H_4\dot{C}H_2$ were present at 77 K, and grew further on annealing. Thus the radical-anions *must* have been present. We conclude that the total hyperfine splitting for the radical-anions is small and that their features were totally concealed by the normal intense solvent features for $\cdot CD_2OD$ and $\cdot CD_3$. The e.s.r. parameters for the *p*-$MeC_6H_4\dot{C}H_2$ radicals agree well with those for this species in the literature.[24]

Aspects of Structure of Radical-anions.—(a) p-*Nitrobenzyl and* p-*nitrocumyl radical-anions.* Comparison of the isotropic and anisotropic coupling constants with those estimated for unit orbital populations[25] give 2*s* and 2*p* populations for the nitrogen atom of *p*-nitrobenzyl and *p*-nitrocumyl compounds ranging from 2.2%—2.7%, and 42%—47.5% respectively (see Table 1). These results are similar to those calculated[22] for nitrobenzene anions (2.4% and 43%, respectively). Thus, there can be little doubt that the parent radical-anions have been produced and, as with nitrobenzene[22] in contrast to aliphatic analogues,[18] the nitro moiety must be nearly planar, since the apparent *p*:*s* ratio is *ca.* 19.

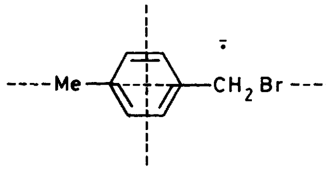
The hyperfine coupling to the bromine and iodine nuclei in (*p*-$NO_2C_6H_4CH_2Br)^{-\bullet}$ and (*p*-$NO_2C_6H_4CH_2I)^{-\bullet}$ establish that there is considerable π–σ overlap between the π-SOMO and the C–Br and C–I orbitals. Similarly, coupling to fluorine $A(F)_{max.}$ = 25.7 G is reported[16] for (*p*-$NO_2C_6H_4CH_2F)^{-\bullet}$, again indicating some π–σ overlap. The data reported for (*p*-$NO_2C_6H_4CH_2SR)^{-\bullet}$, with R = Ph and Me, with small CH_2 splitting (*ca.* 1 G) also suggest that the C–S bond is perpendicular to the ring.

In view of the anionic nature of these radicals it seems probable that the σ–π overlap involves primarily the σ* C–halogen orbital. This corresponds to electron donation towards the halogen which is required for subsequent dissociation. This is the opposite to the normal 'hyperconjugation' effect which involves σ-electron donation in the reverse sense. The absence of any marked temperature dependence for the radical-anion parameters shows that the conformation is fixed over our temperature range.

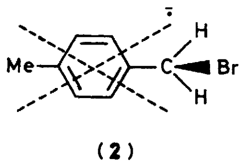
If this form of the SOMO is accepted, it seems reasonable to postulate that only one radical-anion is possible; separate structures with the unpaired electron either in an aromatic/NO_2 π*-SOMO, or in a C–halogen σ* SOMO being only extreme valence bond forms of the actual structure.[21]

Theoretical calculations[26] give support to our observations and conclusions. MNDO (modified neglect of diatomic overlap) calculations on the *p*-nitrobenzyl chloride system show that when the C–Cl bond is orientated perpendicular to the ring there is significant overlap with the LUMO (*i.e.* the orbital that is the SOMO on electron addition). Furthermore, the orbital has high density on the NO_2 group, in accord with our results.

(b) *Radical-anion of* p-*methylbenzyl bromide.* The results for this compound are of some interest. The SOMO for the most stable form of the *p*-xylene radical-anion has a node through the two methyl groups (**1**), and a similar SOMO is possible in this case. The total splitting for the four ring protons should be small (*ca.* 20.0 G) and the features could well be concealed by solvent radical features. However, for this structure there is no incentive for the bromide to dissociate. We conclude either that the alternative SOMO (**2**) is the favoured SOMO, the inversion being induced by the electron-withdrawing character of bromine. In the CD_3OD experiments outer broad features Σ(*A*) ≈ 100 G were detected, which could be explained in terms of radical-anions of structure (**2**). These were present in addition to those for the neutral benzyl radicals, and were lost at *ca.* 100 K. If this is correct, exchange between structure (**1**) and (**2**) must be slow on the e.s.r. time-scale at 77 K, or (**1**) is not a major component of the system. Unfortunately, features for the benzyl radical derivative were always present so only the outermost lines for the possible radical-anion with structure (**2**) were observed.



(**1**)



(**2**)

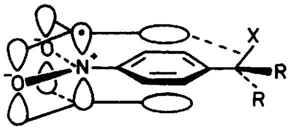
(c) *Radical-anion of* 3,5-*dinitrobenzyl chloride*. Results for the dinitro derivative are very similar to those for 3,5-dinitrobenzene radical-anions in CD_3OD,[27] and for 3,5-nitrobenzyl chloride radical-anions in the liquid phase.[15] In all cases there is high spin density on the nitro group and on the sites *ortho* and *para* – thereto. The spin density at the CH_2Cl site is zero, or nearly so. Thus, there is little incentive for loss of halide anion, which is the reason why these anions are relatively stable in the liquid phase, in contrast with the *para*-derivatives.

We call attention to the observation that the 3,5-dinitro derivatives have an unsymmetrical SOMO, with high spin density on one NO_2 group and almost zero density on the other. We have previously explained[27,28] this unexpected result in terms of asymmetric solvation of the ion, such that one NO_2 group is strongly solvated thereby encouraging the negative charge to remain on this group at the expense of the other. This is a static effect in the solid state,[27] but is dynamic in protic solvents in the liquid phase.[28]

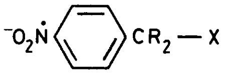
Aspects of Mechanism.—Good evidence[17,20] has been provided to show that the only radiation process that we need to consider for the substrates in dilute solutions is electron-capture. At 77 K only the parent radical-anions are observed, suggesting that electron-capture by the nitro group takes place without dissociation in the radiation process, as opposed to the dissociative electron-capture observed for the 2-nitropropyl analogues.[18] Dissociation of some of the radical-anions [equation (2)] is observed on annealing, showing that dissociation increases with temperature as expected. The rate of dissociation would therefore be predicted to be rapid at the temperatures used for liquid-phase studies. Anion return does not appear to be a major factor.

From our limited data, the effect of solvation on dissociation appears to follow that observed for the aliphatic analogues,[18] *i.e.* that the radical-anions are less stable in the methanol than the ether matrix. This observation can be explained by strong anion (X^-) solvation which would strongly oppose anion return, *i.e.* the reverse of equation (2). One of us has established that solvation of small anions is rapid in methanol glasses even at 77 K.[29] This explanation may only hold in solid matrices in which thermodynamic control is dominant and diffusion is precluded. In liquid-phase, protic solvation, or in the extreme, protonation,[30] has been shown to retard the dissociation of these radical-anions, or their aliphatic analogues,[31] by removal of electron density from the C–X bond towards the nitro group. Dissociation in the liquid phase is under kinetic control and anion return is unfavourable due to diffusion.

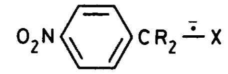
Dissociation of the Radical-anions.—The results of our studies establish that there is considerable overlap between the NO_2/aromatic π^* orbitals and the C–X σ^*-orbitals as represented in structure (3). As we have previously proposed for the radical-anions of 2-substituted 2-nitropropanes $[Me_2C(X)NO_2]^{-\bullet}$[19] and α-substituted 2-methyl-5-nitrofurans,[1] we suggest that dissociation of $(p\text{-}NO_2C_6H_4CR_2X)^{-\bullet}$ radical-anions proceeds by smooth reorganisation of molecular orbitals to the required transition state for loss of X^-. Other mechanisms have been proposed, such as an internal elimination[5] of X^-. The proposals of intramolecular electron-transfer[30,32,33] between π^*-MOs and the C–X σ^*-orbitals prior to dissociation do not essentially differ from our proposals except that two distinct radical-anion species as represented by structures (4) and (5) do not exist, however this is in contrast to dissociation of halogenoarene radical-anions $[(PhX)^{-\bullet}]$ where two distinct radical-anions, an aromatic π^*-species $[^{\bullet-}(Ph)\text{–}X]$ and a C–X σ^* species $[Ph^{-\bullet}\text{–}X]$, have been detected.[17] The π^* and σ^* orbitals in the halogenoarenes do not overlap. Dissociation is thought to take place *via* the σ^* species and mechanistic correlation between the two species is still unclear.[7]



(3)



(4) π^*



(5) σ^*

The free radical, $p\text{-}NO_2C_6H_4\dot{C}Me_2$, resulting from dissociation of the parent radical-anion is unlikely to have an sp^3-hybridised centre at any stage, and we consider that planarity of the 'benzylic'-carbon will be achieved during the course of the dissociation process.

The *p*-nitrobenzyl and *p*-nitrocumyl radical-anions show surprising stability in comparison to the analogous radical-anions[18] of 2-substituted 2-nitropropanes $[Me_2C(X)NO_2$ with X = Br, Cl, NO_2, and SCN]. The latter radical-anions exhibit considerable dissociation at 77 K[18] whereas the *p*-nitrobenzyl radical-anions show little, if any, dissociation even on annealing. The two *p*-nitrocumyl radical-anions did show some dissociation on annealing, indicating lower stability than the *p*-nitrobenzyl analogues as would be expected from bond strength predictions.

Factors which Influence Dissociation.—(a) *Nature of the ring substituents.* The stability of the radical-anions will depend on the electron-affinity of the substituent. We report two extreme cases; nitro groups with high electron affinity, leading to stable radical-anions, and methyl groups with low electron affinity which allow high electron-density close to C–X, leading to fast dissociation. However, the nature of the SOMO is also of importance (see discussion above). *p*-Cyanobenzyl halides have been shown by kinetic photometric pulse radiolysis[34] to capture electrons to form radical-anions which dissociate with rates at least five orders of magnitude higher than those for the analogous nitro compounds.

(b) *Position of the ring substituents.* The *ortho*- and *para*-nitrobenzyl analogues have the highest spin density in the nitro group,[26] but also on the *ortho*- and *para*-carbons, allowing overlap into the C–X bond, thereby allowing rapid dissociation. However, there is little spin density on the *meta*-carbons, and therefore overlap in $(m\text{-}NO_2C_6H_4CH_2X)^{-\bullet}$ of the π^*-MOs into the C–X σ^* bond is very low, resulting in very much slower dissociation (4—6 orders of magnitude slower).[30,34]

(c) *Nature of the benzylic substituent* (X). Our limited results indicate that $(p\text{-}NO_2C_6H_4CH_2I)^{-\bullet}$ dissociates faster than Br, Cl, or SCN analogues. The relative rates of dissociation of *p*-nitrobenzyl radical-anions, $(p\text{-}NO_2C_6H_4CH_2X)^{-\bullet}$, have been reported,[30,33,35] showing that I > Br > Cl > SCN > F. This order correlates with bond strength, *i.e.* the C–I bond is weakest and breaks fastest *etc.*, Neta and Behar[30] reported a ratio of dissociation rates of 1:40:140 for Cl:Br:I, which they comment is surprisingly similar to the relative solvolysis rates of the corresponding aliphatic halides (1:40:110). This observation is interesting support for Bunnett's[7] early comparison of the $S_{RN}1$ and S_N1 mechanisms.

(d) *Nature of the* α-*alkyl group.* We have shown that $(p\text{-}NO_2C_6H_4CMe_2Br)^{-\bullet}$ dissociates considerably faster than $(p\text{-}NO_2C_6H_4CH_2Br)^{-\bullet}$. This observation supports the proposals[36,37] that alkyl substitution increases the rate of dissociation because of the decrease in C–X bond energy caused by stabilisation of the resulting $p\text{-}NO_2C_6H_4\dot{C}R_2$ radicals. Methyl substitution[38] increases the rates by a factor of 20 for both the chloro and bromo derivatives. However, when the α-substituent is t-butyl, the rate *versus* that for methyl decreases by a factor of 240 for the chloride and 56 for the bromide.[38] This observation is explained by rotation of the side-chain to allow the large t-butyl group to go into a position perpendicular to the ring in order to relieve steric strain; the C–X bond is thereby rotated away from the orientation which allows maximum overlap of π*-and σ*-MOs. These results confirm our proposal for the structure of (p-$NO_2C_6H_4CR_2X$)$^{-\bullet}$ radical-anions, *i.e.* a single species with considerable overlap between π*- and σ*-MOs and that dissociation takes place from this species. Hence, when overlap between the π*- and σ*-MOs is reduced, so is the rate of dissociation.

In conclusion, we have obtained confirmatory evidence for the first two steps of the $S_{RN}1$ reactions of p-$NO_2C_6H_4CR_2X$ derivatives; electron-capture by p-$NO_2C_6H_4CR_2X$ to form radical-anions [Scheme 1, equation (1)], and dissociation of these radicals anions to the corresponding radical intermediates, p-$NO_2C_6H_4\dot{C}R_2$ [Scheme 1, equation (2)].

Experimental

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

Materials.—*p*-Nitrocumyl bromide was prepared by standard *N*-bromosuccinimide bromination of *p*-nitrocumene using dibenzoyl peroxide as the radical chain initiator. 2-Nitro-2-(4-nitrophenyl)propane was prepared by the method of Kornblum[37] by reaction between 1,4-dinitrobenzene and the sodium salt of 2-nitropropane in dimethylformamide. All other materials used in this study were purchased commercially.

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