

ELECTRON-LOSS AND ELECTRON-CAPTURE PROCESSES IN IRRADIATED SYSTEMS

Martyn C. R. Symons

Department of Chemistry, Leicester University, Leicester, LE1 7RH, Great Britain

Abstract - The use of ionizing radiation as a method for electron extraction and electron attachment under conditions in which the products are matrix-isolated are outlined, and the utility and simplicity of the method is stressed. A range of electron-loss and electron-gain mechanisms are discussed in terms of molecular relaxation, bond-making and bond-breaking processes, with particular reference to solvation effects.

INTRODUCTION

During the past 26 years I and my collaborators have explored the use of e.s.r. spectroscopy in the study of matrix isolated neutral radicals and radical-ions (Ref. 1). It has turned out to be a powerful technique, leading not only to clear identification in many instances, but also to mechanistic insights that would be difficult to obtain by other means. In particular, we have tried to exploit the use of ionizing radiation as a method, not only for obtaining radicals, but specifically for inducing electron-loss and electron-gain under low temperature conditions. The advantage of using low-temperature rigid matrices is that highly reactive species are rendered impotent by immobility, whilst unimolecularly unstable species have their lives prolonged by the low temperature and sometimes by the inhibitory effects of the matrix on the tendency to fragment.

IONIZATION BY HIGH-ENERGY RADIATION

We are only concerned with the initial chemical effect of ionizing radiation. For most purposes this can be viewed as an initial, indiscriminate, ionization, the ejected electron being in an effective "conduction band", and hence considerably delocalised. At thermal energies, these electrons may be physically trapped, as for example, in anion vacancies in alkali halide crystals, or they may react with available electron acceptors. Failing these events, they may return to their cations (Fig. 1). This generally leads to electronically and vibrationally excited parent molecules (or ions) which may undergo homolysis rather than falling to the ground-state. The overall process may then closely resemble a normal photolysis. An interesting example is the radiolysis of pure nitromethane, the main primary products being $\cdot\text{CH}_3$ and $\cdot\text{NO}_2$ radicals, rather than $(\text{CH}_3\text{NO}_2)^+$ and $(\text{CH}_3\text{NO}_2)^-$ ions (Ref. 2). These ions or products therefrom can be formed in suitable media. This must mean that the rates of electron- and hole- transfer in the pure solid are faster than the deformation rates that are required for trapping, as indicated in Fig. 2. I am not concerned herein with this mechanism (Fig. 1), but note in passing that such solid-state homolyses often lead to pairwise trapping, and this effect is indeed observed for nitromethane.

Electron-loss centres may be stabilised by relaxation to new shapes, or by bond-making or breaking. Any of these changes will inhibit mobility *via* electron-transfer. If electron-return occurs following bond-breaking a new species will be formed, and if this is matrix isolated, pairwise interaction may again be observed. We proposed such a mechanism, for example, in our study of pairwise trapped phenoxy-radicals in irradiated resorcinol (Ref. 4).

Electrons may be stabilised by physical trapping, or by electron-capture. Trapping is long-lived provided the resulting relaxation rate is fast, and leads to sufficiently deep traps. This may take the form of bond stretching or bending, or bond breaking (dissociative electron-capture) or even bond-making. Only if both hole and electron centres are trapped in this way will they be detected by e.s.r. spectroscopy.

It is not widely appreciated that this technique is very powerful for the preparation and study of electron-gain and electron-loss species. Electrons are removed or added without the need of oxidizing or reducing agents whose presence often leads to complications, such as the formation of charge-transfer complexes. Also complications associated with the use

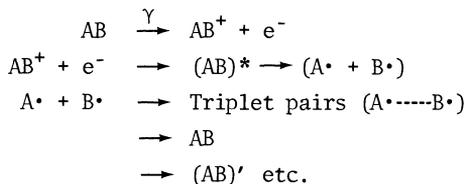
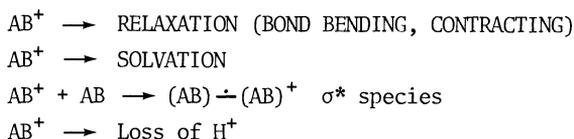
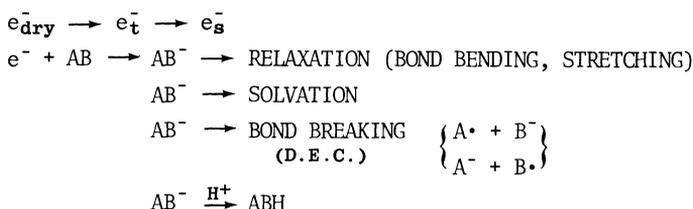


Fig. 1. Electron Ejection and Return



All prevent $AB + AB^+ \rightleftharpoons AB^+ + AB$ AND HENCE, MOBILITY.

Fig. 2(a). e^- -Loss-Centre Changes

All prevent $AB^- + AB \rightarrow AB + AB^-$ AND HENCE, MOBILITY.

Fig. 2(b). e^- -Gain-Centre Changes

of electrodes are avoided. When pure materials are used, both types of centre may be trapped, and spectral interpretation and identification may be difficult. In that case, dilute solutions of the precursors in solvents or in ionic crystals may be chosen such that only electron-gain or electron-loss centres are formed from the additives. Some examples are given in Fig. 3. In many cases conditions can be controlled such that only electron-addition or only electron-loss occurs for the substrate. Of course, solvent radicals are then formed in abundance, but since their e.s.r. spectra are usually well documented, these can be subtracted. In some cases, use of perdeuterated solvent molecules reduces the solvent contribution to a very small region in the $g=2$ region (cf. CD_3OD , or adamantane d_{16}). The great advantage of using rotator solids is that free rotation often sets in before migration occurs. Isotropic e.s.r. spectra are frequently far better resolved and easier to interpret than anisotropic "powder" spectra, so the use of such matrices can be most advantageous.

When the precursors are ions, suitable ionic hosts can be used for the same purpose. For example, ClO_3^- doped into carbonate hosts gave $\cdot ClO_3^{2-}$ on irradiation (Ref. 4), whilst NO_3^- gave $\cdot NO_3^{2-}$ (Ref. 5). Conversely, PO_4^{3-} in calcium tungstate gave PO_4^{2-} (Ref. 6). In all these cases, the substrate attains the charge of the host anions on irradiation, and this is undoubtedly one of the factors contributing to stabilisation.

RADICAL NOMENCLATURE

There is considerable confusion in the literature, and I would therefore like to propose the nomenclature indicated in Fig. 4 as a reasonable way of resolving most of the ambiguities.

- [1] SPECIFIC e^- GAIN:-
 DILUTE SOLUTIONS IN: H₂O GLASS
 CH₃OH(CD₃OD) GLASS
 MeTHF GLASS
 + IONIZING RADIATION
 + PHOTO-IONIZATION [Fe(CN)₆⁴⁻; TMPD]
 HOLE TRAPPED, e^- MOBILE.
- [2] SPECIFIC e^- LOSS:-
 DILUTE SOLUTIONS IN CCl₄, FREON
 + IONIZING RADIATION
 e^- TRAPPED (CCl₄ + e^- → •CCl₃ + Cl⁻)
 HOLE - MOBILE
- [3] ROTATOR SOLIDS → ISOTROPIC SPECTRA
 e.g. TMS, ADAMANTANE.

Fig. 3. Solvent Systems

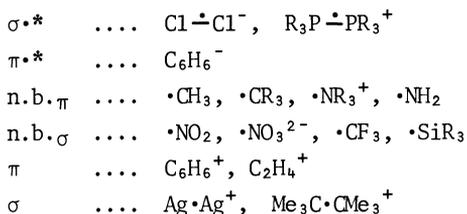


Fig. 4. Nomenclature for Radicals

This nomenclature uses the form of the unpaired electron's orbital as a label for the radical. Since this electron is largely responsible for the reactivity of the radical, this seems to be a logical approach. I suggested some time ago (Ref. 7) that radicals such as •NO₂ should be described as σ -radicals to distinguish them from π -radicals, the major point of difference being the presence or absence of s -character in the orbital. This approach sprang naturally from the fact that reasonably good estimates of the s and p character on a given atom can be obtained from the e.s.r. parameters (Ref. 8 & 9). However, with the realisation that σ^* radicals (Fig. 4) are of great importance (Ref. 9 & 10), this nomenclature becomes confusing. I therefore favour using σ , π and non-bonding (n.b.) orbitals as a basis and hence •NO₂ becomes n.b. σ whilst CH₃, for example, is n.b. π .

ELECTRON LOSS PROCESSES

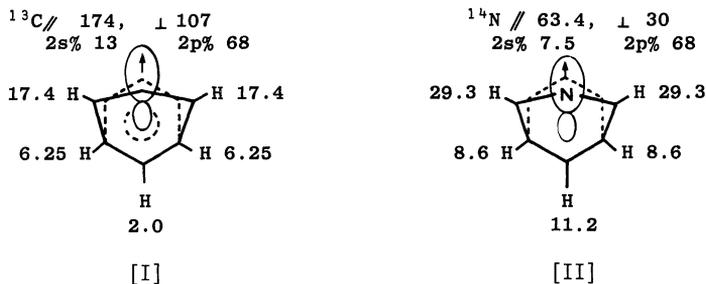
(a) Shape-change

Loss of an electron leads to a new molecule or ion that initially retains the shape of the parent molecule. Provided dissociation does not occur, the shape will rapidly adjust to that of the new species. However, the route taken is not necessarily direct, and in certain cases at low temperatures intermediate species may be detected. For example, there may be competition between bending and stretching modes, the kinetically favoured distortion occurring at low temperatures with the thermodynamically favoured distortion occurring only on annealing.

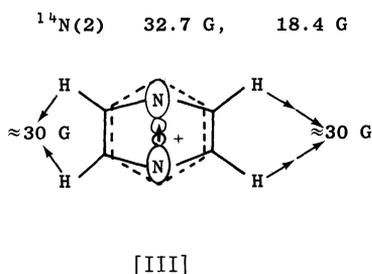
In many cases, shape changes are predictable and unambiguous. Thus, for example, electron loss from NO₂⁻ to give •NO₂ involves mainly an increase in θ from ca. 120° to ca. 132° (Ref. 8). In others, it may be quite subtle. For example, the benzene cation is not symmetrically distorted, although normal e.s.r. parameters seem to indicate this. In fact, because of the degeneracy of the two outer orbitals containing three electrons, the cations

undergo linear distortions which lift this degeneracy: these are interchanging rapidly so that the spectrum is that of the symmetrical ion. Unfortunately, ion-pair effects complicate the study of this type of distortion.

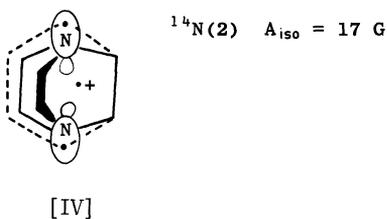
The recently discovered pyridine radical-cation displays an interesting distortion (Ref. 11). This cation [I], isoelectronic with the phenyl radical [II], was formed in a Cl_3CF matrix at 4 K, the usual Freon mixtures being ineffective. The e.s.r. spectrum for the cation was difficult to interpret, even with the aid of deuterium substitutes. Nevertheless, the parameters indicated in [II] are probably close to the true parameters, especially the ^{14}N



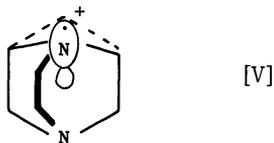
hyperfine components. Shida and Kato made no comparison of the magnitudes of these parameters with those of the phenyl radical. This comparison is interesting on two counts. One is the marked fall in 2s character on going from carbon to nitrogen. I suggest that this reflects an increased distortion for $\text{C}_5\text{H}_5\text{N}^+$ of the type implied in [II]. This presupposes a close correlation between orbital hybridisation and bond angle which has been called into question (Ref. 12), but which we have strongly defended (Ref. 13 & 14). Space does not permit a review of the arguments herein, and I assume that this correlation is good for the purposes of this Review. Such an increased distortion is to be expected: for example, on going from $\cdot\text{CO}_2^-$ to $\cdot\text{NO}_2^-$ there is an increase in the p:s ratio, and hence in θ (Ref. 8). Similarly on going from $\cdot\text{AlR}_3^-$ to $\cdot\text{SiR}_3^-$ and $\cdot\text{PR}_3^+$ there is a steady flattening (Ref. 15). The marked increase in hyperfine coupling to the ortho protons is also expected if delocalisation can be viewed as a form of hyperconjugation, or electron donation from the C-H σ -orbital. In that case the positive charge effect is expected to increase the delocalisation (Ref. 16). A similar, but smaller increase is found on going from $\text{Me}_3\text{C}^\cdot$ to Me_3N^+ , for example (Ref. 17). Probably the extra flattening also enhances hyperconjugative delocalisation. The large increase in hyperfine coupling to the para-proton is surprising (see inserts [I] and [II]): I tentatively suggest that it is also a consequence of flattening at nitrogen, and that it reflects slight σ -delocalisation across the ring. Such delocalisation is evident in the pyrazine cation [III], also studied by Shida and his co-workers (Ref. 18), since the two nitrogen atoms share the electron equally. [This is also



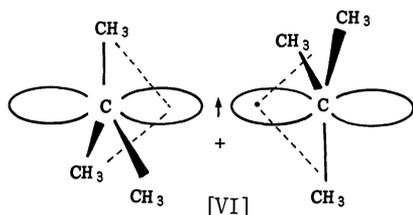
true of the ortho and meta derivatives (Ref. 18).] The results are reminiscent of those for the cation of tetraethylene diamine (TED^+) [IV], which also shares the 'hole' equally between the two nitrogen atoms (Ref. 19). I stress that these symmetrical structures are not formed



of necessity. It would be quite acceptable for TED^+ to have the localised structure [V], with a rapid electron and distortion transfer. Our low-temperature results probably rule out this alternative (Ref. 19).



Another potentially interesting example of a specific change in shape is thought to occur when 2,2,3,3-tetramethyl-butane undergoes electron-loss (Ref. 20). Although my original identification of this cation (Ref. 21) was clearly in error (Ref. 22), nevertheless, using electron trapping media such as CBr_4 , a novel spectrum has been obtained which is probably due to the cation (Ref. 20). I suggest that the distortion involves specific stretching of the central carbon-carbon bond with concomitant flattening of the two Me_3C units as indicated in [VI]. This is not sufficiently precise to explain the e.s.r. spectrum however,



since hyperfine coupling to six protons was very much greater (32 G) than that to the remainder (4.5 G) (Ref. 20). We suggest that crowding of the six methyl groups restricts their rotation so that the 18 protons are no longer equivalent. A conformation in which one C-H bond from each methyl group overlaps favourably with the lone σ -electron is postulated since models show that strain can thereby be minimised.

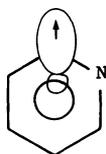
This result, if correct, is important, since it is the first clear example of an e.s.r. spectrum for an alkane cation radical. Previously, broad central singlet features have been assigned to such cations (Ref. 23), but these are in no sense proof of their formation, nor are they structurally informative. I selected the molecule $\text{Me}_3\text{C-CMe}_3$, specifically because I expected to detect a well defined e.s.r. spectrum (Ref. 21). For most of the hydrocarbons studied, the hole is expected to be widely delocalised since there are many equivalent C-C bonds. Hence complex hyperfine patterns with very small splittings are expected, and it seems that these are not normally resolved in solid-state studies (Ref. 23). If the postulated distortion is correct, this is a rare example of a σ -radical. Other examples are $\text{H}_3\text{B}\cdot\text{BH}_3^-$ (Ref. 24) and $[(\text{MeO})_3\text{B}\cdot\text{B}(\text{OMe})_3]^-$ (Ref. 25).

(b) Proton Loss

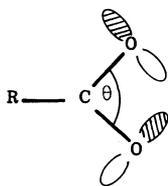
This is a common mode of breakdown, especially for radical cations. Thus, for example, the ethane cation is a strong acid and readily transfers a proton to give ethyl radicals. [This was another reason for my selection of $\text{Me}_3\text{C-CMe}_3$, since its cation cannot gain stabilisation by proton loss.] Besides alkane cations, examples abound: $\text{H}_2\text{O}^+\cdot \rightarrow \cdot\text{OH}$, $\text{ROH}^+\cdot \rightarrow \text{RO}\cdot$, $\text{RCO}_2\text{H}^+\cdot \rightarrow \text{RCO}_2\cdot$, etc. Our early attempts to prepare the pyridine cation resulted in proton loss to give the pyridyl radical [VII] (Ref. 26), in which the unpaired electron is delocalised onto nitrogen, but is primarily on carbon, our estimate of spin densities being 15% $2s$ + 45% $2p$ on carbon and 6% $2s$ + 16% $2p$ on nitrogen. These values make an interesting comparison with those derived for the isoelectronic pyridazine cation (Ref. 18), viz 10.3% $2s$ and 34% $2p$ on each nitrogen. The total spin-density is about the same. The fact that the spin is largely on the less electronegative element for [VII] establishes the N-C anti-bonding character of the molecular orbital. The greater overall $2s$ character for [VII] accords well with the results for phenyl relative to those for the pyridine cation discussed above.

(c) Bond-Breaking

In general, protons are lost most readily, but other bonds may also break after electron loss. A well known example is loss of CO_2 from $\text{RCO}_2\cdot$ radicals. In the parent radical the unpaired electron is in the in-plane, largely non-bonding $2p$ -orbitals on oxygen [VIII]. As the R-C bond stretches, so θ must increase thus encouraging overlap with the R-C bond, and further bond-stretching. An interesting variation on this structure has been revealed in a very thorough study by Iwasaki and co-workers (Ref. 27). The primary electron-loss centres in various α -amino acids, especially glycine and α -aminoisobutyric acid are, as expected,

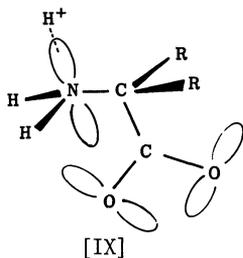


[VII]



[VIII]

$\text{RCO}_2\cdot$ radicals, but there is considerable interaction with the R group, especially the nitrogen of the $-\text{NH}_3^+$ group, which appears to lose a proton as a result. The structure, which is well supported by extensive evidence, is thought to be [IX]. This ultimately gives



[IX]

way to the normal $\text{H}_2^+\dot{\text{N}}\text{CR}_2\text{CO}_2^-$ radical by complete electron and proton transfer. This species appears to be a sort of "transition state", and it is curious that it is stable at 77 K. One slightly disturbing fact is that on prolonged irradiation at 77 K, normal $\text{H}_2^+\dot{\text{N}}\text{CR}_2\text{CO}_2^-$ radicals are formed. This change with dose is unusual. In my experience, if an increase in dose results in a change in radical products this often means that the initial radical species were formed by electron- or hole- scavenging impurities. These are used up during the initial stages and then centres characteristic of the pure compound are formed. Despite this reservation, the results do seem to be genuinely related to the pure substrates.

(d) Bond-Making

This appears to be a very common method of gaining stability. One of the first examples was for irradiated trialkyl phosphines (Ref. 28), the reaction being



The "dimer" cation is a σ^* radical, which can be compared with the well known di-sulphur anions, $\text{RS}^{\cdot-}\text{SR}^-$. These are normally formed by electron addition to RS-SR molecules, but can also be formed by electron loss from RS^- ions (Ref. 29):

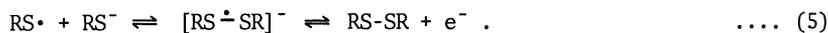


The σ^* orbitals appear to be quite strongly localised to the two central atoms. One major difference between the results for $\text{RS}^{\cdot-}\text{SR}^-$ ions and for the related species $\text{RI}^{\cdot-}\text{IR}^+$ (Ref. 30) and $\text{R}_2\text{S}^{\cdot-}\text{SR}_2^+$ (Ref. 31), compared with $\text{R}_3\text{P}^{\cdot-}\text{PR}_3^+$ cations is that they all involve (p_z-p_z) type orbitals, whereas those involved in $\text{R}_3\text{P}^{\cdot-}\text{PR}_3^+$ cations are close to being sp^3 hybrid orbitals. This difference follows simple expectation, and relates to a similar difference for the parent radicals. Thus $\text{R}_3\text{P}^{\cdot+}$ ions are pyramidal (n.b. σ) species, whereas RS^{\cdot} , $\text{RI}^{\cdot+}$ and $\text{R}_2\text{S}^{\cdot+}$ ions are all n.b. π .

It is not, of course, necessary that the two halves of such dimers be equivalent. We have been able to detect mixed species such as $\text{R}_3\text{P}^{\cdot-}\text{SR}_2^+$, $\text{R}_3\text{P}^{\cdot-}\text{hal}$ and $\text{R}_2\text{S}^{\cdot-}\text{hal}$ when $\text{hal} = \text{Cl}, \text{Br}$ or I . The propensity for forming σ^* radicals in this way seems to be far greater for elements not in the first row of the Periodic Table. For example, we have searched for $\text{R}_3\text{N}^{\cdot-}\text{NR}_3^+$ species which might be expected to form in the radiolysis of tertiary amines, but to no avail. Similarly, $\text{R}_2\text{O}^{\cdot-}\text{OR}_2^+$ or $\text{RO}^{\cdot-}\text{OR}^+$ species have not been detected in the radiolysis of ethers, alcohols or alcoholates. Nevertheless, F_2^- is formed just as readily as Cl_2^- , etc., so there is clearly no innate reason for their lower stability. Possibly

steric factors are important.

It is also worth stressing that these σ^* species can be formed by both oxidative and reductive routes: for example -



Both routes can frequently be detected by e.s.r. spectroscopy. Some mechanistic implications are considered in the section below. Some examples of electron-loss centres reacting to give σ^* radicals are given in Fig. 5.

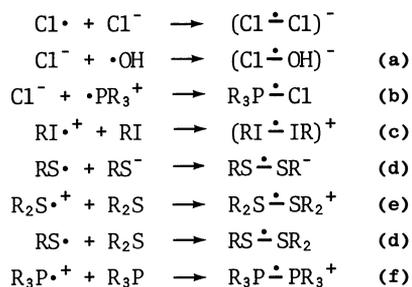


Fig. 5. Some examples of σ^* radicals formed by electron-loss processes

- (a) R. C. Catton and M. R. C. Symons, *J. Chem. Soc. (A)*, 1968, 2155; 1968, 446;
 (b) M. C. R. Symons and R. L. Petersen, *J.C.S. Faraday I*, 1979, 210;
 (c) Ref. 30; (d) Ref. 29; (e) Ref. 31; (f) Ref. 28.

ELECTRON-GAIN PROCESSES

(a) Physical Trapping and Solvation

The best defined units are the F-centres, which comprise electrons trapped at anion vacancies. A good working model for electrons trapped in rigid matrices (e_t^-) is comparable, the electrons being centred on cavities or molecular sized vacancies in the solid. This is why glassy solids usually give far higher yields of e_t^- on irradiation than do their crystalline counterparts (Ref. 32). A good model for solvated electrons (e_s^-) can be obtained by imagining the removal of an anion such as I^- from solution and replacing it with an electron without any major change in the orientation and positions of the solvating solvent molecules. In glassy protic media such as ethanol e_t^- units are converted into e_s^- units on annealing between 4 and 77 K despite the rigidity of the medium. The e_s^- units are, of course, far more stable than e_t^- units, and are probably also more confined to the cavities involved. This physical trapping actively competes with electron capture by molecules: if the 'solvent' molecules can themselves react rapidly with electrons, such trapping may be completely inhibited, but if electron scavengers are dilutely dispersed, physical trapping will compete statistically with capture. Pre-trapped electrons, often described as 'dry electrons' (e_{dry}^-) are in general more reactive, the order of reactivity being $e_{dry}^- > e_t^- > e_s^-$ as expected. Thus, for example, alcohols react with e_{dry}^- to give $RO^- + H\cdot$ or $R\cdot + OH^-$, but do not react with e_t^- or e_s^- (Ref. 33).

(b) Resonant Capture

When electrons interact with molecules in the gas-phase, it is necessary to consider the need for energy matching, the efficiency of capture, or capture cross-section being large only when matching is precise (resonant capture) (Ref. 34). In liquid- and solid-state studies this is of much less importance, although it certainly has kinetic repercussions (Ref. 35). However, in our studies, it seems that provided electron capture is energetically feasible, it will generally be detected. An important factor is the broadening of energy levels in the solid-state, as evidenced by the great widths of the optical absorption curves for e_t^- and e_s^- . Also, substrate energy levels are broadened usually to the extent that individual vibrational levels overlap extensively.

(c) Kinetic Aspects

Although the kinetic course of these reactions is not my prime concern herein, it is clearly a matter of wide significance. The field has been greatly extended by the recent application of pulse radiolysis techniques to low temperature solids (Ref. 36). Controversy centres on the way in which e_t^- manages to reach the substrate S. In particular, Miller and co-workers (Ref. 37) favour the idea that direct tunnelling from the initial trap to S is

sufficient to explain the results, whereas Buxton and co-workers (Ref. 38) maintain that trap to trap migration occurs until $e\ddot{t}$ is within a prescribed encounter distance (r) of S, r being a function of S. It seems to me that the former concept is too restrictive: if e^- can tunnel to S, why can it not tunnel to other traps? I imagine that migration between shallow traps would occur with relatively high probability because there is little modification of the trap by the electron. In cases in which $e\ddot{t}$ changes to $e\ddot{s}$ as a result of solvent reorientation, then migration to other traps would be energetically unfavourable and hence improbable. Hence very different behaviour should be observed for different solvent systems as is indeed the case (Ref. 38). In LiCl glasses varying amounts of $e\ddot{t}$ and $e\ddot{s}$ centres are formed depending on the concentration, and these react differently with different scavengers. In NaOH glasses, only deep, $e\ddot{s}$ type, traps are present. If these are preformed (anion vacancies) then trap to trap migration should be quite efficient. Other factors which in my view should be considered are the charge type of the scavenger, and the extent to which it deforms on electron capture. During trap to trap migration, charged scavengers, such as Cu^{2+} ions or CrO_4^{2-} ions, should strongly influence the direction of migration, especially in neutral glasses, the cations being favoured over the anions. However, solvent orientation about the anions is already favourable, and this should facilitate capture once the electron is close to the encounter distance. Again, if a major deformation is induced by the added electron as, for example, when planar NO_3^- becomes pyramidal $\cdot NO_3^{2-}$, there will be a major barrier unless the electron affinity of the undeformed scavenger is high. However, for ions like CrO_4^{2-} , which do not undergo a major change in shape on e^- addition, this problem does not arise. These concepts may help to explain some of the highly complex behaviour so far recorded, but this is not an appropriate place for such an examination.

(d) Shape Change

Many of the comments made about electron-loss centres apply equally well here. For example, $C_6H_6^-$ ions are expected to be slightly deformed relative to C_6H_6 . Often the major change involves bond bending, as in the formation of bent $\cdot CO_2^-$ from linear CO_2 , or pyramidal $\cdot NO_3^{2-}$ from planar NO_3^- . Whilst e.s.r. data give clear information about such bending changes, they do not give any measure of bond-stretching, which is the other major mode of distortion. For example, electron capture by O_2 to give O_2^- must involve a considerable increase in bond-length, but e.s.r. spectra do not directly probe this change. Similarly, e^- capture into σ bonds to give σ^* radicals must involve considerable bond stretching, but this is not revealed by e.s.r. studies (it is directly probed by u.v. studies of the $\sigma \rightarrow \sigma^*$ transitions and also by resonance Raman spectroscopy).

My own interest has centred on competition experiments rather than kinetic studies. These sometimes involve different modes of distortion with no further change, but often one or more routes involve bond-breaking (usually described as dissociative electron capture or d.e.c.) or protonation. I therefore outline these processes before discussing our competition studies.

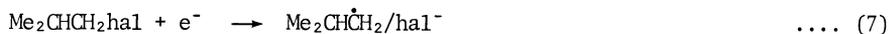
(e) Bond Breaking (D.E.C.)

Most chemists would accept that reaction (6) will occur readily, with no intermediate radical anion, $(R-\dot{a}l)^-$:



(where R = alkyl, and hal = F, Cl, Br or I). This is probably correct, but the conclusion is not obvious. Certainly in fluid or even rigid protic media this reaction should proceed, but in aprotic solvents, and especially in inert solvents the halide ions are highly reactive, and σ^* radicals $(R-\dot{a}l)^-$ might well be expected to form, especially at low temperatures. So far, no such radicals have been detected for R = alkyl, but in rigid aprotic media there is often a clear hyperfine coupling to the halogen nuclei indicating a weak residual interaction between the radical $R\cdot$ (whose e.s.r. spectra indicates a small loss of spin-density) and the adjacent halide ions (Ref. 39). In my view, the fact that these adducts are stable at low temperatures rules out the possibility of stable intermediate σ^* radicals (Ref. 40) - since the reactants are in contact and there are no obvious barriers to reaction, why doesn't it occur? The situation envisaged is indicated in Fig. 6. In support of this contention is the fact that adducts have never been detected for systems which do give σ^* anions on electron capture. [Some examples are shown in Fig. 7.]

I mention in passing that species formed from Me_2CHCH_2Br and Me_2CHCH_2I in adamantane on irradiation at 77 K and warming to ca. 120 K (Ref. 41) are almost certainly $Me_3C\cdot Br^-$ and $Me_3C\cdot I^-$, formed by reactions (Ref. 42 & 43):



The spectra, which are isotropic showing very weak interaction with the halide nuclei, when previously assigned to $Me_2\dot{C}CH_2hal$ radicals (Ref. 41). These very small isotropic coupling constants show that the interaction is charge-transfer in nature rather than being covalent.

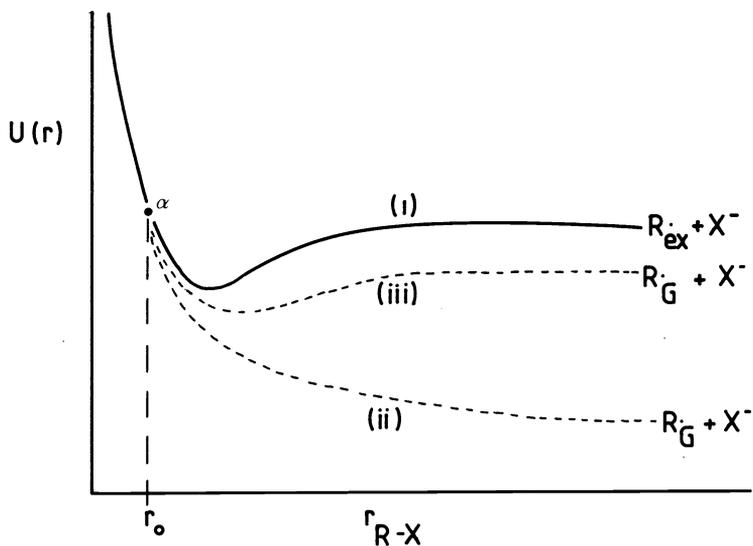


Fig. 6. Qualitative potential energy curves for the dissociation of R-X after electron capture; r_0 is the bond length of the parent molecule and α is the initial energy of the anion. Curve (i) is hypothetical, with no change in the configuration of R. This gives R_{ex} on dissociation, where the configuration of R in the parent molecule is retained. Curves (ii) and (iii) are potentially real cases in which the configuration of R changes with demand, the end product being the ground-state, R_G .

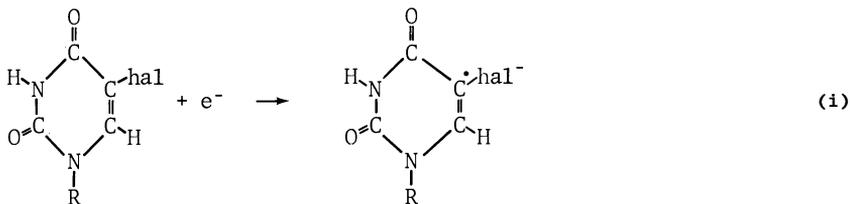
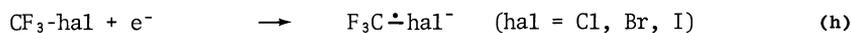
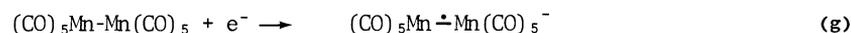
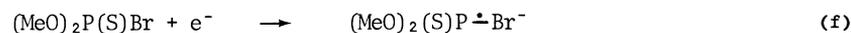
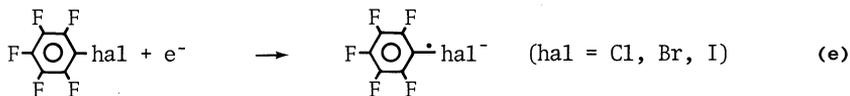
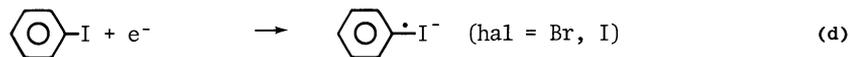
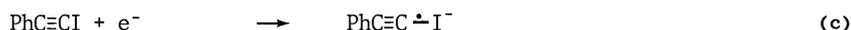
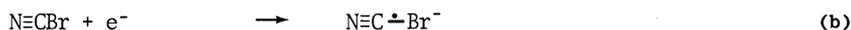
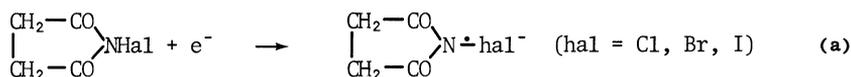


Fig. 7. Some electron-addition reactions leading to σ^* anions.

- (a) Ref. 59; (b) Ref. 60; (c) Ref. 46; (d) Ref. 52; (e) M. C. R. Symons *J.C.S. Chem. Comm.*, 1977, 408; M. C. R. Symons, *J.C.S. Perkin II*, 1980, in press; (f) M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226; (g) S. W. Bratt and M. C. R. Symons, *J.C.S. Dalton*, 1977, 1314; (h) Ref. 47; (i) Ref. 61; (j) G. W. Eastland and M. C. R. Symons, *J.C.S. Perkin II*, 1977, 833.

They also establish that the perpendicular halogen coupling for non-rotating systems must be negative.

Some examples of reactions which lead to true σ^* anions are given in Fig. 7. The isotropic coupling constants (A) [which are now large] can be converted into approximate s -orbital populations, whilst the anisotropic coupling constants (2B) can be converted into p -orbital populations using standard procedures (Ref. 9). Some results are displayed in Fig. 8. Results for Cl, Br and I derivatives correlate remarkably well when the A° values recommended by Morton and Preston (Ref. 44) are used. The points α given in Fig. 8, for various $R\cdot/\text{hal}^-$ adducts, show clearly that their e.s.r. parameters are not commensurate with σ^* anions.

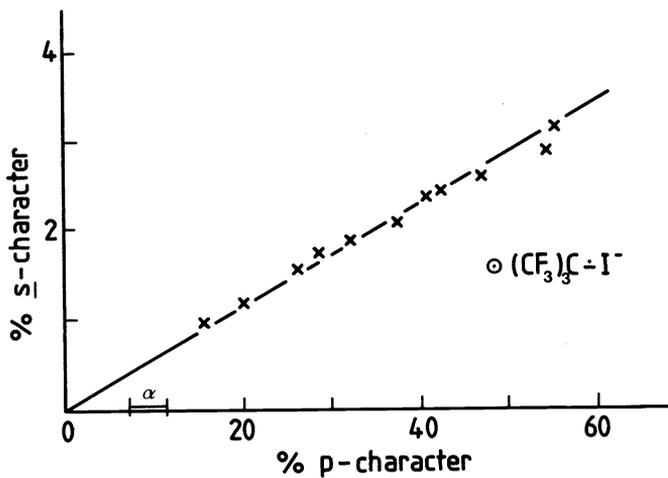


Fig. 8. Correlation of s - and p -character for a range of $R\cdot\text{-Cl}^-$, $R\cdot\text{-Br}^-$ and $R\cdot\text{-I}^-$ σ^* radicals. The s -character was obtained from A_{iso} for Cl, Br or I using the corrected A° values of Morton and Preston whilst the p -character was obtained using values obtained from the wavefunctions of Froese. The line α covers data for a range of alkyl radical adducts, $R\cdot/\text{hal}^-$.

I pointed out some time ago that one of the reasons why this dicotomy exists stems from the tendency for certain groups R to undergo a major change in shape during the process of dissociation (Ref. 45 & 46). Thus, for example, as the C-Cl bond begins to stretch to accommodate the excess electron in $(\text{MeCl})^-$, so the $-\text{CH}_3$ group begins to flatten. This continuous flattening leads to a continuous weakening of the C-Cl bond and no minimum is reached prior to effectively complete dissociation. On the other hand, for $(\text{F}_3\text{C-Cl})^-$ as the C-Cl bond stretches, the $\text{F}_3\text{C-}$ group does not alter its shape to any great extent. Hence the orbital hybridisation at carbon is not modified greatly and there the probability of a 3-electron bond being retained is greater. Indeed, $(\text{F}_3\text{C}\cdot\text{-hal})^-$ σ^* radicals have been studied by e.s.r. spectroscopy (Ref. 47). It has recently been stated that there is a "basic flaw" in this argument, and that my mechanism is "in violation of the principle of microscopic reversibility" (Ref. 48). We should therefore consider the reverse processes. For $\text{Me}\cdot + \text{Cl}^-$, as the C-Cl bond begins to form the $\cdot\text{CH}_3$ radical must become pyramidal, retracing curve (ii) in Fig. 6. This is energetically unfavourable and contributes to the upward trend in the curve. For $\cdot\text{CF}_3 + \text{Cl}^-$ this particular energy contribution is less involved and a minimum is achieved prior to electron ejection [curve (i) or (iii) in Fig. 6]. I am unable to understand why there is any basic flaw in these schemes, and propose to continue to invoke them as a useful guide to understanding these experimental results.

Obviously, there are several other factors that need to be taken into account, a major one being the way in which the three electrons are disposed within the carbon-halogen bond for

any potential σ^* anion. For the hypothetical $(\text{Me}^{\ominus}\text{Cl})^-$ anion, the two σ electrons will strongly favour the chlorine atom, leaving the σ^* electron largely on carbon. This is indicated in the partial energy level diagrams in Fig. 9. This is apparently still true for

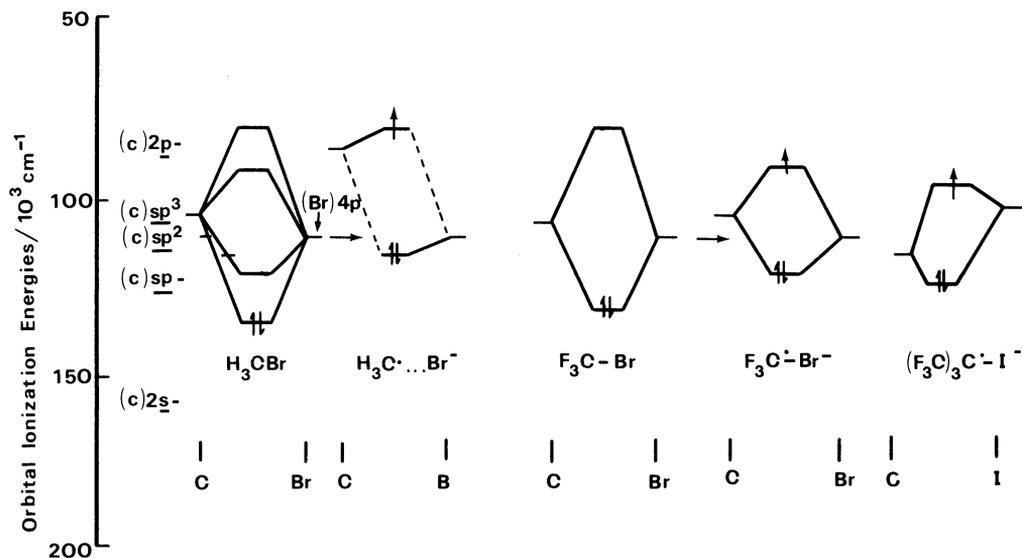


Fig. 9. Energy level diagram for the C-hal bonding in $(\text{H}_3\text{C}-\text{Br})^-$ and $(\text{F}_3\text{C}-\text{Br})^-$, showing how the fact that the CH_3 group becomes planar as the bond stretches influence the extent of bonding.

$(\text{F}_3\text{C}-\text{hal})^-$ anions, since they dissociate to give $\text{F}_3\text{C}\cdot$ radicals on annealing (Ref. 47). Clearly my argument, based on shape change and orbital re-hybridisation becomes less and less significant as the electron affinity of the R group in R-hal increases. If it is greater than that for hal, the stretched bond in $(\text{R}^{\ominus}\text{hal})^-$ will be moving towards the dissociation $\text{R}^- + \cdot\text{hal}$, and the tendency of R^- to change shape will be greatly reduced since R^- anions usually resemble R in R-hal compounds. This may be the case for $(\text{F}_3\text{C})_3\text{C}-\text{I}$, which clearly forms a σ^* anion (Ref. 48). I suggest that on dissociation, this may well give $(\text{F}_3\text{C})_3\text{C}^- + \cdot\text{I}$, though $(\text{F}_3\text{C})_3\text{C}\cdot$ radicals might well be formed in protic media.

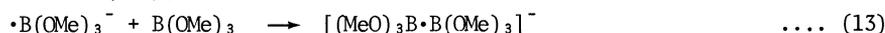
Some of the most stable σ^* radicals are the "dimers" such as $(\text{RS}^{\ominus}\text{SR})^-$ discussed above. These often dissociate reversibly, and their reactivity may be largely due to this dissociation. Thus $(\text{RS}^{\ominus}\text{SR})^-$ is a source of $\text{RS}\cdot$ radicals. I stress that these σ^* anions involve bonds between p-orbitals rather than hybrid orbitals. Thus there is no innate reason why p-orbitals should not be used by carbon.

(f) Bond-Making

There is probably less tendency to bond formation for electron-gain centres than for electron-loss centres, except for their tendency to protonate. A potentially important route to bond formation is the formation of σ -radicals, as exemplified by reactions of silver atoms (Ref. 49):



An interesting example is



discovered by Hudson and Williams (Ref. 25).

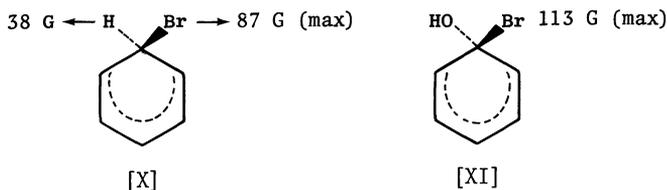
(g) Protonation

This is an important route to the stabilisation of electron-gain centres. Some random examples studied by e.s.r. spectroscopy are discussed herein. Cyanide ions in aqueous glasses give HCN^- and H_2CN^- (Ref. 50).



Similarly cyanoalkanes, R-CN give $\text{H} \begin{array}{l} \text{R} \\ \diagup \\ \text{C} = \dot{\text{N}} \end{array}$ (Ref. 51). Evidently RCN^- anions are relatively strong bases.

Aromatic π^* anions are readily protonated in acidic media to give cyclohexadienyl derivatives. An interesting example is the protonation of bromo- or iodo- aromatic anions, which gave mainly *ipso*-protonation, so far as we can judge (Ref. 52). Thus there was no sign of the usually distinctive features from the CH_2 group of normal cyclohexadienyl radicals, but species with a single large proton coupling together with a large hyperfine coupling to bromine or iodine nuclei were detected (Insert X). An interesting feature of our results was that in deuterated solvents, $\text{C}_6\text{H}_5\text{Br}$ still gave a product with a large proton hyperfine coupling, whereas in protic solvents, $\text{C}_6\text{D}_5\text{Br}$ gave a product which exhibited no proton coupling. This is interpreted in terms of a facile migration of Br around the ring, giving a statistical distribution. This concept nicely explains the tritiation studies of Gold and co-workers (Ref. 53). In a related study, *p*-bromo- and *p*-iodo-phenols gave the *ipso*-product [XI], which again implies migration of halogen to this preferred site after protonation (Ref. 52).



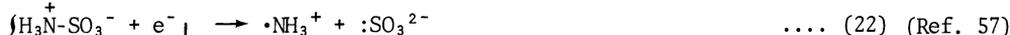
An interesting new example of protonation taken from the inorganic field is for $\text{Pt}(\text{CN})_4^{2-}$ anions. Photolysis of TMPD to give photo-electrons in aqueous media containing $\text{Pt}(\text{CN})_4^{2-}$ gave no detectable yield of the expected $\text{Pt}(\text{CN})_4^{3-}$ anion, but high yields of $\text{H} \cdot \text{Pt}(\text{CN})_4^{2-}$ anions, the excess electron being almost equally shared between H and Pt [$A(^1\text{H}) = 175 \text{ G}$] (Ref. 54).

(h) Competition Reactions and Solvation

We often find that more than one type of electron-capture process occurs. For example, electron addition to various phosphate esters, $(\text{RO})_3\text{PO}$, gave $\text{R} \cdot$, $(\text{RO})_3\text{PO}^-$ phosphoryl radicals and $\cdot\text{P}(\text{OR})_2\text{O}$ phosphoryl radicals (Ref. 55):

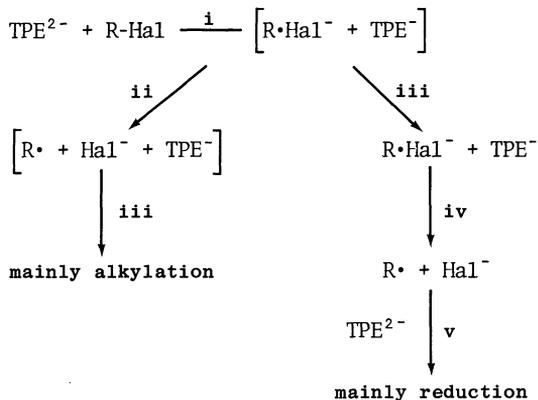


Our results showed that $\text{R} \cdot$ and $\cdot\text{P}(\text{OR})_2\text{O}$ radicals were not formed *via* the phosphoryl anions. In other words, during the initial flirtation between the ester and the electron, a statistical choice is made between C-O bond stretching to give $\text{R} \cdot$, P-O bond stretching to give $\cdot\text{P}(\text{OR})_2\text{O}$, and O-P-O bond opening to give the phosphoryl radical [XII]. Other examples of such competitions include



The course of these reactions is strongly influenced by solvation. Thus reactions (20) and (24) are favoured in inert solvents, whilst (21) and (25) are favoured in protic media (Ref. 56 & 58). Clearly solvation of the leaving group is of significance, even in our solid-state experiments.

Many of the reactions shown in Fig. 7 are in competition with other modes of electron



SCHEME II - Reactions between alkyl halides and disodium tetraphenylethanedide.

Sometimes it is necessary to use light to initiate the chain, or it may be electrochemically induced. A simpler, but related sequence comprises reaction (27) between $\text{R}\cdot$ and the nucleophile Nu^- to give $\text{RNU}\cdot^-$, followed by loss of the electron to give RNU and e_s^- , for solvents such as ammonia or hexamethylphosphoramide. Clearly, some of the results discussed above are indeed significant since they shed light on the electronic structures expected for many of the $\text{RX}\cdot^-$ and $\text{RA}\cdot^-$ intermediates in these chain sequences.

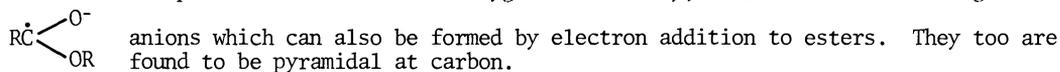
Consider the reactions studied by Kim and Bunnett (Ref. 65):



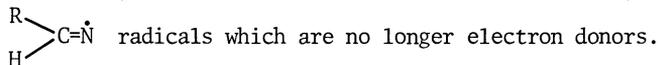
Our results show that initially the electron may give π^* and σ^* anions, but only the latter will break down to give $\text{Ar}\cdot$, this being favoured by protic solvents. $\text{Ar}\cdot + \text{NH}_2^-$ probably proceeds initially towards a σ^* species, but this probably gives the π^* anion via an electron switch.

When the nucleophile is saturated, the attacking radical can only give long-lived $\text{RNU}\cdot^-$ provided there is a site for the excess electron. This may be in the σ^* orbital, and I have given many examples in which such species are quite stable at low temperatures (cf. Fig. 5 & 7). They are generally only formed readily with non-first row elements. This fits in with the observation that if the nucleophile is fully saturated, it is most effective when it is 'soft'.

When the nucleophile is unsaturated, radical addition can, of course, occur, and electron-loss or transfer will then occur provided the balance of potentials is correct. Several of the anion radicals thus formed have also been formed in rigid systems by electron addition. Thus, for example, $\text{R}'\cdot + \text{R}_2\text{C}=\text{NO}_2^-$ gives $\text{R}'\text{R}_2\text{C}\cdot\text{NO}_2^-$. Radical anions of nitroalkanes are readily formed in irradiated systems, and have been shown to be pyramidal at nitrogen, with considerable spin-delocalisation onto oxygen. Similarly, RCO_2^- ions add $\text{R}'\cdot$ to give



Protonation could well interfere with electron transfer. Thus, for example, $\text{R}\cdot$ addition to CN^- ions gives $\text{R}\cdot\text{C}\cdot\text{N}^-$ radicals, but these have a high proton affinity and will readily give



ELECTRON-CAPTURE BY METALLO-ENZYMES

The use of ionizing radiation in the study of electron-gain and -loss processes in biological systems is gravely limited by the complexity of the resulting e.s.r. spectra, especially if solid systems are used. Nevertheless, by using model compounds and single crystals, considerable progress has been achieved. We have exploited the fact that electron addition

to metal ions in metallo-enzymes often gives rise to paramagnetic centres whose e.s.r. features are well removed from the central ($g=2$) region, and hence more readily analysed. This is because the electronic energy levels in such systems are relatively close together, and being coupled by the magnetic field the g -values are well shifted from $g=2$.

So far, we have obtained interesting results with oxy-myoglobin and oxy-haemoglobin (Ref. 67), with xanthine oxidase (Ref. 68) and with haemocyanine (Ref. 69). Work is in progress with superoxide dismutase. Electron addition at the metal ion centres turns out to be remarkably efficient. After electron addition, various reactions can be studied as the systems are annealed towards room-temperature. For example, with oxy-haemoglobin the added electron is in an M.O. comprising iron and oxygen orbitals. There is a clear difference between α -chain and β -chain centres, and these undergo well-defined conformational changes followed by protonation and ultimately, loss of HO_2^- with the formation of high-spin Fe(III) centres. With xanthine oxidase, addition occurs primarily at Mo(VI) and one of the (Fe_2S_2) units (I). The first formed Mo(V) unit is unstable and changes on annealing to a new centre which exhibits hyperfine coupling to a single proton. Electron transfer then occurs from $\text{Fe}_2\text{S}_2(\text{I})$ to $\text{Fe}_2\text{S}_2(\text{II})$ and later from Mo(V) to $\text{Fe}_2\text{S}_2(\text{II})$ possibly via $\text{Fe}_2\text{S}_2(\text{I})$. Thus, electron transitions between the various acceptor centres can readily be studied by our technique, in the absence of any chemical reagents.

I hope that these examples show that irradiation will prove to be a useful method for the selective addition of electrons to metal ions in biological systems.

REFERENCES

1. See, for example, Unstable Intermediates Parts 1-193 mainly in J.C.S. Faraday I & II, J.C.S. Dalton and J.C.S. Perkin II.
2. Unpublished results.
3. D. Campbell and M.C.R. Symons, *J. Chem. Soc. (A)*, 428 (1969).
4. R.S. Eachus and M.C.R. Symons, *J. Chem. Soc. (A)*, 2433 (1968).
5. R.S. Eachus and M.C.R. Symons, *J. Chem. Soc. (A)*, 790 (1968).
6. S. Subramanian, M.C.R. Symons and H.W. Wardale, *J. Chem. Soc. (A)*, 1239 (1970).
7. M.C.R. Symons, *J. Chem. Soc.* 2276 (1965).
8. P.W. Atkins and M.C.R. Symons, *The Structure of Inorganic Radicals*, Elsevier, Amsterdam (1967).
9. M.C.R. Symons, *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, Van Nostrand Reinhold Co. Ltd. (1978).
10. A.R. Lyons, G.W. Neilson and M.C.R. Symons, *J.C.S. Chem. Comm.* 507 (1972).
11. T. Shida and T. Kato, *Chem. Phys. Letters* 68, 106 (1979).
12. C.L. Reichel and J.M. McBride, *J. Amer. Chem. Soc.* 99, 6758 (1977); J.M. McBride, *ibid.*, 99, 6760 (1977).
13. B. Burton, T.A. Claxton, S.J. Hamshe, H.E. Marshall, R.E. Overill and M.C.R. Symons, *J.C.S. Dalton* 2446 (1976).
14. D. Griller and M.C.R. Symons, *J. Mag. Resonance* (1980) in press.
15. A. Begum, A.R. Lyons and M.C.R. Symons, *J. Chem. Soc. (A)*, 2290 (1971).
16. J.A. Brivati, R. Hulme and M.C.R. Symons, *Proc. Chem. Soc.* 385 (1961); R. Hulme and M.C.R. Symons, *J. Chem. Soc.* 1120 (1965).
17. J.A. Brivati, K.D.J. Root, M.C.R. Symons and D.J.A. Tinling, *J. Chem. Soc. (A)* 1942 (1969).
18. T. Kato and T. Shida, *J. Amer. Chem. Soc.* 101, 6869 (1979).
19. G.W. Eastland and M.C.R. Symons, *Chem. Phys. Letters* 45, 422 (1977).
20. M.C.R. Symons and I.G. Smith, *J. Chem. Research (S)* 382 (1979).
21. M.C.R. Symons, *J.C.S. Chem. Comm.* 686 (1978); 640 (1979).
22. H. Shiraishi, H. Kadoi, K. Hasegawa, Y. Tabata and K. Oshima, *Bull. Chem. Soc. Japan* 47, 1400 (1974); J.T. Wang and F. Williams, *Chem. Phys. Letters* 68, 202 (1979); M.C.R. Symons, *Chem. Phys. Letters* 69, 198 (1980).
23. J. Ceulemans, *Discuss. Faraday Soc.* 63, 192 (1977).
24. T.A. Claxton, R.E. Overill and M.C.R. Symons, *Mol. Phys.* 22, 1081 (1971).
25. R.L. Hudson and F. Williams, *J. Amer. Chem. Soc.* 99, 7714 (1977).
26. H.J. Bower, J.A. McRae and M.C.R. Symons, *J. Chem. Soc. (A)* 2696 (1968).
27. H. Muto, M. Iwasaki and Y. Takahashi, *J. Chem. Phys.* 66, 1943 (1977).
28. A.R. Lyons and M.C.R. Symons, *J.C.S. Faraday II* 68, 1589 (1972).
29. D.J. Nelson, R.L. Petersen and M.C.R. Symons, *J.C.S. Perkin II* 2005 (1977).
30. S.P. Mishra and M.C.R. Symons, *J.C.S. Perkin II* 1492 (1975).
31. R.L. Petersen, D.J. Nelson and M.C.R. Symons, *J.C.S. Perkin II* 225 (1978).

32. M.C.R. Symons, Chem. Soc. Reviews **5**, 337 (1976).
33. K.V.S. Rao and M.C.R. Symons, J. Radiat. Phys. Chem. **10**, 35 (1977);
M.C.R. Symons and G.W. Eastland, J. Chem. Research (S) 254 (1977) (M) 2901 (1977).
34. See, for example,
L.G. Christophorou, Radiat. Phys. Chem. **12**, 19 (1978).
35. A. Henglein, Canad. J. Chem. **55**, 2112 (1977).
36. See, for example, papers in
Proc. 6th. Internat. Congress of Radiation Research, Radiation Research **6**, (1979).
37. J.R. Miller and J.V. Beitz, Radiation Research **6**, 301 (1979).
38. G.V. Buxton, Radiation Research **6**, 317 (1979).
39. E.D. Sprague and F. Williams, J. Chem. Phys. **54**, 5425 (1971);
S.P. Mishra and M.C.R. Symons, J.C.S. Perkin II 391 (1973).
40. M.C.R. Symons, J.C.S. Chem. Comm. 408 (1977).
41. R.V. Lloyd, D.E. Wood and M.T. Rogers, J. Amer. Chem. Soc. **96**, 7130 (1974); R.V. Lloyd
and D.E. Wood, ibid, **97**, 5986 (1975).
42. M.C.R. Symons and I.G. Smith, J.C.S. Perkin II 1362 (1979).
43. M.C.R. Symons, Radiat. Phys. Chem. **15**, 453 (1980).
44. J.R. Morton and K.F. Preston, J. Mag. Resonance **30**, 577 (1978).
45. M.C.R. Symons, Faraday Discuss. Chem. Soc. **63**, 209 (1977); J.C.S. Chem. Comm. 408
(1977).
46. D.J. Nelson and M.C.R. Symons, Chem. Phys. Letters **47**, 436 (1977).
47. A. Hasegawa, M. Shiotani and F. Williams, Faraday Discuss. Chem. Soc. **63**, 157 (1977).
48. J.T. Wang and F. Williams, J. Amer. Chem. Soc. **102**, 2861 (1980); [this point is
attributed to Professor J.A. Pople, but in a private communication Professor Pople
tells me that he can find nothing wrong with my arguments].
49. L. Shields and M.C.R. Symons, Mol. Phys. **11**, 57 (1966);
R.S. Eachus, I. Marov and M.C.R. Symons, J.C.S. Chem. Comm. 633 (1970).
50. I.S. Ginns and M.C.R. Symons, J.C.S. Dalton 185 (1972).
51. S.P. Mishra and M.C.R. Symons, J.C.S. Perkin II 394 (1973).
52. S.P. Mishra and M.C.R. Symons, J.C.S. Perkin II submitted;
J. Edwards, D.J. Hills, S.P. Mishra and M.C.R. Symons, J.C.S. Chem. Comm. 556 (1974).
53. C.L. Brett and V. Gold, J.C.S. Perkin II 1437; 1453 (1973);
C.L. Brett, V. Gold and G. Perez, ibid, 1450 (1973).
54. J.L. Wyatt and M.C.R. Symons, J.C.S. Chem. Comm. submitted.
55. D.J. Nelson and M.C.R. Symons, J.C.S. Perkin II 286 (1977);
A. Begum, S. Subramanian and M.C.R. Symons, J. Chem. Soc. (A) 1334 (1970).
56. S.P. Mishra, M.C.R. Symons and B.W. Tattershall, J.C.S. Faraday I 1772 (1975).
57. S.P. Mishra and M.C.R. Symons, J. Chem. Research (S) 48 (1977) (M) 0572 (1977).
58. S.P. Mishra and M.C.R. Symons, J. Chem. Research (S) 147 (1977) (M) 1660 (1977).
59. G.W. Neilson and M.C.R. Symons, J.C.S. Faraday II 68, 1582 (1972); Mol. Phys. **27**, 1613
(1974).
60. S.P. Mishra, G.W. Neilson and M.C.R. Symons, J.C.S. Faraday II **70**, 1280 (1974).
61. H. Riederer, J. Hüttermann and M.C.R. Symons, J.C.S. Chem. Comm. 313 (1978).
62. J.F. Garst, R.D. Roberts and J.A. Pacifici, J. Amer. Chem. Soc. **99**, 3528 (1977);
J.F. Garst, J.T. Barbas and F.E. Barton, J. Amer. Chem. Soc. **90**, 7159 (1968).
63. M.C.R. Symons, J. Chem. Research (S) 360 (1978).
64. R.C. Kerber, G.W. Urry and N. Kornblum, J. Amer. Chem. Soc. **86**, 3904 (1964); **87**, 4520
(1965).
65. J.K. Kim and J.F. Bunnett, J. Amer. Chem. Soc. **92**, 7463; 7464 (1970);
J.F. Bunnett, Acc. Chem. Res. **11**, 413 (1978).
66. G.A. Russell and W.C. Danen, J. Amer. Chem. Soc. **88**, 5663 (1966); ibid, **90**, 347 (1968);
G.A. Russell, R.K. Norris and E.J. Panek, ibid, **93**, 5839 (1971).
67. M.C.R. Symons and R.L. Petersen, Proc. Roy. Soc. B **201**, 285 (1978); Biochim. Biophys.
Acta **535**, 241 (1978); **537**, 70 (1979).
68. M.C.R. Symons and R.L. Petersen, J. Chem. Research (S) 382 (1978) (M) 4572 (1978).
69. M.C.R. Symons and R.L. Petersen, Biochim. Biophys. Acta **535**, 247 (1978).