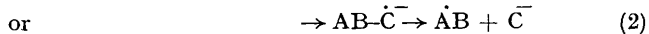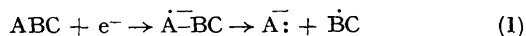# Factors Controlling the Site of Electron-capture and the Mode of Dissociation following Molecular Electron-capture: an Electron Spin Resonance Study

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Summary γ-Ray induced electron-capture processes by molecules ABC, either to give $\dot{A}\text{-}BC$ and $AB\text{-}\dot{C}$ in which the added electron is confined to specific and separate sites in the molecule, or to undergo dissociation to $A^- + BC$ or $AB + C^-$, are described and discussed.

For electron-capture processes involving radical-anion formation or dissociative electron capture, ambiguity can arise if there is more than one trapping site or potential leaving group. This we generalise for the molecule ABC as in equations (1) and (2). Implicit in this description is

$$ABC + e^- \rightarrow \dot{A}\text{-}BC \rightarrow \dot{A}\text{:}^- + \dot{B}C \quad (1)$$

or $$\rightarrow AB\text{-}\dot{C}^- \rightarrow \dot{A}B + C^- \quad (2)$$

lack of overlap between the alternative trapping centres, so that the two anionic forms represent distinct structures.

For example, Bockestein et al.[1] demonstrated that the anions $PhP(OR)(Me_2)^-$ and $PhP(OR)(OMe)_2^-$ have the unpaired electron located on the aromatic rings rather than on phosphorus. In contrast, we found that $PhP(O)Cl_2$ and $PhP(S)Cl_2$ added electrons to give the corresponding phosphoranyl radicals having axial chlorine ligands.[2] Also,[3] $PhPO(OH)_2$, $PhPH(O)OH$, and $Ph_2P(O)OH$ underwent electron addition to the aromatic rings but for $PhPH(O)OH$ the phosphoranyl radical $[Ph\dot{P}H(O)OH]^-$ was also detected.

(We suggest that the name 'phosphoranyl radical' should not be used for the substituted benzene anions,[1] since two quite separate entities are involved.)

The direction of electron addition must depend upon the relative electron affinities of the two sites, and, for low temperature studies, upon the extent to which distortion is required to produce the most stable conformation. In these examples, the aromatic rings probably distort only slightly on electron addition, but the electron affinity of the 'tetrahedral' phosphorus atom must be much less than that of the fully distorted unit having the normal trigonal bipyramidal configuration of phosphoranyl radicals. Since, under our conditions, addition must occur prior to any extensive distortion, it is not surprising that addition to the aromatic ring is often favoured. Since initial electron capture to the 'tetrahedral' phosphorus centre will involve a σ^* orbital, it is probably the high electronegativity of chlorine that renders such addition favourable for the dihalides.

Sometimes, electron addition to ABC molecules results directly in dissociation for one centre but in stable anion formation for the other. For example, $Cl\text{-}CH_2\text{-}POCl_2$ in CD_3OD solution gave e.s.r. spectra after γ-irradiation characteristic of $H_2\dot{C}POCl_2$ radicals and of $\cdot POCl_2(CH_2Cl)^-$ radicals having two axial chlorine ligands. For the undiluted compound the latter radical predominated. Simi-

larly, pure $ClCH_2CN$ gave mainly $\cdot CH_2CN$ radicals, but in protic solvents $H(CH_2Cl)C=N\cdot$ radicals were also well characterised. If, as we suggest, the latter are formed by protonation of the anion $(CH_2Cl)\dot{C}-N^-$, it seems that again two modes of interaction with electrons are possible.

Another mode of reaction is for both centres to dissociate directly. We found that $BrCH_2Cl$ gave $\cdot CH_2Cl$ radicals[4] primarily when the pure compound was irradiated, but a roughly equal mixture of $\cdot CH_2Cl$ and $\cdot CH_2Br$ radicals[5] when in CD_3OD solvent. Similar results were obtained with $BrCHCl_2$ and $BrCCl_3$.

Finally, a variant of these reactions occurs for AB molecules which can form only one anion, but which can dissociate in two ways [equations (3) and (4)]. Generally,

$$AB^- \rightarrow A^- + \cdot B \qquad (3)$$

$$\rightarrow A\cdot + B^- \qquad (4)$$
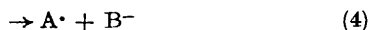
there is no ambiguity, the atom or group with higher electronegativity being the only one to be ejected as a stable anion. However, as the electronegativity difference is reduced, other factors such as distortion, solvation, and charge-delocalisation become significant. For example, CCl_3-NO_2 gave only NO_2 radicals in the pure state or in aprotic glasses [equation (5)]. However, in protic glasses such as CD_3OD,

$$CCl_3-NO_2 + e^- \rightarrow :CCl_3^- + \cdot NO_2 \qquad (5)$$
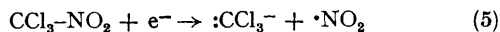
NO_2 formation was completely suppressed, the major radical species being $\cdot CCl_3$ [equation (6)]. We suggest that,

$$CCl_3-NO_2 + e^- \rightarrow \cdot CCl_3 + NO_2^- \qquad (6)$$
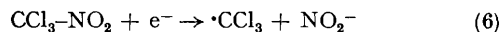
for protic solvents, solvent molecules are preferentially hydrogen bonded to oxygen rather than to chlorine, and that after irradiation, this serves to stabilise the ejected nitrite ion. Otherwise, the greater charge delocalisation for $:CCl_3^-$ is the controlling factor.

For NH_3SO_3 at 77 K, the radical anion $(NH_3SO_3)^-$ was detected by its ^{33}S hyperfine coupling, together with a high yield of $\cdot NH_3^+$ radicals. However, on annealing, the parent anions were rapidly lost, giving way to $\cdot SO_3^-$ radicals, again well characterised by their ^{33}S hyperfine features [equation (8)]. Thus addition to the undistorted molecules gives

$$NH_3SO_3 + e^- \rightarrow [NH_3SO_3]^- \rightarrow NH_3 + \cdot SO_3^- \qquad (8)$$
$$\searrow$$
$$\cdot NH_3^+ + SO_3^{2-}$$
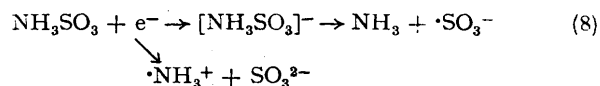
ejection of sulphite or distortion to the anion. However, the latter prefers to eject ammonia rather than sulphite on dissociation.

[1] G. Bockestein, E. H. J. M. Jansen, and H. M. Buck, J.C.S. Chem. Comm., 1974, 118.
[2] S. P. Mishra and M. C. R. Symons, J.C.S. Dalton, 1973, 1494.
[3] S. P. Mishra and M. C. R. Symons, Tetrahedron Letters, 1973, 4061.
[4] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, J.C.S. Faraday II, 1973, 69, 1425.
[5] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, J. Amer. Chem. Soc., 1973, 95, 605.