

Review Article

# $\sigma^*$ Radicals Formed by Electron-Capture and Electron-Loss†

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$\sigma^*$  Radicals ( $A^{\cdot-}B^-$ ), sometimes called three-electron-bonded radicals, are now known to be important intermediates in a range of reactions. In this review, general methods for preparation and study are described, and it is shown how EPR spectroscopy can be used to obtain very detailed information about the SOMO for these species. This is shown to be strongly confined to the two atoms that are directly involved in the  $\sigma^*$  orbitals.

Examples are drawn from homonuclear species ( $A^{\cdot-}A^-$ ), which are generally the most stable, and from heteronuclear species ( $A^{\cdot-}B^-$ ). (The negative charge used herein is arbitrarily selected for illustrative purposes only: these radicals may, in fact, be negative, neutral or positive). For the former, the ‘parent’  $\sigma^*$ -radical,  $H_2^{\cdot-}$  leads on to the  $V_K$  centres (e.g.,  $Cl_2^{\cdot-}$ ),  $RS^{\cdot-}SR^-$  and  $R_2S^{\cdot-}SR_2^+$ ,  $R_3P^{\cdot-}PR_3^+$  and certain  $SiSi^{\cdot-}$  centres. For the latter, discussion moves from the limiting case of  $R_3C^{\cdot-}hal^-$ , (where R = alkyl), which is better represented as  $R_3C^{\cdot-}hal^-$  with a very weak, ‘charge transfer’ interaction, to the isoelectronic  $R_3N^{\cdot-}hal^-$  species which are clearly  $\sigma^*$  radicals. Qualitative reasons for this difference are outlined. Other species discussed are hydrogen derivatives,  $H^{\cdot-}X$ , the species  $RS^{\cdot-}SR_2$ , which may possibly be important in organosulfur chemistry and a novel species formed from the salt  $Ph_3PH^+Br^-$ .

## 1. Introduction

Many years ago, I became interested in solvated electrons (mainly metal ammonia solutions in those days),<sup>1</sup> and that led me to F-centres in alkali halide crystals.<sup>2</sup> The latter, in turn, led me to think about  $V_K$  centres in alkali-halide crystals and to puzzle over the amazing contrasts involved. EPR spectroscopy (the terms ESR and EPR are synonymous) had already proved its worth in this area, as had ENDOR spectroscopy,<sup>3,4</sup> the results being absolutely convincing, and incidentally, serving to underline the brilliance of the physicists who had already arrived at the correct models for both these types of centre.<sup>5,6</sup> However, although the field of ‘trapped and solvated electrons’ moved rapidly into the domain of chemistry, that of  $V_K$ -centres, or of three-electron bonded centres, remained firmly ‘trapped’ within the field of ionic crystals for many years. The structural implications were clear [see Fig. 1(a)]: The unpaired electron was in an orbital (SOMO) comprising 50% of the two halogen  $p_z$  orbitals, lying exactly along the hal–hal directions,

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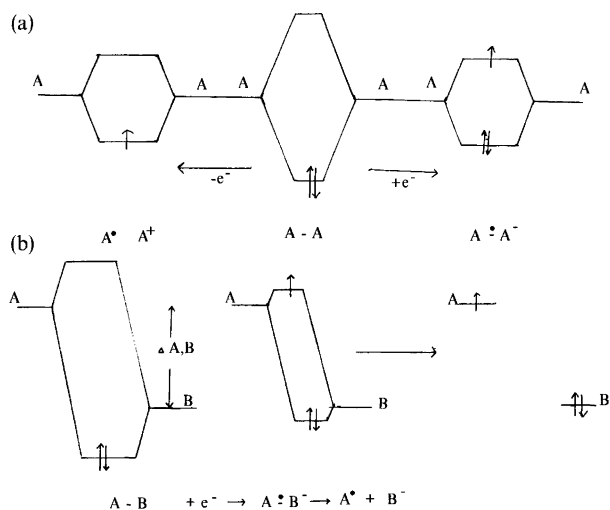


Fig. 1. Qualitative orbital energy level diagrams for A–A (a) and A–B (b) showing only the  $\sigma$  and  $\sigma^*$  orbitals. For (a), the electron-loss ( $A^{\cdot+}$ ) and electron-captive ( $A^{\cdot-}A^-$ ) centres are shown, indicating the great reduction in bond strengths for these species. For (b), this reduction increases as  $\Delta A,B$  increases and this may well lead to bond-breaking, giving, for electron-addition,  $A^{\cdot+}B^-$

with very little s-admixture. Thus the halogen atoms (generated, for example, by ionizing radiation) must have moved towards a neighbour, which, in turn, moved in to form the bond (Fig. 1).

Then we,<sup>7</sup> and others,<sup>8-10</sup> began to realise that such species, which I labelled  $\sigma^*$ -radicals, formed very readily indeed, and hence must be of great importance in chemistry. Even more recently, those interested in reaction kinetics and products have begun to formulate reactions in terms of initial attack of radicals to form such three-electron  $\sigma^*$  systems.<sup>11</sup> For example, in the reaction of chlorine atoms with pyridine, Breslow and co-workers concluded that instead of adding to the ring to give normal  $\pi$ -addition, as with benzene, addition was on nitrogen to give the in-plane  $\sigma^*$  species. We subsequently prepared this species and showed unambiguously by EPR spectroscopy that this is indeed the correct structure of the primary adduct.<sup>12</sup>

The aim of this review is to show how EPR spectroscopy has been used to establish the structures of such centres, the tendency for them to form under a variety of conditions, and the way that they can switch to give alternative, non- $\sigma^*$  structures in some cases. Their great mechanistic importance is rapidly becoming clear and hopefully, that can be seen within the confines of this review. UV-VIS spectroscopy has also been widely used, especially by Asmus and co-workers,<sup>10,13</sup> and was originally used to define  $V_K$ -clusters.

## 2. Methods of formation

There are at least three, interlinked, mechanisms generally encountered, namely, electron-gain, electron-loss, and radical-addition. These are summarised in reactions (1)–(3).



I stress that the  $\sigma^*$  intermediates may or may not be very stable (i.e.,  $A \dot{-} B^-$  may break down to give  $A \cdot + B^-$  or  $A^- + B \cdot$ ) but even so, they need always to be considered, especially if the reverse can occur [Fig. 1 (b)]. Thus, many so-called 'dissociative electron-capture (DEC) reactions' occur via such  $\sigma^*$  intermediates, which should not be ignored. Electron-gain and -loss reactions are common in radiation chemistry and in photo-ionization processes, as well as in certain redox reactions or electrochemical processes.

## 3. Methods of detection

The two methods most widely used are EPR and optical spectroscopy. The former has been especially successful using matrix isolation methods, whilst the latter is especi-

ally useful in time-resolved spectroscopy if the  $\sigma^*$  intermediates have short lifetimes.

EPR spectroscopy has the great advantage of giving remarkably detailed structural information, in addition to precise identification and high sensitivity. However, optical detection is also very sensitive because the  $\sigma \rightarrow \sigma^*$  transition (Fig. 1) is always of low energy and high intensity, because this is a strongly allowed transition. However, firm identification is less compelling. Ideally, both techniques are used together.

## 4. Examples of homonuclear (A-A) species $H_2$

I was delighted when I recognised that an unidentified doublet appearing in the EPR spectrum of irradiated para-hydrogen must be the  $|0, 0\rangle$  and  $|1, 0\rangle$  for either  $H_2 \dot{-}^+$  or  $H_2 \dot{-}^-$  centres.<sup>14</sup> The major centres detected are hydrogen atoms having unexceptional properties. However, two narrow features separated by ca. 12.4 G\* and centred on  $g=2.007$  were tentatively interpreted in terms of radical-pairs.<sup>15</sup> Using the observed separation ( $\delta$ ) and the equation  $\delta = (A^2/\nu)(g/g_e)$  2.8, I estimated a hyperfine coupling ( $A$ ) of 203 G for two exactly equivalent protons. The total splitting of 406 G is far less than that for  $H \cdot$  atoms (508 G) and hence is in good accord with the expectation for  $H_2 \dot{-}^-$  and rules out  $H_2 \dot{-}^+$ . In simple terms this arises because the effective radius of the 1s orbital is very sensitive to charge. The positive charge for  $H_2 \dot{-}^+$  causes this radius to contract, thereby greatly increasing the nuclear contact term and the hyperfine splitting. The negative charge for  $H_2 \dot{-}^-$  has the reverse effect, as observed. Accordingly, I asked Professor Miyazaki to look for the outer  $\pm 1$  features, and was delighted when he told me that they were, indeed, present, with a separation of 407 G<sup>16</sup> (Fig. 2). Thus, the identification is firm, and the 'parent'  $\sigma^*$  radical now seems to be established (my only remaining reservation is that the apparent  $g$ -value is greater than 2.0023).

The radical  $He_2 \dot{-}^+$ , studied extensively in the gas-phase by Carrington and co-workers,<sup>17</sup> is isoelectronic with  $H_2 \dot{-}^-$ . Their interest in such centres is with highly excited vibrational levels, very close to the dissociation limit. Under these conditions, if dissociation were to occur, the three electrons have to make a choice between the two nuclei, such that one gets two electrons and the other gets one. It seems that this choice is already being made in these excited states, and this is where their interest lies. Unfortunately for the chemists, details of the ground-state species are not readily (or reliably) derived from these data. So far as I know, ground-state  $He \dot{-}-He^+$   $\sigma^*$  radical cations have not yet been studied.

All other such  $A \dot{-}A$  centres involve p- or sp-hybrid  $\sigma$  bonds. The dimer cations  $Xe \dot{-}-Xe^+$  seem to form quite readily, and have been fully characterized.<sup>18</sup> These are isoelectronic with  $I_2 \dot{-}^-$  centres, and have very similar EPR parameters.<sup>19</sup> It would be interesting to prepare the

\* 1 G = 0.1 mT.

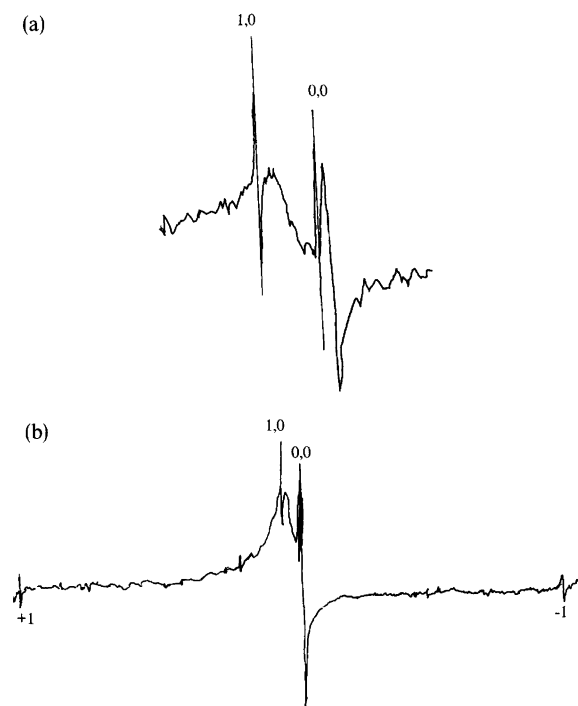


Fig. 2. First derivative EPR spectra for irradiated parahydrogen at 4 K. (a) Shows the two features separated by 12 G and centred on  $g=2.007$  that were thought to be due to radical-pairs,<sup>14</sup> but which were reassigned to the 1, 0 and 0, 0 features for  $H_2^{\cdot-}$  radical-anions.<sup>15</sup> (b) Shows the outer,  $\pm 1$  features subsequently detected.<sup>16</sup>

mixed centre I'-Xe, but I know of no such centres. In fact I' atoms in an Xe matrix do not seem to form such  $\sigma^*$  centres.<sup>20</sup>

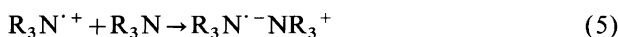
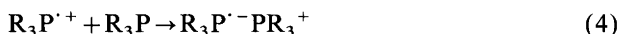
The two centres  $RS-SR^{\cdot-}$  and  $R_2S-SR_2^{\cdot+}$  are both well characterised.<sup>21,22</sup> Both have  $\sigma$ -bonds that comprise, primarily,  $p_z \pm p_z$  orbitals with little s-admixture, as established by the  $^{33}S$  hyperfine splitting. The former is thought to be of importance in biology, when interconversions between two RSH units and the corresponding RSSR dimer is often of structural importance, for example in the activation/deactivation of enzymes.

The diphosphorus centres,  $R_2P-PR_2^{\cdot-}$  are isoelectronic with these  $R_2S-SR_2^{\cdot+}$  units, with the expected  $p_z \pm p_z$  bonding. However, the species  $R_3P^{\cdot-}-PR_3^+$  differ in that the  $\sigma/\sigma^*$  P-P bonds now involve considerable admixtures of 2s atomic orbitals. This dramatically modifies their EPR spectra, with large increases in the  $^{31}P$  hyperfine splittings. The change arises because the  $R_3P$  units remain strongly pyramidal in these dimers. So far as we can judge from the EPR spectra, the units are quite symmetrical with all six ligands remaining equivalent, as in the parent unit,  $R_3P-PR_3$ .<sup>24,25</sup> This is a limiting case in which movement towards phosphoranyl radicals does not seem to occur (see below). Even so, MO theory on the  $H_3P^{\cdot-}-PH_3^+$   $\sigma^*$  species suggest a marked distortion that would make two of the hydrogen ligands quite different from the other four, implying a trend towards a 'phosphoranyl'-type structure.<sup>26</sup> This is

not seen on the EPR timescale even at low temperatures, but it serves to underline the close energetic balances that can exist in these systems. Fortunately, EPR spectroscopy can normally detect such differences unambiguously.

Our own experience and those of others strongly suggest that these dimer species ( $A^{\cdot-}-A$ ); ( $B^{\cdot-}-B$ ) are more stable than corresponding  $A^{\cdot-}-B$  centres. In simple terms, this is to be expected, as can be judged from the qualitative energy-level diagrams (shown in Fig. 1). As  $\Delta A/B$ , indicated there, increases, so the system must move towards the  $A^{\cdot-}+B^{\cdot-}$  limit, and the  $\sigma^*$  'intermediate' must cease to have any significance.

Another aspect of the theoretical calculations is that first row dimers are predicted to be much more stable than those of second and subsequent rows.<sup>26</sup> Thus, for example,  $D_A$  calculated for  $H_2O^{\cdot-}-OH_2^+$  (45.8 kcal mol<sup>-1</sup>) is far greater than that for  $H_2S^{\cdot-}-SH_2^+$  (29.7) and that for  $H_3N^{\cdot-}-NH_3^+$  (39.8) is much greater than that for  $H_3P^{\cdot-}-PH_3^+$  (ca. 26). These estimated differences of ca. 15 kcal mol<sup>-1</sup> must surely be correct, and yet experimental results seem to support the reverse! Thus, in our solid-state studies, formation of relatively stable dimers, such as  $R_3P^{\cdot-}-PR_3^+$  cations is difficult to avoid, but the corresponding  $R_3N^{\cdot-}-NR_3^+$  cations are unknown, except for  $H_3N^{\cdot-}-NH_3^+$ ,<sup>27</sup> formed by  $e^-$ -addition to  $H_3N-NH_3^{2+}$  cations, despite many attempts to prepare them. In other words, reaction (4) is facile and complete, whilst (5) has never been observed, despite all our endeavours.<sup>28</sup>



We suggested that one major controlling factor is that  $R_3P^{\cdot-}$  radicals retain the pyramidal character of the parent molecules, whilst  $R_3N^{\cdot-}$  radicals are planar, and hence need to become pyramidal on moving in to form the  $\sigma^*$  dimer.<sup>28</sup> Another possibility is that steric requirements of the R-groups are more restrictive. However, both these factors are presumably built into the theoretical computations, which nevertheless suggest that the nitrogen dimer be much more stable than that of phosphorus. We have also failed to prepare  $RO^{\cdot-}-OR^-$  or  $R_2O^{\cdot-}-OR_2^+$  centres, despite the stability of the sulfur analogues. Thus, for example, the  $\sigma^*$  radical-anion,  $HO^{\cdot-}-OH^-$ , does not seem to form on electron-addition, and even at low temperatures in glassy systems,  $\cdot OH$  radicals are formed by DEC from  $H_2O_2$ . However, there is evidence for the mixed species  $HO^{\cdot-}-Cl^-$ .<sup>29</sup>

## 5. Examples of heteroatomic, A-B centres

*Hydrogen atom centres.* These are of considerable importance since they may play a role in modifying the reactions of hydrogen atoms. The key question is, do they interact with water molecules to give  $H^{\cdot}-OH_2$  centres? Some time ago we suggested that an intense UV band found for  $H^{\cdot}$  atoms in water is the  $\sigma-\sigma^*$  transition

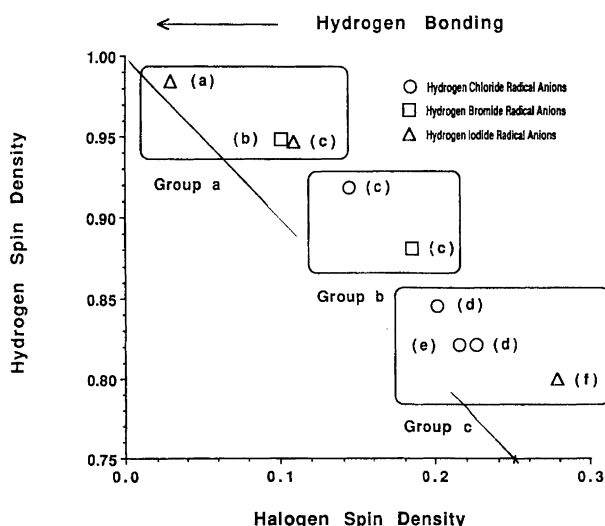


Fig. 3. Trends in the spin-densities on hydrogen and halogen for H-hal<sup>-</sup> radical-anions, estimated from their EPR spectra. The line shows the 'ideal' trend for unit spin-densities. Although all points deviate such that this total is slightly too large, nevertheless, the steadily increasing delocalization on going through the series is clear. Groups a, b and c represent different crystalline matrices in which the radicals were generated.

for such units.<sup>30</sup> I understand that this idea is now thought to be incorrect,<sup>31</sup> but I find the evidence for this statement inconclusive. This, however, is not the place for such controversy. Fortunately there can be no doubt about the reality of H<sup>-</sup>hal<sup>-</sup> centres. Recognition of the H<sup>-</sup>Cl<sup>-</sup> centre<sup>32</sup> was followed by a systematic study, in which H<sup>-</sup>F<sup>-</sup>, H<sup>-</sup>Br<sup>-</sup> and H<sup>-</sup>I<sup>-</sup> centres were also formed in various matrices.<sup>33,34</sup> The results show the expected trend (Fig. 3). Judging from the <sup>1</sup>H hyperfine splitting, H<sup>-</sup>F<sup>-</sup> may be just H<sup>-</sup> trapped adjacent to a single F<sup>-</sup> ion, as for R<sup>-</sup>hal<sup>-</sup> adducts (see below). Even so, the <sup>19</sup>F hyperfine features were clearly defined. For the remainder, there can be no doubt – these are genuine  $\sigma^*$  centres.

*The organic halide story.* Until the most interesting discovery of Williams and co-workers,<sup>35</sup> it was usually assumed that simple alkyl halides (R<sub>3</sub>C-hal) reacted in one step with electrons, to give R<sub>3</sub>C<sup>-</sup> radicals and halide ions. However, some envisaged a two-step process.<sup>36</sup> The new EPR results showed, fairly conclusively, that only one step is involved.<sup>37</sup> The key point is that, for solid matrices at low temperature, the parent products do not separate. This is clear from the well defined halogen hyperfine-coupling (Fig. 4).<sup>38</sup> Despite this coupling, the hyperfine parameters for the R<sub>3</sub>C<sup>-</sup> units were just those expected for the normal radicals. We argued that, if there were a genuine  $\sigma^*$  intermediate, distinct from these 'adducts' these systems would have to move back to such structures even if there were sufficient kinetic energy to induce DEC initially.<sup>39</sup>

Later, Williams and co-workers also showed that the

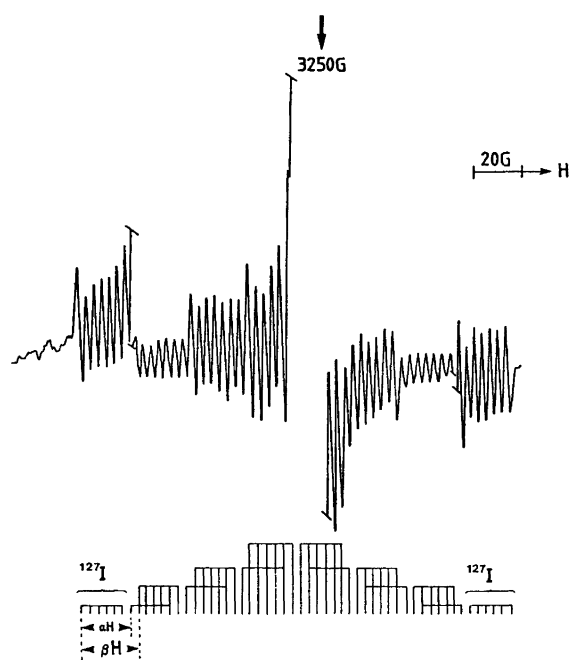


Fig. 4. First-derivative EPR spectrum for (CH<sub>3</sub>)<sub>2</sub>CH-I in adamantane after exposure to ionizing radiation, showing features assigned to (CH<sub>3</sub>)<sub>2</sub>CH<sup>-</sup> radicals weakly associated with I<sup>-</sup> anions. The small sextet splitting is from <sup>127</sup>I (*I*=5/2).

electron adduct formed by F<sub>3</sub>C-I is a true  $\sigma^*$  species, F<sub>3</sub>C<sup>-</sup>I<sup>-</sup>, with relatively high spin-density on iodine.<sup>40</sup> This raised the interesting question, when will C-hal units form  $\sigma^*$  intermediates? One factor is surely that of electronegativity difference ( $\Delta$  in Fig. 1), with the F<sub>3</sub>C-unit more electronegative than R<sub>3</sub>C-units. Another, more subtle, but important difference stems from the orbital switch that occurs for the central carbon on going from R<sub>3</sub>C-hal (roughly sp<sup>3</sup>) to R<sub>3</sub>C<sup>-</sup> (pure p).<sup>41,42</sup>

This constitutes a considerable switch in the energy of the orbital involved in the  $\sigma^*$  unit: as the R<sub>3</sub>C-hal bond stretches to accommodate the extra electron, so the energy is smoothly raised from sp<sup>3</sup> to p and the bond continues to stretch. However, the 'CF<sub>3</sub> radical is markedly pyramidal, so this trend does not occur, thereby greatly stabilising the  $\sigma^*$  structure. The origins of these phenomena are, of course, the same, and hinge on the high electronegativity of fluorine.

The (CF<sub>3</sub>)<sub>3</sub>C-I<sup>-</sup> situation highlights this contrast. In this case, the (CF<sub>3</sub>)<sub>3</sub>C<sup>-</sup> radical is probably planar, but, the electron distribution in the  $\sigma^*$  orbital is quite evenly balanced and the resulting three-electron bond is therefore relatively strong. Hence the planarity issue is not important. This  $\sigma^*$  radical provides an interesting example of a 'structure-switch', discussed in the next section.

These considerations led us to probe situations in which the 'sp<sup>x</sup> → p' relaxation cannot occur, in the hope that genuine  $\sigma^*$  C-X centres would then be formed. We were successful with certain aromatic centres, in which any major change in bond angle is blocked, and also for

HC≡C-I, where the orbital on carbon remains roughly sp-hybridised even for complete dissociation.<sup>40-43</sup>

Another interesting extrapolation was to the isoelectronic nitrogen species, R<sub>3</sub>N<sup>-</sup>-hal. It seems probable that the increase in electronegativity on going from R<sub>3</sub>C<sup>-</sup> to R<sub>3</sub>N<sup>-</sup> would be sufficient to induce σ\* stability.<sup>44</sup> In the event, the required experiments had already been done, although the results<sup>45</sup> had not been interpreted in this way. We then went on to show that these nitrogen analogues all have 'respectable' σ\* structures rather than the limiting 'contact' structures of the alkyl derivatives.<sup>46</sup> Returning to the R<sub>3</sub>C<sup>-</sup>-hal<sup>-</sup> adduct, it is interesting to note that the degree of halide-ion interaction, gauged from the hyperfine splitting, falls off rapidly with increase in the extent of solvation, and, at least for methyl iodide, the <sup>127</sup>I hyperfine splitting was lost entirely when methanol was used as the solvent, even at 77 K.<sup>47</sup>

*Other A-B centres.* Some of the range of σ\* centres with which I have been involved, and which have been characterised firmly by EPR spectroscopy, are listed in Table 1. I draw attention to three of these, which have their own special interest.

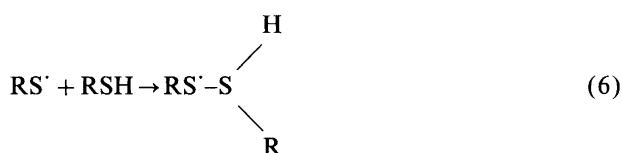
The first was the nitrogen centre in diamond.<sup>48</sup> These centres can be envisaged as follows. The excess electron is confined to a single C-N bond, which is very clearly defined by the <sup>14</sup>N and <sup>13</sup>C coupling constants. Proof that the SOMO is a σ-bond comes from the fact that the major axes lie exactly along the C-N directions. The fact that it is an antibonding orbital is established by the fact that the spin-density on carbon is clearly greater than that on nitrogen. Thus the trapping distortion is the stretching of just one of the four C-N σ-bonds.<sup>48</sup> Migration of the electron between these four bonds becomes fast on the EPR timescale only at very high temperatures. This is not only a beautiful example of a σ\* bond, but it also provides a fascinating contrast with the far more 'famous' structural analogue of phosphorus atoms in silicon. Here the electron is delocalised over a very large silicon sphere with the tetrahedral P<sup>+</sup> unit at its centre. Hence only the isotropic <sup>31</sup>P splitting is detected, and this corresponds to an extremely low effective spin-density on phosphorus.

The next centre is typified by the *N*-bromosuccinimide radical anion. We showed some years ago that the centres are genuine σ\*, linear >N<sup>-</sup>-Br<sup>-</sup> species, with very well

defined hyperfine coupling to <sup>14</sup>N and <sup>81/79</sup>Br.<sup>49</sup> This centre was of special interest to us because of an intriguing controversy regarding the structure/reactivity of the succinimidyl radical.<sup>50</sup> This could be either a π\* centre or a σ centre with the electron in an in-plane sp<sup>2</sup> orbital on nitrogen. It was generally agreed that the ground state should be π\* and this was nicely established by EPR spectroscopy.<sup>51</sup> However, in this case the mode of generation involved π-electron loss from the parent succinimide, followed by proton loss, so the species was 'born' as the π-centre.

In contrast, dissociation of the σ\* centres that we had prepared might lead, initially, to the σ\* centre that Skell and co-workers felt might be an important 'excited-state' intermediate with significant lifetime,<sup>50</sup> hence we studied a wide range of spectra in the hope of detecting the σ-intermediate. Unfortunately these σ\* centres proved to be too unstable and we detected neither species on warming. Recently, Kasai and co-workers<sup>52</sup> have demonstrated that, even at 4 K, the σ-intermediate cannot be detected, so the σ → π\* switch, though forbidden, must be very rapid.

The last of these mixed σ\* species that was of special interest to us is a ubiquitous sulfur centre characterised by a distinctive EPR spectrum with *g*-values of ca. 2.059, 2.025 and 2.001, and often a small doublet splitting in the 9 ± 1 G region. This centre (called species X) was originally identified as an RS' radical since it was readily formed from RSH derivatives.<sup>53</sup> I argued that, in view of the precise nature of the *g*-values in different environments, this identification was surely incorrect, and I suggested instead that the initial RS' radicals moved within the solid to form weak σ\* bonds to neighbouring RSH units, eqn. (6).<sup>54</sup>



These are expected to have considerable RS' character, but, because of the bonding, the *g*-shifts should be relatively small. Later, we detected species with far greater *g*<sub>||</sub> shifts which, we felt, were genuine RS' centres.<sup>54</sup> Gordy and co-workers then established that there were indeed two quite different sulfur atoms present (using <sup>33</sup>S), but concluded that the species was RSS' rather than RS'-S(H)R.<sup>55</sup> And so this duality of structures remains – I still like my original structure, principally because it would be so readily formed compared with the RSS' centres. But many others favour this latter structure. Coincidences must arise sometimes, even in science and I sometimes wonder if both centres have, fortuitously, similar *g*-values. However, a centre formed from RS-S-Cl molecules by electron capture has quite distinct *g*-values, and, since there was no <sup>35</sup>Cl/<sup>37</sup>Cl hyperfine splitting, we consider that this really is RSS'. In this case, species X is not an RSS' centre!

Table 1. Examples of A-A and A-B σ\* species (which have been studied in my laboratories)

hal-hal <sup>-</sup>	R <sub>2</sub> S-SR <sub>2</sub> <sup>+</sup>
hal-OH <sup>-</sup>	RS-SR <sup>-</sup>
RCONH-hal <sup>-</sup>	R <sub>2</sub> S-hal
Br-CN <sup>-</sup>	R <sub>3</sub> P-hal
HC≡C-I <sup>-</sup>	Rhal-halR <sup>+</sup>
C <sub>6</sub> H <sub>5</sub> -hal <sup>-</sup>	Imidazole-hal <sup>-</sup>
C <sub>6</sub> F <sub>5</sub> -hal <sup>-</sup>	Uracil-hal <sup>-</sup>
R <sub>3</sub> N-hal	H <sub>3</sub> N-NH <sub>3</sub> <sup>+</sup>
R <sub>3</sub> P-PR <sub>3</sub> <sup>+</sup>	

## 6. Structure switches

By this I mean unimolecular electronic structural changes in which a  $\sigma^*$  structure is involved. One of the clearest arises for aryl halides on electron addition. This is expected to involve initial addition into the  $\pi$ -system, in part because this usually involves only minor geometric changes. However, if the C–hal bond stretches, the electron can switch from  $\pi^*$  to  $\sigma^*$  (a formally forbidden transition) and DEC may then occur. We probed the situation, and in some cases were able to detect the  $\sigma^*$  Ar–hal<sup>-</sup> intermediates.<sup>41,42</sup> This dichotomy had been proposed by many. However, it was also proposed that a similar switch between  $\pi^*$  and  $\sigma^*$  levels should arise for the corresponding benzyl derivatives Ar–CH<sub>2</sub>–hal.<sup>56</sup> In our view, however, it is not a comparable situation.<sup>57</sup> In part, this is because R<sub>3</sub>C–hal<sup>-</sup>  $\sigma^*$  species have no potential energy minimum, as stressed above, and partly because hyperconjugative ( $\sigma$ – $\pi$ ) mixing is expected, so that there is no real orbital switch. Indeed one can view structures of this type as being  $\pi^*$ – $\sigma^*$  ‘hybrids’. There is a tendency for such  $\beta$ -halogen atoms to prefer the out-of-plane site, as we and others have shown for R<sub>2</sub>C<sup>-</sup>–CH<sub>2</sub>(hal) radicals. So, if DEC occurs, it involves a smooth stretching of the C–hal bond and flattening of the ArCH<sub>2</sub> unit without any extra intermediate (in my view!).

An inverse switch, from an initial  $\sigma^*$  structure, was postulated for e<sup>-</sup>-addition to cyanogen bromide, N≡C<sup>-</sup>–Br.<sup>58</sup> As with RC C–I,<sup>40</sup> the initial product was the linear  $\sigma^*$  anion, N≡C–Br<sup>-</sup>. However, a new species, with a greatly reduced spin-density on bromine, was formed from this  $\sigma^*$  centre on annealing. The EPR data support the idea that this is the ‘ $\sigma$ ’, bent, species, N=C<sup>-</sup><sub>Br</sub>. Thus, in this case it seems that bond-stretching was favoured over bending, but that the greater ‘non-bonding’ character of the SOMO for the bent species makes this structure more stable.

*Phosphoranyl and related radicals.* Just this situation also arises for various phosphorus-centred radicals. Also, surely, for many similar systems – but we, and others, have used phosphorus in these studies, because the <sup>31</sup>P hyperfine coupling parameters are so easy to pick up by EPR spectroscopy, and are relatively easy to interpret. So I use the term ‘phosphoranyl-type radical’ to cover species thought to have trigonal-bipyramidal structures, in which the unpaired electron is in a (formally) non-bonding sp-hybrid occupying one of the trigonal sites. (I stress that is a limiting structure, used for convenience.) The EPR data show that there are two (equal) axial ligands that couple strongly, and two (equal) equatorial ligands that couple weakly if at all.

When a radical, R<sup>•</sup>, adds to three-coordinated phosphorus, I expect, on the principle of microscopic reversibility, that initial formation of a  $\sigma^*$  radical will result. (I stress that, in this nomenclature, such  $\sigma^*$  radicals are *not* ‘phosphoranyl radicals.’) Subsequently, these  $\sigma^*$  centres may switch, by bond bending, to a phosphoranyl

structure. This switch is best if R goes into the axial site: it may subsequently migrate to the equatorial site if this is favoured.<sup>59</sup>

For electron addition to an R–PL<sub>3</sub> species, this requirement is not so firm, and either type of radical may initially be formed. However, when ‘R’ is strongly electro-negative, for example R=hal, then  $\sigma^*$  radicals are frequently initial products. A different ‘switch’ occurs for A–B<sup>-</sup> type  $\sigma^*$  radicals, when the electron is fairly equally distributed within the  $\sigma^*$  SOMO. Here dissociation can give either A<sup>•</sup> + B<sup>-</sup> or A<sup>-</sup> + B<sup>•</sup>, and a simple change in solvent may tip the scales from one mode to the other. A nice example proved to be the (F<sub>3</sub>C)<sub>3</sub>C<sup>-</sup>–I<sup>-</sup> centre discussed above. Thus, even in solvent methanol, which might be expected to favour formation of I<sup>-</sup>, we obtained clear evidence for iodine *atom* formation.<sup>61</sup> ‘Free’ iodine atoms are normally very difficult to detect by EPR spectroscopy<sup>20</sup> but the tendency to form  $\sigma^*$  species came to our aid, CH<sub>3</sub> and the species detected was thought to be I<sup>-</sup>–O<<sub>H</sub>CH<sub>3</sub> units.<sup>61</sup> These are, of course, close to being I<sup>•</sup> atoms, but the weak  $\sigma$ -interaction is enough to quench the orbital angular momentum to a considerable extent.

## Conclusions

The major conclusion must be that genuine  $\sigma^*$  species are chemically and mechanistically of real importance, and *must* be considered seriously. They are probably also of biological importance, especially for RS–SR derivatives. Thus, for example, we found that electrons, generated in proteins containing S–S bonds, readily migrate thereto to form RS<sup>•</sup>–SR<sup>-</sup> centres.<sup>62</sup>

I think that EPR spectroscopy has played a major role in establishing structure. Hence these centres are remarkably well understood structurally. One of the great puzzles is why first row–first row units seem to be so difficult to form, when they are predicted to be the most stable of all. This remains a real structural puzzle – at least to me. Even so, structural factors are, largely, well understood. However, it is the mechanistic implications, such as those stressed by Breslow and co-workers<sup>11</sup> that are so important.

## Mechanistic implications – there are many!

They include (i) providing alternative reactions to those expected; (ii) reducing the rates of such reactions; (iii) increasing selectivity when more than one reaction occurs. In (i),  $\sigma^*$  species may go on to give products that would not have formed had not such adducts been involved. In (ii) H–X adducts, for example, may be so stable that they fail to give the reactions of ‘free’ H<sup>•</sup> atoms. This greatly reduces the [H<sup>•</sup>] and hence the observed rates. In (iii) H–X adducts for example react directly, but only in the most favourable processes.

### Why are σ\* species more significant than σ<sub>1</sub> centres?

I think that the main reasons are clear. For many molecules and ions, the π\* orbitals are partially or totally filled. These are always well separated from the σ-bonding orbitals and hence electron-loss is expected to be from the π\* (or even the π) orbitals rather than from a σ-orbital. However, the σ\* and π\* levels may be quite close, and specific bond-stretching may well lower the σ\* below the π\* levels. Hence electron loss from σ levels is mainly favoured only when there are no π levels, as, for example, for saturated hydrocarbons. Extensive EPR studies of radical-cations have strongly supported this contention.<sup>63,64</sup> In contrast, the σ\* and π\* orbitals may well be close – especially as the σ-bond stretches to lower the σ\* level – and hence σ\* centres abound, as I have tried to show, herein.

Two final points. One is to stress that throughout my lengthy studies of radicals using EPR spectroscopy, going back for over 40 years, the key to my understanding has always been a qualitative version of MO theory, at the LCAO level, such as the arguments used herein. Our early ideas are expressed in my book with Peter Atkins.<sup>65</sup> I make no apologies for this: it *works*, and that, surely is justification enough. Theoreticians today are inclined to criticise this approach as being ‘old fashioned’. I *do* realise that modern computers will do infinitely better, but one can end up with no deeper understanding than simple MO theory provides. I have never known it to fail, and it has opened many doors for me and others. I see no point in abandoning this method of thinking, at least until something else as clear comes along, for simple-minded people such as myself.

*Acknowledgements.* Finally, I apologise to all those whose work *should* have been cited in a review of this sort. Much that we have done has been built on their work: however, this is a ‘mini’-review with limited space, and my terms of reference were to use our own work in this area. It has been extensive, and I thank all my collaborators, senior and junior, who did so much.

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