

E.S.R. Studies of Electron Addition to *p*-Nitrobenzyl Bromide and *p*-Nitrobenzyl Chloride

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The radical-anions of *p*-nitrobenzyl bromide and *p*-nitrobenzyl chloride, produced by irradiation of *p*-nitrobenzyl bromide and *p*-nitrobenzyl chloride with ⁶⁰Co γ -rays at 77 K, have been identified by e.s.r. spectroscopy.

The study of the radical-anion reactions of *p*-nitrobenzyl halides has been central to the development of the $S_{RN}1$ and related electron-transfer mechanisms.¹ The $S_{RN}1$ mechanism was first proposed from evidence obtained from the alkylation of *p*-nitrobenzyl halides by the anion of 2-nitropropane.^{2,3} Considerable evidence for the intermediacy of the radical-anions of *p*-nitrobenzyl halides in electron-transfer reactions has been accumulated.¹ The rates of dissociation of the *p*-nitrobenzyl halides have been reported^{4,5} and are in the order I > Br > Cl > F.

Attempts to observe electron-capture by *p*-nitrobenzyl halides to yield the corresponding radical-anions using e.s.r. spectroscopy have proved unsuccessful.^{2,6} Suggestions have been made to explain the mechanism of dissociation of the radical-anions of *p*-nitrobenzyl halides. An internal elimination mechanism has been described (equation 1),¹ and an

alternative proposal⁵ suggests that the electron is initially captured in the nitro π^* MO and undergoes intramolecular transfer to the C-X σ^* MO, followed by immediate dissociation (equation 2).

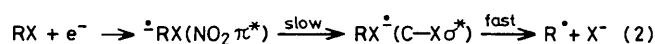
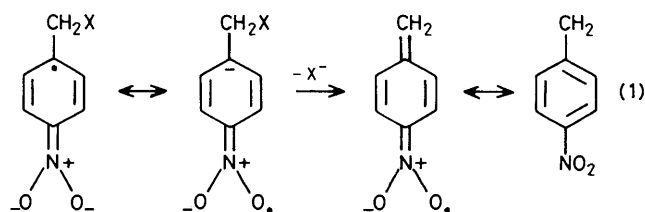


Table 1. Observed e.s.r. parameters for the radical-anions of *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide.

Anion	¹⁴ N Hyperfine coupling/G ^a			Approximate unit orbital population/%		
	<i>A</i>	<i>A</i> _⊥	<i>A</i> _{iso}	2s	2p	%
PhNO ₂ ^{•-} ^b	27.6	6.5	13.5	2.4	43	45.4
O ₂ NC ₆ H ₄ CH ₂ Cl ^{•-}	38.5	ca. 5 ^d	12.8	2.3	47	49.3
O ₂ NC ₆ H ₄ CH ₂ Br ^{•-} ^c	26.5	ca. 5 ^c	12.1	2.2	44	46.2

^a *G* = 10⁻⁴ T. ^b See ref. 10. ^c *A*_z (⁸¹Br) = 26.5; *A*_x and *A*_y have not yet been estimated. The values are small and the large nuclear quadrupole interaction dominates the form of the spectrum, making data extraction difficult. ^d Estimated from the line width.

E.s.r. spectroscopy at low temperature of matrix-isolated radical-anions has been used successfully to obtain information regarding unstable radical-anion intermediates in *S*_{RN1} and related electron-transfer mechanisms for aromatic halides⁷ and aliphatic α -substituted nitro-compounds.⁸ The advantage of these solid-state studies is that the first-formed intermediates are often detectable, and that for strongly coupled nuclei, anisotropic hyperfine 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, especially CD₃OD and methyltetrahydrofuran (MeTHF), it has been established that the major reaction exhibited by dilute solutes is electron addition.⁹

The e.s.r. spectrum obtained from dilute solutions of *p*-nitrobenzyl bromide in MeTHF after annealing to remove solvent features comprised a set of parallel features exhibiting hyperfine coupling to ¹⁴N and (⁷⁹Br + ⁸¹Br) (Table 1). For the chloride, only the nitrogen coupling was observed, but the lines were broader, presumably as a result of weak coupling to chlorine.

The form of the interaction with ¹⁴N is very similar to that obtained from nitrobenzene radical-anions in rigid media.¹⁰ Comparison of the resulting isotropic and anisotropic coupling constants with those estimated for unit orbital populations¹¹ gives 2s and 2p populations of ca. 2.2% and 45%. The results are similar to those deduced for nitrobenzene radical-anions (2.4% and 43% respectively). Thus there can be no doubt that the parent radical-anions have been produced. To our surprise, annealing to the softening points of these glasses failed to give any loss of signal prior to the onset of diffusion. Thus the parent radical-anions are quite stable in this temperature range, despite the rapid loss of halide anions in fluid solution.

The analogous radical-anions⁸ of 2-bromo- and 2-chloro-2-nitropropane show considerable dissociation under the same conditions, which indicates that the radical-anions of *p*-nitrobenzyl halides are more stable than their 2-nitropropyl analogues.

The large coupling to the bromine nuclei establishes that there is considerable σ - π overlap and that the bromine atom does not lie close to the plane of the aromatic ring. The absence of any marked temperature dependence shows that the conformation is fixed over our temperature range.

These results establish the considerable stability of the parent radical-anions, and give important information about their structures. They show that the SOMO includes a significant contribution from bromine, and we suggest that since these are electron-rich radicals this is *via* electron donation into the σ^* C-Br bond, rather than the more familiar

electron donation from that bond. If this is the dominating mode of delocalisation it seems unreasonable to postulate two separate structures (equation 2) since these are, in effect, extreme valence-bond forms of the actual structure.

Therefore, we suggest that the rate determining step of the *S*_{RN1} chain reactions for these compounds is the dissociation of the radical-anions. We hope that by careful choice of matrix it may prove to be possible to measure these rates using e.s.r. spectroscopy.

Finally, it seems most unlikely that there should be an intermediate radical having an sp³ hybridized Ar \dot{C} H₂ centre. There can be little doubt that the preferred structures are planar, as deduced for example from e.s.r. spectroscopy, and we consider that planarity will be achieved during the course of the dissociation process.

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