The Electron Paramagnetic Resonance Spectra of Organic Radical Ions

Alwyn G. Davies

Chemistry Department, University College London, 20 Gordon Street, London, WC1H OAJ, U.K.

1 Introduction

Organic radical ions have played a key role in organic EPR spectroscopy. Neutral radicals in fluid solution usually self-react at a diffusion-controlled rate and have a lifetime of much less than a second. If their EPR spectra are to be recorded, they therefore have to be continually generated within the cavity by special methods such as *in situ* irradiation with electrons or with UV light, or by flow mixing of the reagents as they enter the cavity.

Radical anions and cations on the other hand are usually longer lived, sometimes indefinitely so, and it is relatively easy to obtain strong, well-resolved spectra.

It was natural then that much of the early work on the EPR spectra of organic radicals should be focused largely on radical ions. The first set of papers, by Weissman in 1953,[1] included the naphthalene, anthracene, and mono-, di-, and tri-nitrobenzene radical anions and Wurster's nitrogen-containing radical cation, and the second set, by Fraenkel in 1955,[2] was concerned with the semiquinone and semidione radical anions.

Most of the principles concerning hyperfine coupling which are used today were derived from studies on radical anions in the 1950s and 1960s and are discussed in Gerson's book on High Resolution EPR Spectroscopy (1970),[3] and in Kaiser and Kevan's edited volume on Radical Ions (1968).[4] Since then there have been few major developments in matters of principle, but the experimental techniques have improved greatly, particularly in relation to radical cations, and the studies have been extended to many more structural types. An extensive, though not comprehensive, listing of the EPR data on organic radical ions, with references, is given in three editions of Landolt–Börnstein.[5]

The major development in technique has been the generation of radical ions by gamma-irradiation of dilute solutions of substrates in frozen matrices such as ethers for radical anions, or Freons for radical cations.[6] As the radical ions are immobilized, the spectra are anisotropic; this anisotropy provides further information about the electron configuration, but it also causes the lines to be relatively broad. The technique is most useful for smaller molecules, and it can be used for generating radical cations from compounds with high ionization energies, such as alkanes.[5] It is less useful for generating the radical cations from larger π-conjugated compounds, where the resolution of complex spectra containing a large number of closely spaced lines is often important.

A second technique which is being increasingly used is the generation of radical cations in activated zeolites.[7] It can be used for substrates with ionization energies up to about 11 eV. The reactant must be small enough to enter the channels of the zeolites, and the hindering of rotation may again give rise to anisotropic spectra.

This review will concentrate on the EPR spectra of radical ions in fluid solution.

2 Generation

The orbital occupancy by the electrons of a π-conjugated molecule and its corresponding radical anion and cation are illustrated in Figure 1. In principle, the radical anion is formed by addition of an electron into the LUMO, and the radical cation by removal of an electron from the HOMO, but less direct routes to the radical ions can often be used if the parent compound is not available.
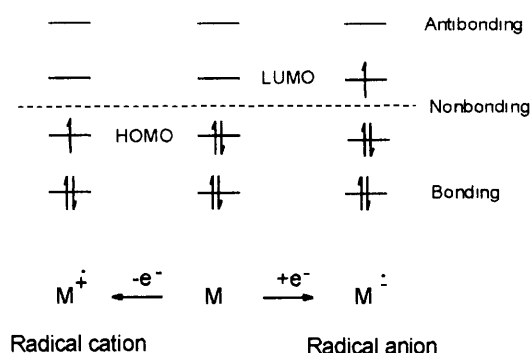

Figure 1 Orbital occupancy in M, M$^{\cdot+}$, and M$^{\cdot-}$.

A fundamental problem in generating a radical anion or cation from a substrate M is that of avoiding back electron transfer from the radical anion to the oxidized reductant, or to the radical cation from the reduced oxidant. For the radical anions this problem is easily solved by using an alkali metal as the reductant (see below), and up to about 1980 many more radical anions than cations had been studied. In recent years new techniques for generating radical cations have been developed, and that situation has now been partly redressed.[8]

2.1 Radical Anions

The principal techniques for generating radical anions in fluid solution are shown in Table 1.

Table 1 Generation of radical anions

(1) Reduction with an alkali metal
(2) Photoassisted electron transfer
(3) Deprotonation of a neutral radical
(4) Electrolysis

Professor Davies did his B.Sc. degree at University College London, and his Ph.D. with Sir Christopher Ingold. His research has included work on organic peroxides, organometallic chemistry, and free radical reactions, and the EPR spectra of organic radicals and radical ions. He is a Fellow of the Royal Society, and holds the Organic Reaction Mechanisms prize of the Royal Society of Chemistry, and is the present Chairman of the ESR Group. He will be spending a year from November 1993 at the University of Freiburg as the holder of a Humboldt Award.

Experimental Methods for Generation of Radical Ions

If UV irradiation is to be used, the working part a of the cell must be made of high grade silica ($e\ g$ Suprasil, ca 3 mm o d) which will not itself develop a signal under irradiation The silica cell a is joined to the Pyrex upper section through the graded seal b Solvents can be transferred by pipette or syringe, or on a vacuum line Typical procedures are as follows

Radical Cations The solvent ($e\ g$ TFAH, ca 0 5 cm³), Hg(TFA)₂ (ca 10 mg), and the substrate (1—2 mg) are successively added to the cell A, and then flushed with nitrogen or degassed on the vacuum line The cell is stoppered at c or sealed at d, and transferred to the EPR cavity which is equipped for *in situ* photolysis

Radical Anions In straightforward cases, it may be sufficient to add the substrate (1—2 mg) to the cell A, and a clean piece of potassium at b, too large to pass into the silica section a The solvent ($e\ g$ potassium–dried THF, ca 0 5 cm³) is then distilled into the cell on the vacuum line and sealed at d The solution is washed over the metal until the colour and the spectrum of the radical ion develop, sonication in a cleaning bath may be used to accelerate the process

For more demanding substrates, the apparatus B may be used, the purpose of the coarse sintered glass filter e is to prevent fragments of metal passing into the working part of the cell a, and that of the bypass f is to avoid an air lock The sample is introduced into a and the metal into the side arm h which is then stoppered The cell is connected to the vacuum line at d and then sealed under vacuum at i The side arm g is warmed with a luminous flame to distil the metal as a mirror onto the walls at j The side arm h is removed by sealing at k,
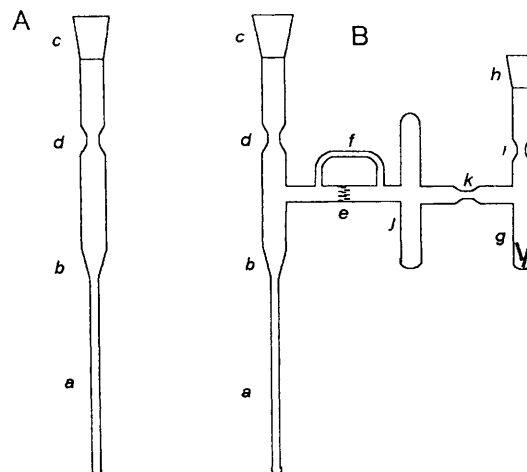
the solvent is distilled into a on the vacuum line and the cell is sealed at d The radical anion is then generated as before

After use, the cell should be cut open, and the residual metal cautiously dissolved in an alcohol, t-butyl alcohol should be used for potassium The cell can then be reconstructed and reused

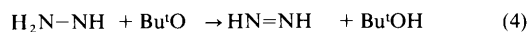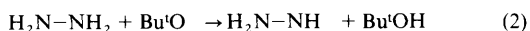The formation of a radical anion by treating a substrate with an alkali metal is very general (e g equation 1)

$$C_6H_6 + K \rightarrow C_6H_6^{-} + K^{+} \qquad (1)$$

All the alkali metals can be used, including sodium/potassium alloy, and sodium amalgam, and a more polar solvent ($e\ g$ diethyl ether or tetrahydrofuran rather than a hydrocarbon) helps to solvate the ions which are formed A good ligand for the metal cation, particularly a crown ether, will further stabilize the metal cation, and the electron transfer can be assisted by sonication

The alkali metals all have nuclear spin, and frequently hyperfine coupling can be observed to the metal counter cation This is discussed below

If the parent molecule M is not accessible, the radical anion M⁻ can sometimes be prepared by photo-induced electron transfer

An example is illustrated in Figure 2 Photoionization of hydrazine in liquid ammonia/THF in the presence of potassium t-butoxide leads to the formation of the diazene radical anion by the sequence of reactions shown in equations 2—4 [9]

$$H_2N-NH_2 + Bu^tO^- \rightarrow H_2N-NH^- + Bu^tOH \qquad (2)$$

$$H_2N-NH^- \xrightarrow{h\nu} H_2N-NH\cdot + e_{solv}^- \qquad (3)$$

$$H_2N-NH\cdot + Bu^tO^- \rightarrow HN=NH^- + Bu^tOH \qquad (4)$$

The spectrum shows hyperfine coupling by two equivalent nitrogen atoms [$I = 1$, a(2N) 7 9 G], and two equivalent protons [a(2H) 11 3 G], together with, at high field, the singlet due to the solvated electron

A radical anion can be regarded as the conjugate base of a protic neutral radical, and equation 5 illustrates the application of this principle in the preparation of the radical anion of di-t-butylsilanone[10] by the abstraction of a hydrogen atom and a proton from the corresponding silanol by a t-butoxyl radical (from the photolysis of di-t-butyl peroxide) and a t-butoxide anion respectively

$$Bu^t_2Si\begin{smallmatrix}H\\\\OH\end{smallmatrix} \xrightarrow[Bu^tO^-]{Bu^tO\cdot} Bu^t_2Si = O^{-} \qquad (5)$$
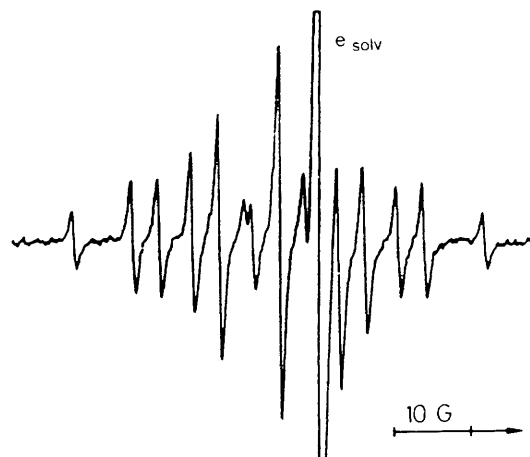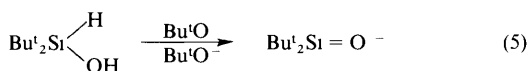
Figure 2 EPR spectrum of the diazene radical anion in liquid NH₃/THF, showing, as marked, the singlet due to the solvated electron (Taken, with permission from ref 9)

Few chemists appear to be confident in both electrochemistry and EPR spectroscopy, and the electrolytic generation of radical anions and cations deserves more attention A convenient cell for *in situ* electrolysis has been described by Ohya-Nishiguchi [11] The technique has the advantage of being applicable under neutral conditions over a wide range of temperature It has been particularly successful for preparing radical ion salts for X-ray crystallography, the salt may separate on the appropriate electrode, and be used without further handling [12]

2.2 Radical Cations

There is no single method equivalent to the alkali metal route to radical anions, by which radical cations can be prepared A variety of methods is available as shown in Table 2,[8] and the choice between these is still largely empirical The electron transfers in methods 1—5 may all be promoted by photolysis

Mere dissolution of a substrate in a protic acid (CF₃CO₂H, H₂SO₄, CF₃SO₃H/SO₂, FSO₃H/SO₂), may be sufficient to

Table 2 Generation of radical cations

(1) With protic acids
(2) With Lewis acids
(3) With oxidizing metal ions
(4) With π-conjugated electron acceptors
(5) With aminium radical cations
(6) Protonation of a neutral radical
(7) Electrolysis

generate the radical cation, the substrates with the higher ionization energies need the use of the stronger acids For example, the NMR and EPR spectra of anthracene in FSO_3H/SO_2 show that the cation resulting from addition of a proton at the 9-position, and the radical cation resulting from removal of an electron, are both present [13] When trifluoroacetic acid (TFAH) is used as the solvent, nucleophilic attack on either species may have the result that the EPR spectrum of the aryltrifluoroacetate [e g 9-trifluoroacetoxy- and 9,10-bis(trifluoroacetoxy)-anthracene $^+$] is observed [14]

The mechanism or mechanisms by which protic acids bring about oxidation is not certain (and the possible effect of daylight has often been ignored) The suggestions which have been made include electron transfer to ground state or photoexcited substrate (equation 6),[15] and electron transfer from the photoexcited substrate to the dimer of trifluoroacetic acid, which avoids back electron transfer by dissociating into trifluoroacetate anion and dihydroxytrifluoroethyl radical (equation 7) [16]

$$M + MH^+ \rightarrow M^+ + MH \qquad (6)$$

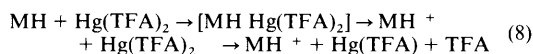$$M^* + (CF_3CO_2H)_2 \rightarrow M^+ + CF_3C(OH)_2 + CF_3CO_2 \qquad (7)$$
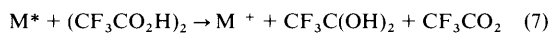
A variety of Lewis acids behave in the same way Aluminium trichloride has been most widely used, particularly in dichloromethane, and, without photolysis, will bring about the oxidation of substrates with ionization energies less than ca 8 eV Other reagents which have been used include $AsCl_5$, BF_3, BCl_3, $SbCl_3$, and $SbCl_5$ [7]

Oxidation with metal ions has been carried out with silver(i), cobalt(iii),[17] cerium(iv),[18] mercury(ii),[19] and thallium(iii),[20] usually in TFAH, and with lead(iv) in FSO_3H,[7] the oxidizing power is in the sequence $Ce^{IV} > Tl^{III} > Hg^{II}$

Cobalt(iii) and cerium(iv) have been used only under flow conditions which is expensive in solvent, reagent, and substrate, but is sometimes uniquely effective Modifications of this method, using other cobalt and cerium salts under static, photolytic conditions might repay investigation

Mercury trifluoroacetate or thallium trifluoroacetate in static, usually photolytic systems have been used extensively The mechanism is illustrated for $Hg(TFA)_2/TFAH$ in equation 8, it involves photoassisted electron transfer within a charge-transfer complex, energy-wasting back electron transfer being avoided by loss of trifluoroacetate ion from the reduced metal complex [21]

$$\begin{aligned} MH + Hg(TFA)_2 &\rightarrow [MH \; Hg(TFA)_2] \rightarrow MH^+ \\ &+ Hg(TFA)_2 \rightarrow MH^+ + Hg(TFA) + TFA \end{aligned} \qquad (8)$$

Under these conditions, a number of substrates undergo mercuration in the aromatic ring,[22] the reaction occurs at the CH ring position where, in the SOMO, the electron density (and hence the hyperfine coupling constant) is highest The ionization energies of the mercurated species are often close to those of the parent molecules, and the EPR spectra which are observed may be of MH $^+$, or MHg(TFA) $^+$, or both With some substrates, the mercuration under photolytic conditions is faster than that in the dark, and hence the reaction can apparently proceed through the interaction of the radical ion pair as well as through the neutral molecules, both processes giving the same Wheland intermediate $M(H)Hg(TFA)_2$ (equation 9) There appears to be

no report of the observation of the analogous arylthallium radical cations in experiments with $Tl(TFA)_3$


$$+ \; TFAH \quad (9)$$
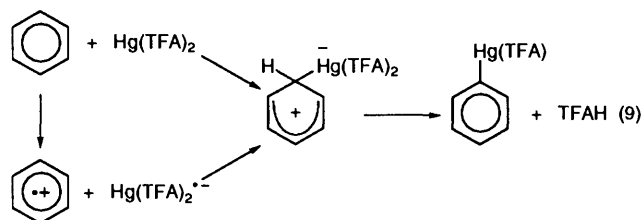
The generation of radical cations by electron transfer to π-electron acceptors has not been widely used, and should be capable of being extended For example, when a few drops of TFAH are added to a solution of thianthrene and of 2 3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dichloromethane, a purple colour develops, and the spectrum of the thianthrene radical cation can be observed [23] Presumably protonation of the DDQ radical anion to give the neutral radical overcomes the reversibility of the electron transfer

$$(10)$$

$$(11)$$
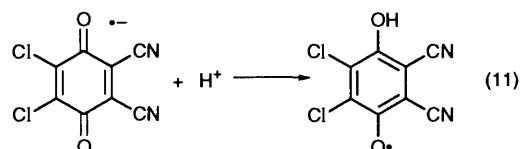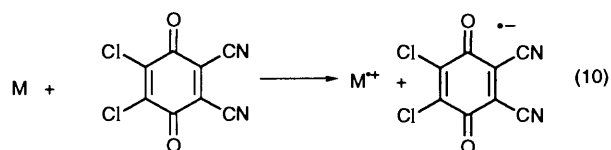
Triarylaminium radical cations, Ar_3N $^+$ will remove an electron from a substrate with an appropriately low ionization energy, and provide a useful route to radical cations under mild conditions Tris(4-bromophenyl)aminium hexachloroantimonate, $(4\text{-}BrC_6H_4)_3N$ $^+$ $SbCl_6$), is commercially available, and the tris(2,4-dibromophenyl)aminium hexachloroantimonate is readily prepared Solutions of the aminium salt and substrate are mixed at low temperature, then allowed to warm when the spectrum develops [24]

The formation of a radical cation by the protonation of a neutral radical is a useful concept, though many of the reactions which might appear to follow this mechanism in fact adopt an alternate route For example, the photolysis of pentamethylcyclopentadiene under neutral conditions shows the formation of the pentamethylcyclopentadienyl radical, and it was predicted that the same reaction in TFAH should show the spectrum of the pentamethylcyclopentadiene radical cation (equation 12) [15] Indeed it does, but the reaction appears to involve oxidation of the substrate Me_5C_5H by the photoexcited cation $Me_5C_5H_2^+$

$$(12)$$
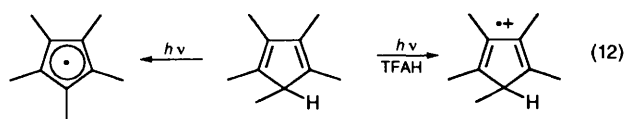
As mentioned above the electrolytic technique appears to be capable of further development One of its advantages is that it can avoid the strongly acid conditions of most of the other techniques, and in principle it can be used for acid-sensitive substrates such as organometallic compounds However, one of the principal decay routes of radical cations involves loss of a proton to give a highly reactive neutral radical, and acid conditions may be necessary to avoid this problem

3 Interpretation of Spectra[3]

The hyperfine coupling (a) for a proton in the α- or β-position to an unpaired electron is given by the McConnell and Heller–McConnell equations (equations 13 and 14) where ρ is the electron spin density at the carbon centre, and Q is the McConnell constant

$$a(H_a) = \rho C_a Q_a \qquad (13)$$

$$a(H_\beta) = \rho C_a(A + B\cos^2\theta) \qquad (14)$$

In equation 14 θ is the dihedral angle between the axis of the $2p$ orbital and the CH bond, if, in a series of related compounds, θ may be assumed to be constant, equation 14 can be reduced to equation 15

$$a(H_\beta) = \rho C_a Q_\beta \qquad (15)$$

If any two of the three terms in equation 13 or 15 are known, the third can be calculated, and in a conjugated system, the spin densities over all the π-centres should sum to unity One use of these relationships is to predict and to help in the analysis of the spectra of new radical ions, a second is to check the performance of MO calculations of local electron densities
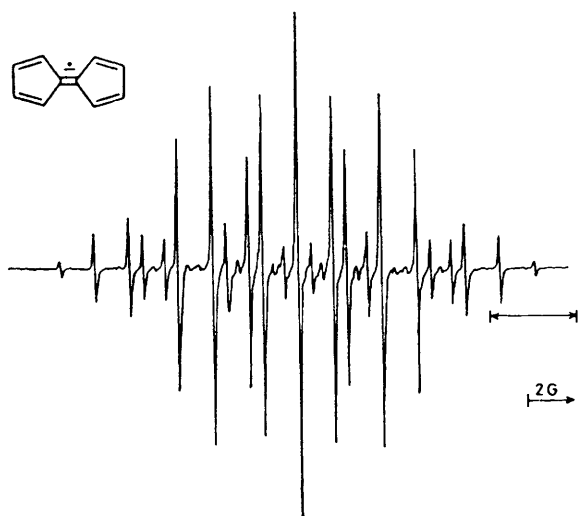
As a first approximation, the spin density may be taken to be equal to the Huckel electron density (c^2) at the π-centre, but in a conjugated system it will depend also on the electron density at the other π-centres, and allowance for this can be made by McLachlan's method [3]

Values of the constant Q_a have been derived by Gerson[3] from the regression lines of plots of observed coupling constants against HMO electron densities or McLachlan spin densities, and are $(-)26\ 9$ and $(-)21\ 8$ G respectively for radical anions, and $(-)35\ 1$ and $(-)25\ 4$G respectively for radical cations The larger values for the radical cations are ascribed to the effect of the positive charge on the spatial distribution of the p orbital on carbon, or the s orbital on hydrogen The predictive value of the two calculations is illustrated in Table 3 for the spectrum of the radical anion of fulvalene[25] which is shown in Figure 3 Pro-

grammes for the calculation of Huckel electron densities and McLachlan spin densities, and for the simulation of EPR spectra are available for microcomputers

In strong simple spectra, the satellite lines due to ^{13}C hyperfine coupling in natural abundance can sometimes be observed The analysis can be based on relative intensities and on the values predicted by a calculation which sums the spin polarization contributions from the spin densities on the α- and β-carbon atoms in the π-system An example (for the biphenylene radical cation) is given in reference 26
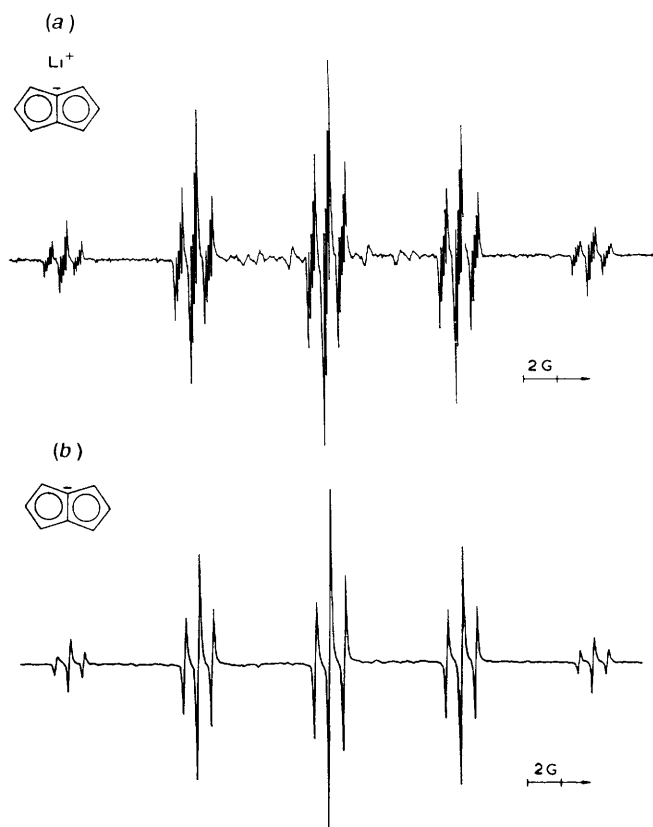
4 Counterion Coupling

As mentioned above, radical anions may show hyperfine coupling to an alkali metal counterion [^7Li (92 6%), ^{23}Na (100%), ^{39}K (93 1%), all with $I = 3/2$, ^{85}Rb (72 8%) $I = 5/2$, ^{87}Rb (27 2%) $I = 3/2$, ^{133}Cs (100%) $I = 7/2$]

An example is shown in Figure 4 [27] Irradiation of the dianion of dihydropentalene with UV light induces electron transfer to the lithium cation (equation 16), and the spectrum of the pentalene radical anion can be observed There is a nodal plane in the SOMO passing through the 2- and 5-positions The spectrum therefore consists of a quintet [a(4H) 7 76 G] of narrowly spaced triplets [a(2H) 0 90 G] (at $-48\ ^\circ$C), and each line is further split into a 1 1 1 1 1 quartet by coupling with the lithium counter ion (Figure 4a), if 12-crown-4 is added, this complexes the lithium cation and breaks the coupling, and the quartets are reduced to singlets (Figure 4b)

(16)
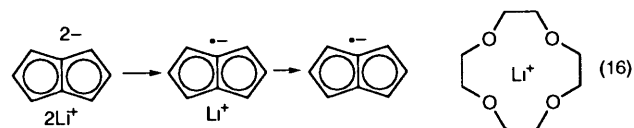
The interaction with the counterion is usually reduced at lower temperature (as the dielectric constant of the solvent

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Table 3 Observed and calculated values of $a(H\alpha)/G$ in the fulvalene radical anion

	a(H-2,2′,5,5′)	a(H-3,3′,4,4′)
Observed	1 55	3 7
Calculated (HMO)[a]	$-1\ 85$	$-3\ 31$
Calculated (HMO/McLachlan)[a]	$-1\ 05$	$-3\ 25$

Taking $Q = -30$ G as it is in the cyclopentadienyl radical

Figure 3 EPR spectrum of the fulvalene radical anion

Figure 4 EPR spectrum of the pentalene radical anion showing (a) the presence of hyperfine coupling to the lithium counterion and (b) the absence of this coupling when 12-crown-4 is added

increases) and when the coordinating power of the solvent is increased (e g when THF is replaced by DME)

The effect that the counter cation has on the spin distribution, and hence the hyperfine coupling constants, in the radical anion is usually small, but in some special cases it may lead to a concentration of the unpaired electron density in one particular region of the molecule This appears to be the cause of the complications which are observed in the EPR spectrum of the tetraphenylene radical anion [28]

It is interesting that there appear to be no reports of the observation of hyperfine coupling of a counteranion with a radical cation Part of the explanation may be that whereas the alkali metal cations are poor electrophiles for the carbanions, the common counter anions are better nucleophiles for the radical cations, and lead to chemical reaction such as the mecuration or trifluoroacetoxylation which is mentioned above

5 Chemical Interactions and Reactions

It must be remembered that the EPR technique is very sensitive – the spectra illustrated in Figures 2 and 4 are derived from solutions ca 10^{-6} M in radical ions The spectrum which is observed will be that of the substrate in solution with the lowest ionization energy or electron affinity, and impurities in low concentrations can cause misleading results For example, tetraphenylene prepared from the thermolysis of biphenylene continues to show the EPR spectrum of the biphenylene radical cation until it is purified by chromatography, and radical anions prepared from sodium or potassium which has been stored under tetralin or decalin may show the spectrum of the naphthalene radical anion

One must equally beware of the interactions and the unimolecular and bimolecular reactions which the radical ions may undergo in solution These are rare with radical anions, but common with radical cations, also of course the strongly acid conditions which are often used for generating radical cations may induce reactions of the substrates also by non-radical routes

The most common phenomenon that is observed is the charge-transfer interaction of a radical cation and its precursor (equation 17)

$$M^{+} + M \rightarrow (M)_2^{+} \qquad (17)$$

The hyperfine coupling constants in, for example, the anthracene dimer radical cation are the same as those which are observed in the cyclophane where two anthracene structures are held in eclipsing positions,[29] and it is assumed that, in the absence of steric repulsion between substituents, the two molecules similarly are eclipsed in the dimers M_2^+, idealizing the overlap of the SOMO and HOMO The electron is equally shared between the two molecules, and the spectrum shows hyperfine coupling to twice the number of protons (or other nuclei) of each type, at approximately half the coupling constant shown by M^+ Thus the benzene radical cation with a(6H) 4 44 G forms $(C_6H_6)_2^+$ with a(12H) 2 16 G, and the anthracene radical cation with a(2H) 6 47 G, a(4H) 3 08 G, a(4H) 1 38 G gives $(C_{14}H_{10})_2^+$ with a(4H) 3 25, a(8H) 1 42 G, a(8H) 0 71 G [7]

In favourable examples M^+ may associate with a number of parent molecules M, and with coronene, complexes up to $(C_{24}H_{12})_4^+$ have been identified by electrolysis at low temperature [30]

If the arene carries substituents, as in pyracene or 1-methylnaphthalene, steric interference between the substituents may lead to dimers with lower structural symmetry [11]

Similar dimer radical cations, M_2^+, are known for sulfur-centred,[31] nitrogen-centred,[32] and phosphorus-centred[33] radical cations

No equivalent interaction to give the dimeric species M_2^- has been reported for radical anions, although when two arenes are held closely parallel in a cyclophane radical anion, the unpaired electron is delocalized over both rings [29] The SOMO would now

have the same symmetry as the LUMO of the substrate and this interaction is apparently less bonding than is the SOMO/HOMO interaction in radical cations One contributory factor may be that in the anion, the p-orbitals are more diffuse than in the cations

The dimers M_2^+ may interact further by covalent bonding For example dialkylacetylene radical cations react with their parents to give tetraalkylcyclobutadiene radical cations (equation 18),[34] and treatment of benzene with $Hg(TFA)_2/TFAH$ leads to the radical cation of biphenyl (equation 19) [35]

(18)

(19)
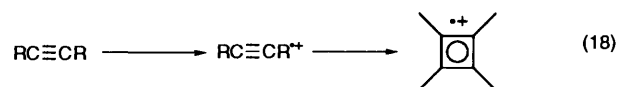
Radical cations may also be formed with intramolecular rearrangement, though it is often not clear whether this occurs through a cation or radical cation Thus di-t-butyl acetylene with aluminium chloride shows the spectrum of the hexamethylbutadiene radical cation (equation 20),[36] diphenylacetylene shows the spectrum of the triphenylazulene radical cation (equation 21),[37] and 1,4-dimethylcyclohexene shows the radical cation of the Diels–Alder adduct between the parent and 2,5-dimethylcyclohexadiene (equation 22) [38]

(20)

(21)

(22)
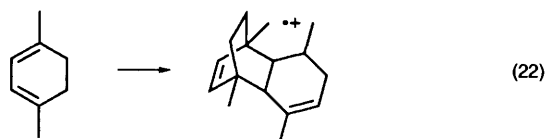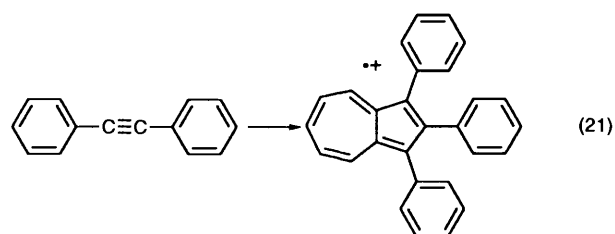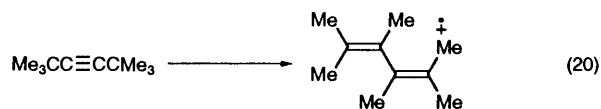
More deep-seated rearrangements can sometimes be observed, and bis(pentamethylphenyl)methane and a variety of related systems containing polymethylated benzene derivatives all show the spectrum as the octamethylanthracene radical cation [39]

6 References

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