

REVIEW

J. Chem. Research (S),
2001, 253–261
J. Chem. Research (M),
2001, 0701–0729

The generation of organic radical cations: a guide to current practice for EPR spectroscopic studies

Alwyn G. Davies*

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK

A wide variety of methods is now available, each with its particular advantages and disadvantages, for generating radical cations for EPR or other spectroscopic studies in fluid solution or in matrix. This field is critically surveyed, together with recent developments in the understanding of the mechanisms of these reactions.

Keywords: radical cations, EPR

1 Introduction

EPR spectroscopy gives a direct insight into the electronic structure of radical ions and can provide evidence for the electron distribution and, often quantitatively, for the various electronic effects by which organic chemists interpret structure and reactivity. The early experiments in this field, almost 50 years ago, provided remarkable confirmation of the predictions of Hückel molecular orbital theory.

As shown in Fig. 1, the electronic configuration of a radical anion corresponds to that of the LUMO of the substrate S, whereas the configuration of the radical cation corresponds to that of the HOMO of S, and is more directly relevant to the properties of molecules in their ground states, which are involved in thermal reactions.

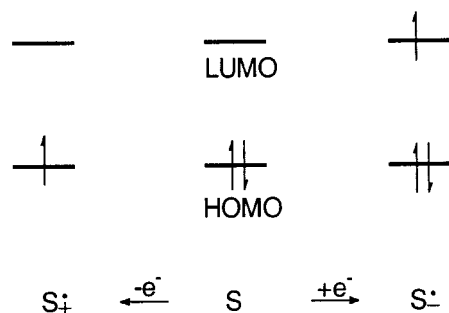
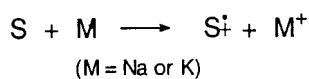


Fig. 1 Electronic configuration of radical anion and cation

It has also become apparent that radical cations may be involved in some reactions that were regarded previously as being purely heterolytic, and that some reactions involving closed-shell reagents can with advantage be directed through their radical cations. Much effort has therefore been put into the methodology of generating radical cations for EPR and other spectroscopic studies.

The radical anions of a wide variety of organic compounds can be prepared in solution by treating the substrates, S, with an alkali metal (Scheme 1), but there is no equivalent general method for generating radical cations.

The early studies of radical cations depended on treating the substrates with concentrated sulfuric acid, or on electrochemical oxidation,¹ but these methods are limited in scope, and it is



Scheme 1

only since about 1980 that techniques have been developed that make it possible to study the less amenable types of compound. The present situation is that a wide variety of techniques is now available for preparing radical cations for spectroscopic studies though all, at least those applying to fluid solutions, have limited scope. Most of these studies continue to be by EPR as it is sensitive and can provide so much structural information, but, increasingly, it is being used in conjunction with UV-VIS or near-IR spectroscopy, (e.g. ref. 2) and both types of measurement can be carried out simultaneously on the same sample.³ NMR Studies are not common; the paramagnetic shift and line-broadening of signals of nuclei in the vicinity of the unpaired electron can yield the sign and magnitude of the EPR hyperfine coupling constants if they are small (e.g. ref. 4), but otherwise the NMR spectra provide little further information.

The choice of which technique to use for the one-electron oxidation of a particular substrate can be guided by considering ionisation energies or electrode potentials, and Bock has proposed a correlation between the two scales for reactions with AlCl₃ in CH₂Cl₂.⁵ These are of limited value, however, because ionisation energies ignore the solvent, the electrode potentials may be solvent dependent, and neither takes account of the fact that, in practice, the electron transfer is often photoassisted. The choice of technique is hence usually based on experience with structurally related substrates, and this article reviews the variety of techniques which is now available, and the classes of substrate to which they can be applied; I hope that this will be useful to other workers in the field in choosing which method to use for a novel substrate.

It is only in recent years that the mechanisms of some of these reactions have become clear; the present situation is briefly reviewed, and some of the pitfalls that may accompany interpretation of the EPR spectra are noted.

2 Experimental methods

Table 1 lists the principal methods, numbered sequentially, that are now available for generating radical cations in liquid or solid solution. Table 2 gives the principal classes of organic compounds, together with the serial number of the method, from Table 1, by which their radical cations have been generated. The abbreviation TFAH is used for trifluoroacetic acid, CF₃CO₂H, and TFA for trifluoroacetate, and an asterisk after the number of the technique indicates that the reaction is usually carried out with simultaneous photolysis of the sample. The references have been chosen to give a guide to the techniques that have been used most widely for each class of compound. A listing, which aims to be comprehensive, of the radical cations that have been prepared and examined by EPR spectroscopy, with their methods of preparation and their spectroscopic details, is given in the various series of Landolt-Börnstein (1965, 1980, 1988, 1990, and due for publication in 2002).¹

Table 1 Methods of generating radical cations

		In liquid solution
Serial number	Oxidant	Medium
Oxidising metals		
1	Hg(TFA) ₂	TFAH CH ₂ Cl ₂ TFAH/FSO ₃ H (CF ₃) ₂ CHOH CH ₂ Cl ₂ /TFAH MeNO ₂ /CF ₃ SO ₃ H
2	Tl(TFA) ₃	TFAH CH ₂ Cl ₂ TFAH TFAH/FSO ₃ H (CF ₃) ₂ CHOH/TFAH Cl(CH ₂) ₃ Cl/CF ₃ CO ₂ H
3	4-MeC ₆ H ₄ Tl(TFA) ₂	(CF ₃) ₂ CHOH (CF ₃) ₂ CHOH/TFAH
4	AgNO ₃	MeCN Me ₂ CO/MeCN
5	AgTFA	THF DMF
6	AgClO ₄	MeCN MeNO ₂ CH ₂ Cl ₂
7	FeCl ₃	CH ₂ Cl ₂
8	Ce(SO ₄) ₂	FSO ₃ H MeCO ₂ H
9	Pb(TFA) ₄	(CF ₃) ₂ CHOH CH ₂ Cl ₂ CH ₂ Cl ₂ /TFAH
10	Pb(OCOCH ₃) ₄	CH ₂ Cl ₂ TFAH Cl ₂ CHCO ₂ H TFAH/CH ₂ Cl ₂
Lewis acids		
11	BF ₃	MeCN
12	AlCl ₃	CH ₂ Cl ₂ CH ₃ CHCl ₂ Cl(CH ₂) ₂ Cl Cl(CH ₂) ₃ Cl SO ₂ Cl(CH ₂) ₂ Cl CHF ₂ Cl MeNO ₂ ClSO ₃ H CF ₃ CO ₂ H
13	GaCl ₃	CH ₂ Cl ₂
14	SbCl ₅	CH ₂ Cl ₂
15	SbF ₅	CH ₂ Cl ₂
Protic acids		
16	TFAH	CH ₂ Cl ₂ CH ₂ Cl ₂ /TFAH/(CF ₃ CO) ₂ O
17	H ₂ SO ₄	TFAH SO ₂ MeNO ₂
18	FSO ₃ H	SO ₂ SO ₂ ClF MeNO ₂
19	MeSO ₃ H	(CF ₃) ₂ CHOH
Stable radicals		
20	(4-BrC ₆ H ₄) ₃ N SbCl ₆	CH ₂ Cl ₂ CH ₂ Cl ₂ /EtOH TFAH TFAH/CH ₂ Cl ₂ TFAH/PhMe (CF ₃) ₂ CHOH
21	(2,4-Br ₂ C ₆ H ₃) ₃ N SbCl ₆	CH ₂ Cl ₂
22	DPPH	MeNO ₂
23	O ₂ SbF ₆	CH ₂ Cl ₂
24	O ₂ AsF ₆	CHClF ₂
Onium salts		
25	Et ₃ O ⁺ SbCl ₆ ⁻	CH ₂ Cl ₂
26	NO ⁺ BF ₄ ⁻	CH ₂ Cl ₂ TFAH/CH ₂ Cl ₂
27	NO ⁺ PF ₆ ⁻	MeCN PrCN MeCN/Et ₂ O (CF ₃) ₂ CHOH
28	NO ⁺ SbCl ₆ ⁻	CH ₂ Cl ₂
29	Thianthrenium ⁺ ClO ₄ ⁻	CH ₂ Cl ₂
Halogens		
30	I ₂	CH ₂ Cl ₂
31	Br ₂ , Cl ₂	CH ₂ Cl ₂ /TFAH, (CF ₃) ₂ CHOH
32	ICl	(CF ₃) ₂ CHOH
33	PhI(TFA) ₂	(CF ₃) ₂ CHOH
Quinones		
34	DDQ	TFAH TFAH/PhMe TFAH/(CF ₃ CO) ₂ O TFAH/MeSO ₃ H
35	TCNQ	CH ₂ Cl ₂
Nitro compounds		
36	C(NO ₂) ₄	CH ₂ Cl ₂ /TFAH
37	N-Nitrosuccinimide	CH ₂ Cl ₂ /TFAH
Anodic oxidation		
38	Electrolysis	CH ₂ Cl ₂
Electromagnetic radiation		
39	X-Ray	
40	Electrons	

Table 1 Methods of generating radical cations *continued*

		In solid solution
	Physical method	Medium
41	γ -Irradiation	CFCl ₃ CF ₃ CCl ₃ CCl ₂ FCCl ₂ F CCl ₂ FCCIF ₂ CCl ₄ C ₄ F ₁₀ c-C ₆ F ₁₀ C ₅ F ₁₂ C ₆ F ₆ c-C ₆ F ₁₂ c-C ₆ F ₁₁ CF ₃ C ₆ F ₁₄ C ₈ F ₁₈ CF ₂ BrCFBrCl CF ₂ BrCF ₂ Br s-BuCl CH ₂ Cl ₂ SiCl ₄ GeCl ₄ SF ₆ Ne
42	X-Irradiation	CH ₂ Cl ₂ CCl ₄ CFCl ₃ C ₆ F ₁₄ C ₈ F ₁₈ CF ₃ CCl ₃ c-C ₆ F ₁₁ CF ₃ CCl ₂ FCCIF ₂ c-C ₆ F ₁₂ PrCN squalane
43	Electron irradiation	C ₁₀ D ₈ or C ₁₄ D ₁₀ in C ₅ H ₁₂ C ₆ H ₁₄ c-C ₅ H ₁₀ PhMe MeCH ₂ CHMeCH ₂ Me MeCH ₂ C(Me ₂)CH ₂ Me Me ₃ CMe ₃ /MeCHMeCH ₂ CH ₂ Me MeCH ₂ CHMeCH ₂ CH ₂ Me
44	Zeolites	H-ZSM-5 Na-ZSM-5 ZSM-34 MCM-14 NaX NaY H-mordenite sodium labonite silicalite mesoporous silicate silica gel

Table 2 Generation of radical cations for various types of compound

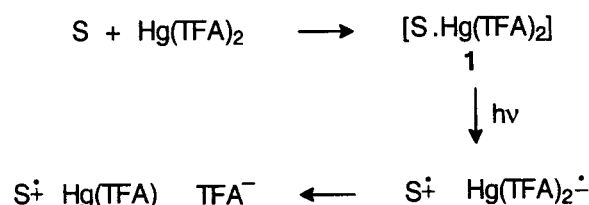
Substrate	Method	Medium	Reference
Alkanes	44	Zeolite	6
	43	Alkane	7
	40	Freon	8
Alkadienes	12	CH ₂ Cl ₂	9
	41	Freon	10
Alkenes	41	Freon	11
	42	Freon	12
Alkyl ethers	41	Freon	13
Alkyl halides	42	Freon	14
Allenes	41	Freon	15
Arenes	1	TFAH	16
Aryl amines	30	CH ₂ Cl ₂	17
Aryl ethers	20	CH ₂ Cl ₂	18
	2	TFAH	19
Aryl fluorides	18	MeNO ₂	20
	41	Freon	21
Arylmercury compounds	1*	TFAH	22
Aryl sulphides	12	CH ₂ Cl ₂	23
Azo compounds	41	CFCl ₃	24
	21	CH ₂ Cl ₂	25
Azulenes	1*	CH ₂ Cl ₂	26
Biaryls	2	(CF ₃) ₂ CHOH	27
Biphenylenes	2	TFAH	28
	25	CH ₂ Cl ₂	2
Cyclophanes	10	TFAH	29
Diazoalkanes	38	CH ₂ Cl ₂	30
Furanes	16*	TFAH	31
Heterocyclic N	41	Freon	32
	6	CH ₂ Cl ₂	33
Heterocyclic N + S	20	CH ₂ Cl ₂	34
	12	SO ₂	35
Hydrazines	27	MeCN	36
	9	CH ₂ Cl ₂	37
Nitrosoarenes	38	MeCN	38
Organosilanes	41	Freon	39
Phenols	18	MeNO ₂	20
Pyrroles	1*	TFAH	31
Tetrathiofulvalenes	12	CH ₂ Cl ₂	40
	6	CH ₂ Cl ₂	41
Thiophenes	38	CH ₂ Cl ₂	42
	17*	H ₂ SO ₄	31
	2	TFAH	43

2.1 Hg(OCOCH₃)₂

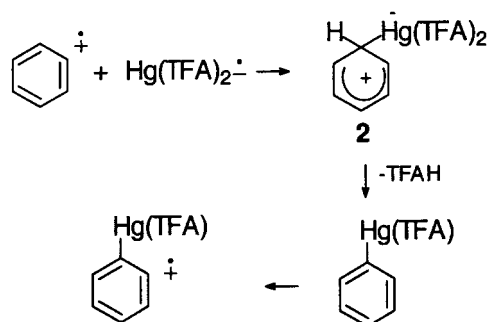
One of the most popular methods for generating radical cations is to treat the substrate with mercury(II) bis(trifluoroacetate) [Hg(TFA)₂] in trifluoroacetic acid (TFAH). Very reactive substrates may be oxidised in the dark, but usually photolysis is necessary to produce a satisfactory ESR spectrum.⁴⁴ Classes of compound for which this method has been

used include mono- and poly-cyclic arenes,⁴⁵ bi-, tri-, and tetra-phenylenes,⁴⁶ azulenes,²⁶ furans,³¹ and pyrroles.³¹

The mechanism of the reaction involving arenes has been elucidated by Kochi,⁴⁷ and presumably similar principles apply to the oxidation of other substrates (Scheme 2). The arene (S) and mercury(II) salt first form a charge-transfer complex, **1**, and that between hexamethylbenzene and mercury trifluoroacetate has been isolated, and its structure determined by X-ray diffraction. Photolysis then induces electron transfer to give the radical ion pair, and back electron transfer is avoided by loss of the trifluoroacetate ion from the mercury radical anion (Scheme 2)

**Scheme 2**

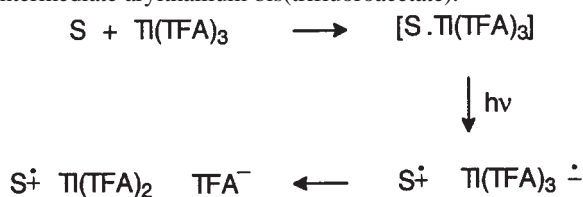
When radical anions are generated by reduction with an alkali metal, the EPR spectrum often shows hyperfine coupling to the metal counteranion. No equivalent hyperfine coupling between an organic radical cation in fluid solution and its counteranion has yet been reported, but in the above process, reaction may occur between the first-formed radical cation and its counter radical anion, leading to mercurideprotonation. Collapse of the radical ion pair gives an alternative route to the familiar Wheland intermediate, **2**, for aromatic substitution, providing a novel, homolytic, route for mercuriation (Scheme 3).

**Scheme 3**

If the substrate contains a number of equivalent reactive positions, progressive mercuriation may be observed, and, for example, biphenylene shows first the EPR spectrum of the biphenylene radical cation, then, sequentially, that of the mono-, di-, tri-, and tetra- β -mercuriated compounds;^{22, 45} at each step, the multiplet pattern from proton coupling simplifies to that of the next higher line in the Pascal's triangle, and the satellites that result from ^{199}Hg coupling become apparent, with the ratio between the hyperfine coupling constants of the entering mercury and the departing proton, $a^{199}\text{Hg}/a^1\text{H}$, equal to *ca* 20.5. Mercuriation also usually leads to a decrease in the *g* value, for example the radical cation of biphenylene and its mono-, bis-, tris-, and tetrakis- β -trifluoroacetoxymercury derivatives show *g* 2.0025, 2.0014, 2.0007, *ca* 2.0003, and *ca* 2.0003 respectively.⁴⁵

2.2 $\text{Tl}(\text{OCOCF}_3)_3$ and $4\text{-MeC}_6\text{H}_4\text{Tl}(\text{OCOCF}_3)_2$

Thallium trifluoroacetate is a rather more powerful oxidising agent than mercury trifluoroacetate.⁴⁸ With a reactive substrate such as durene, the oxidation may occur without photolysis, and the mechanism of the reaction may well be similar to that of mercury bis(trifluoroacetate) (Scheme 4). Thallideprotonation of the substrate, the analogue of the above mercurideprotonation, may occur, but no ESR spectrum of the resulting arylthallium compound has been observed, perhaps because the arylthallium compound has a higher ionisation energy than that of the arene. Trifluoroacetoxylation of the substrate occasionally is observed, for example the reaction with anthracene shows the spectrum of the radical cation of the 9,10-bis(trifluoroacetate), and it is possible that this is formed through an intermediate arylthallium bis(trifluoroacetate).⁴⁹



Scheme 4

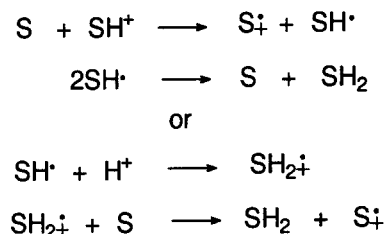
p-Tolylthallium(III) bis(trifluoroacetate), $\text{TolTl}(\text{TFA})_2$, will oxidise arenes with E^0 ($\text{ArH}^{\cdot+}/\text{ArH}$) up to 1.6–1.7V (NHE), and in TFAH, gives radical cations that are longer lived than those generated from $\text{Tl}(\text{TFA})_3$.⁵⁰

Hexafluoroisopropyl alcohol, $(\text{CF}_3)_2\text{CHOH}$ (HFPA), has a low nucleophilicity towards radical cations, and is a particularly good solvent for generating radical cations with strong, persistent, EPR spectra, with $\text{Hg}(\text{TFA})_2$, $\text{Tl}(\text{TFA})_3$, $\text{TolTl}(\text{TFA})_2$, halogens, or $\text{PhI}(\text{TFA})_2$ as oxidising agents.^{51, 52}

2.3 Protic acids

Solutions of many arenes, aryl ethers,⁵³ quinols,²⁰ cyclopentadienes,⁵⁴ furans,³¹ or thiophenes³¹ in strong acids (H_2SO_4 , FSO_3H , $\text{CF}_3\text{SO}_3\text{H}$, TFAH, $\text{CCl}_3\text{CO}_2\text{H}$ etc.) show the EPR spectra of the corresponding radical cations, and the intensity of the spectra are enhanced by photolysis.

The mechanism of the oxidation involves electron transfer from the substrate (S) to the protonated substrate (SH) to generate $\text{S}^{\cdot+}$ and SH^{\cdot} (Scheme 5).^{54–56} The neutral radical goes on to form the dihydride SH_2 , either by disproportionation or by further protonation and electron transfer, and Kochi has shown that 2,2'-biadamantane can be isolated from the oxidation of adamantylideneadamantane in trifluoromethanesulfonic acid.⁵⁶

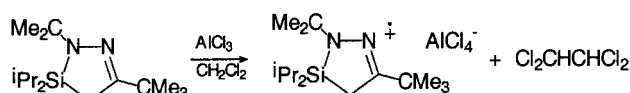
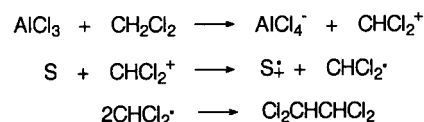


Scheme 5

2.4 Lewis acids

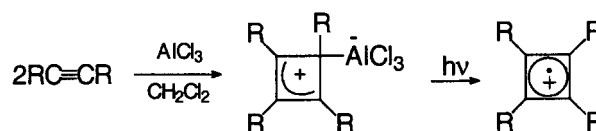
One of the most common methods of generating radical cations is that of treating the substrate with aluminium chloride, usually in dichloromethane or another alkyl chloride, sometimes with photolysis. Without photolysis, radical cations are generated from substrates with ionisation energies less than about 8 eV.⁵ Typical substrates are hydrocarbon arenes,⁵⁷ arenes with substituents bonded through nitrogen, sulfur⁵⁸ or oxygen¹⁹ thiophenes,⁵⁹ furans,⁶⁰ tetrathiofulvalenes,⁶¹ and alkynes (which give radical cations of cyclobutadienes,⁶² azulenes,⁶³ thiophenes⁶⁴ or dithietes,⁶⁵ depending on the components of the system).

The mechanism by which the reaction, and that of other Lewis acids such as BF_3 or SbCl_3 , takes place is by no means clear, and it seems likely that more than one mechanism can operate. It has been suggested that, when dichloromethane is the solvent, electron transfer may take place from the substrate to the dichloromethyl cation (Scheme 6), and indeed the reaction of a diazasilacyclopentene with aluminium chloride gives the corresponding radical cation and 1,1,2,2-tetrachloroethane, which would result from the decay of the dichloromethyl radical (Scheme 6).⁶⁶



Scheme 6

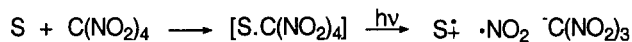
However, radical cations can also be generated with AlCl_3 in nitromethane, sulfur dioxide, or TFAH where such a mechanism seems to be less likely. Under some conditions, adventitious hydrolysis may give HCl which could oxidise the substrate by the protic acid mechanism described above, or a direct reaction between the AlCl_3 and the substrate could occur. This latter mechanism seems possible in the generation of tetra-alkylcyclobutadiene radical cations from dialkynes and AlCl_3 . A cyclobutadiene- AlCl_3 complex, which can sometimes be isolated, is first formed,⁶⁷ then photolysis generates the radical cation (Scheme 7).^{62, 67}



Scheme 7

2.5 Tetranitromethane and *N*-nitrosuccinimide

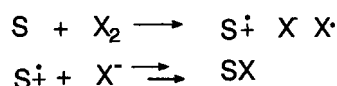
Tetranitromethane has not yet been widely used for generating radical cations, but the reaction mechanism seems to be well established. In HFPA as solvent, a charge-transfer complex is first formed between the substrate and C(NO₂)₄, then irradiation into its absorption band gives the substrate radical cation, the trinitromethyl anion, and nitrogen dioxide (Scheme 8). Presumably *N*-nitrosuccinimide operates in an analogous manner.⁶⁹



Scheme 8

2.6 Halogens

The halogens and positive halogen compounds have not been widely used because they often lead to halogenation of the substrate, but with hexafluoroisopropyl alcohol as the solvent, the rate of the reaction between the radical cation and nucleophilic halide ion is drastically reduced, and the EPR spectrum of the radical cation can be observed (Scheme 9). Under these conditions, ICl, I₂, Cl₂, Br₂, and *N*-bromo- and *N*-chloro-succinimide will oxidise arenes, aromatic ethers, and amines with E° (ArH^{•+}/ArH) ≤ 1.6, 1.5, 1.3, 1.1, 1.5, and 1.2 V (vs Ag/AgCl) respectively.⁷⁰



Scheme 9

Phenyliodine(III) bis(trifluoroacetate), PhI(TFA)₂, is a stronger oxidant with an oxidizing power similar to that of TI(TFA)₃, and in HFPA will generate the radical cations from arenes with E° (ArH^{•+}/ArH) ≤ 2.1 V (vs Ag/AgCl).^{71, 72}

2.7 Ar₃N^{•+} radical cations

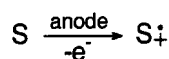
The triarylammonium radical cations (4-BrC₆H₄)₃N^{•+} ("magic blue", which is commercially available) and (2,4-Br₂C₆H₃)₃N^{•+} ("magic green") form stable crystalline hexachloroantimonate salts with E° (Ar₃N^{•+}/Ar₃N) 1.30 and 1.74 V (S.H.E) respectively, in MeCN.⁷³ In solution, they undergo single electron transfer from substrates with a lower electrode potential (Scheme 10), and they have been used, though not very widely, in EPR studies of long-lived radical cations such as those of arenes,⁷⁴ azulenes,⁶³ aryl amines,¹⁸ ethers,⁷⁵ azo compounds²⁵ and diazoalkanes.⁷⁶



Scheme 10

2.8 Anodic oxidation

EPR studies of radical cations generated by anodic oxidation (Scheme 11) are usually carried out in association with electrochemical studies. The design of a suitable EPR cell has been described by Ohya-Nishiguchi,⁷⁷ and one for simultaneous electrochemical and electron spin resonance (SEESR) studies by Bond.⁷⁸ Typically, the solvent is dichloromethane and the electrolyte is tetrabutylammonium tetrafluoroborate, and measurements are carried out between 130 K and room temperature.



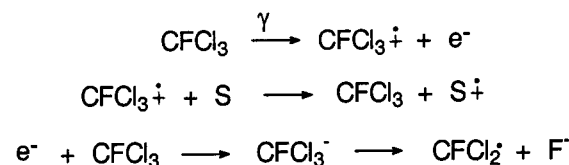
Scheme 11

The method has been applied to compounds of a wide range of structures, including aromatic amines,¹⁸ phosphines,⁷⁹ diazoalkanes,³⁰ nitrosoarenes,³⁸ carotinoids,⁸⁰ azoalkanes,⁸¹ cycloalkenes,⁸² pagodanes,⁸³ and tetrathiofulvalenes.⁴²

2.9 γ -Irradiation in freons

The techniques that are described above are ineffective for generating radical cations when the substrates, for example simple alkyl compounds, have high ionisation energies, or when the radical cations are short-lived in fluid solution. The solution to this problem came in the early 1980s in matrix isolation in frozen Freons (fluorohalogenocarbons).^{84, 85} A solution of the substrate, typically 10⁻³ M, in the Freon (e.g. CFCl₃ or CFCl₂CF₂Cl) at 77K is irradiated with γ -rays from a ⁶⁰Co source. The spectra can be studied up to the softening point of the matrix which is about 120–160 K. The hydrogen anisotropy is neither averaged out as it is in fluid solution, nor resolved as it is in a crystal, and the lines are typically 0.2–0.5 mT broad.

The technique can be applied to essentially any substrate with an ionisation energy below that of the Freon, which is ca. 11 eV, and it has been applied extensively to alkanes,⁸ cycloalkanes,^{86, 87} alkenes,⁸⁸ ethers,¹³ alkyl halides,¹⁴ carbonyl compounds,⁸⁹ nitroso compounds,³⁸ azo compounds,⁹⁰ imines,⁹¹ arenes,⁹² heteroaromatics,⁹³ organometallics,⁹⁴ and compounds of P,⁹⁵ S,⁹⁶ and Te.⁹⁷



Scheme 12

The gamma ray interacts with the Freon give the Freon radical cation with the ejection of an electron. The substrate S transfers an electron to the Freon radical cation to give S^{•+}, which is observed, and the electron is captured by the matrix which then loses a halide ion to leave a neutral matrix-derived radical in which the ¹⁹F anisotropy is large enough to broaden the spectrum beyond detection (Scheme 12). The problem of the large EPR line width can be overcome by the use of ENDOR spectroscopy.⁹⁸

2.10 Zeolites

The intrinsic acidity of some zeolites such as HZSM-5 or H-mordenite is sufficient to oxidise a suitable adsorbate into its radical cation; otherwise the radical cations can be generated in the zeolite by radiolysis.⁹⁹ The zeolites provide microreactors which retain their rigidity and dimensions, and permit EPR measurements to be made at temperatures much higher temperature than those at which Freons soften and melt. The size of the cavities, and the substrate loading can be chosen so that bimolecular reactions can be excluded, or can be studied.

The acidity of the zeolite can be varied by controlling the SiO₂/Al₂O₃ ratio, and Roduner has given evidence that the active sites in dealuminated mordenite are the Lewis acid sites associated with extra-framework alumina.¹⁰⁰ Silica gels have also been used as the medium, but then radiolysis is need to effect the electron transfer.

3 Some complicating factors

EPR Spectra can usually be assigned unambiguously to a particular radical, but the literature contains many examples of incorrect interpretations.

Theoretical calculations provide the first check for identifying a radical. For simple π -conjugated systems, Hückel-McLachlan calculations are usually sufficient;¹⁰¹ for more complex systems, density functional theory (DFT) usually gives good agreement between calculated and experimental hyperfine coupling constants, and is economical in CPU time.¹⁰²

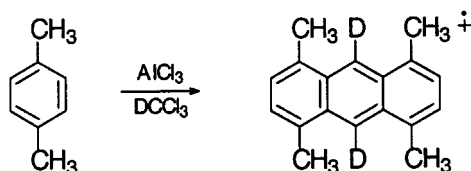
The principal causes of complications are as follows.

3.1 Impurities

In a mixture of compounds, electron loss occurs from the substrate with the lowest ionisation energy, and the presence of a trace of an easily ionisable impurity can give a misleading result. For example, a trace of anthracene in phenanthrene was apparently responsible for the incorrect identification of the phenanthrene radical cation.²⁷

3.2 Reaction with the medium

The reaction between the substrate and the medium may not be limited to simple electron transfer. The use as oxidant of aluminium chloride in a chlorocarbon solvent may introduce Freidel-Crafts complications, *e.g.*, Scheme 13.⁵⁷



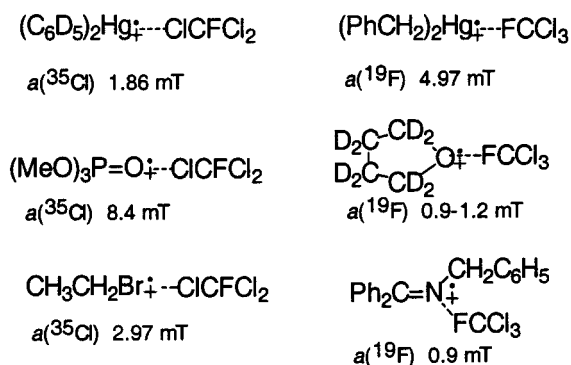
Scheme 13

The mercuriation of arenes that can occur with mercury(II) trifluoroacetate in trifluoroacetic acid is referred to above. It is unlikely to cause any wrong assignments if its possibility is recognised, and it usually occurs with compounds for which it is easy to generate radical cations by an alternative method to check the assignment. There are not many examples of the trifluoroacetoxylation of arenes, but confusion can result from the fact they often show hyperfine coupling to ^{19}F , which may be mistaken for proton coupling. For example, anthracene in $\text{Ti}(\text{OCOCF}_3)_3/\text{CF}_3\text{CO}_2\text{H}$ gives the 9-trifluoroacetate with $a(3\text{F})$ 0.026 mT, and the 9,10-bis(trifluoroacetate) with $a(6\text{F})$ 0.0262 mT.

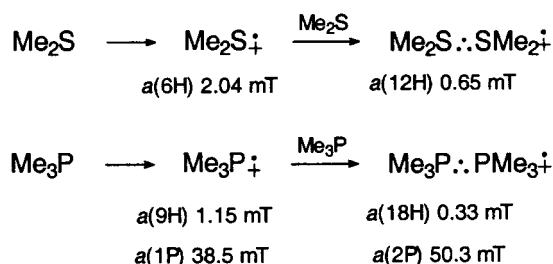
When radical cations are generated in a Freon matrix, a weak interaction may occur between the radical cation and the fluorine or chlorine of the matrix molecule, leading to further hyperfine lines in the EPR spectrum that may be confused with proton coupling. Some examples are shown in Scheme 14.¹⁰³⁻¹⁰⁸ This can be usually be clarified by using a different matrix, or by the appropriate deuteration of the substrate.

3.3 Dimerisation and dehydrodimerisation

Radical cations $\text{S}^{+\cdot}$ sometimes form complexes, $\text{S}_2^{+\cdot}$, with their progenitors S; the equivalent behaviour is not known for radical anions. Sulfides and phosphines associate through a three-electron bond between the heteroatoms, and examples are shown in Scheme 15.¹⁰⁹⁻¹¹¹ This should cause little confusion with compounds of simple structure if the possibility is recognized and the spectra are strong, but it can cause difficulties with more complex compounds such as those containing two phosphorus centers, when the association may be intra- or inter-molecular.¹¹²



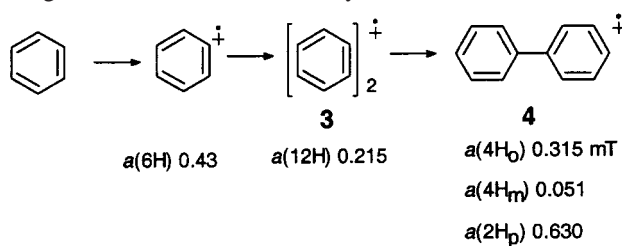
Scheme 14



Scheme 15

Arene radical cations may form dimer (and sometimes higher order) complexes with their parents, and these may go on to give dehydrodimers. For example, the EPR spectrum of monomeric benzene has not been observed in fluid solution, but in CFCl_3 at 100 K (e^- irradiation) it shows $a(6\text{H})$ 0.43 mT.¹¹³ At higher concentrations (γ -irradiation) it shows $a(12\text{H})$ 0.215 mT for the dimer **3**,¹¹⁴ and in fluid trifluoroacetic acid (mercury trifluoroacetate) at 273 K, dihydrodimerisation occurs to give the biphenyl radical cation **4** (Scheme 16).¹¹⁵

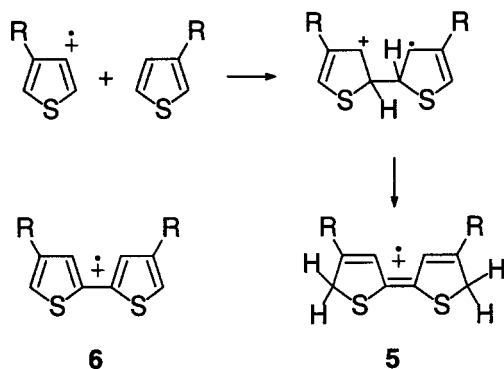
2-Alkylthiophenes form 5,5'-dehydrodimers, and 2,5-dimethylthiophene gives the 3,3'-dehydrodimer.¹¹⁶ 3-Alkylthiophene radical cations similarly form dimers with their parents, but these avoid dehydrogenation and aromatisation by undergoing prototropic shifts to give *cis* and *trans* forms of the dimers **5** (Scheme 17); these had previously been assigned the structures of the dehydrodimers **6**.¹¹⁶



Scheme 16

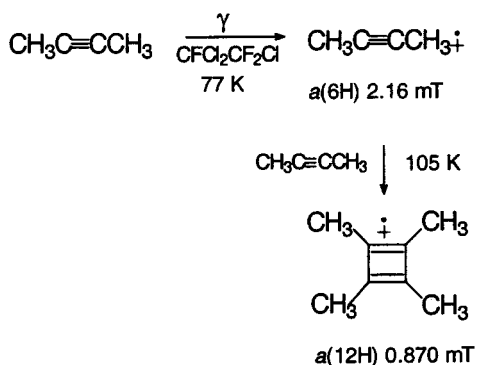
In the arene dimers $\text{S}_2^{+\cdot}$, the unpaired electron is evenly distributed over the two units,² and the hyperfine coupling constants are approximately half those in the monomer $\text{S}^{+\cdot}$. The tendency to form dimers, and the structures of those dimers, are affected by steric factors. For example, whereas the monomeric naphthalene radical cation is unknown in fluid solution, only the monomer and not the dimer is known for octamethylnaphthalene.²

The ESR spectrum of dimethylacetylene has been observed in a Freon matrix when the spin orbit coupling is broken by association with the matrix,¹¹⁷ but at higher temperatures,



Scheme 17

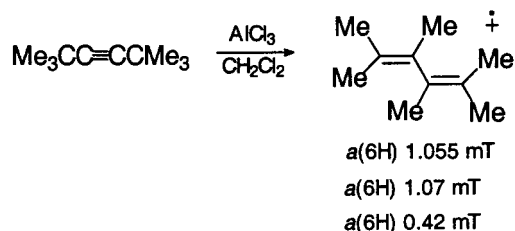
when the matrix softens, irreversible cycloadditive dimerisation occurs to give the tetramethylcyclobutadiene radical cation,¹¹⁸ (Scheme 18) and tetra-alkylcyclobutadiene radical cations in general can be prepared when a fluid solution of a dialkylalkyne and aluminium chloride in dichloromethane is photolysed (Scheme 7)⁶². Arylalkynes undergo a more complicated dimerisation and rearrangement (see below).



Scheme 18

3.4 Rearrangements

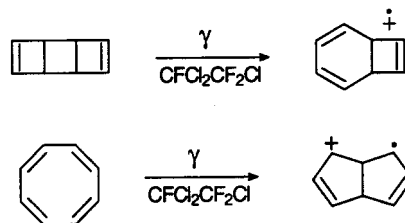
Most of the wrong assignments of the EPR spectra of radical cations have been the result of rearrangement reactions. Some of the rearrangements are obvious from the spectral pattern, though not always expected, *e.g.* Scheme 19.⁹



Scheme 19

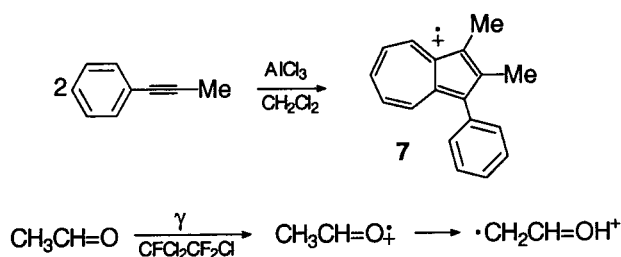
Electrocyclic ring opening reactions are common, and some ring closing reactions are known (*e.g.* Scheme 20).^{119, 120}

Some reactions involve a change in ring size, for example methylphenylacetylene reacts with aluminium chloride by dimerisation to give the dimethylphenylazulene **7**, in which the benzene ring has expanded into a 7-membered ring (Scheme 21).⁶³ Carbonyl compounds may undergo intramolecular hydrogen transfer to give a distonic radical cation in



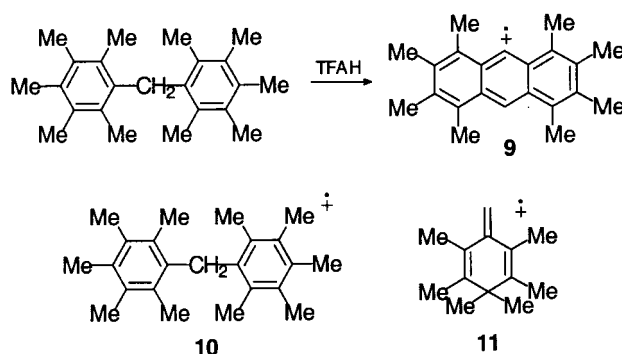
Scheme 20

which the unpaired electron and the positive charge are separated (Scheme 21).¹²¹



Scheme 21

Strong acids can induce the migration of alkyl groups in an aromatic ring by reversible protodealkylation, and this, coupled with the dehydrodimerisation of aromatic rings can lead to the formation of highly alkylated condensed polycyclic aromatics. Thus the radical cation of octamethylanthracene, **9**, is formed when a variety of polymethylated aromatic compounds such as $(\text{Me}_5\text{C}_6)_2\text{CH}_2$,^{70, 122} $(\text{Me}_5\text{C}_6)_2\text{Sn}_2$, or $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{Ge}_2$,¹²³ are treated with $\text{CF}_3\text{CO}_2\text{H}$, and the spectrum of **9**^{•+} has been erroneously ascribed to both to the diarylmethane **10**^{•+} and to the triene **11**^{•+}.



Scheme 22

4 Conclusion

We have reached the situation now where there is a method available for the generation in the condensed phase of radical cations of compounds of essentially any structure. The ionisation energies of most p-electron substrates are low enough to permit the radical cations to be generated in fluid solution by one or more of the many methods that are outlined above. For compounds with higher ionisation energies, the technique of γ - or X-radiolysis in a frozen Freon or in a zeolite cavity, is available, and these compounds can also be studied in fluid solution by the specialised technique of pulse radiolysis or laser flash photolysis coupled with optical detection of the magnetic resonance.

References

- 1 Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, Springer-Verlag, Berlin, Vol.II/1, 1965; Vol.II/9d1, 1980, Vol. II/9d2, 1980; Vol.II/17f, 1988, Vol.II/17h, 1990.
- 2 J.K. Kochi, R. Rathore and P. Le Maguères, *J. Org. Chem.*, 2000, **65**, 6826.
- 3 G. Gescheidt, *Rev. Sci. Instrum.*, 1994, **65**, 2145.
- 4 S.F. Nelsen, L.-J. Chen, P.A. Petillo, D.H. Evans, and F.A. Neugebauer, *J. Am. Chem. Soc.*, 1993, **115**, 10611.
- 5 H. Bock and U. Lechner-Knoblach, *J. Organomet. Chem.*, 1985, **294**, 295.
- 6 K. Toriyama, K. Nunome and M. Iwasaki, *J. Am. Chem. Soc.*, 1987, **109**, 4496.
- 7 D.W. Werst, M.G. Bakker and A.D. Trifunac, *J. Am. Chem. Soc.*, 1990, **112**, 40.
- 8 M. Shiotani, A. Yano, N. Ohta and T. Ichikawa, *Chem. Phys. Lett.*, 1988, **147**, 38.
- 9 J.L. Courtneidge and A.G. Davies, *J. Chem. Soc., Chem. Commun.*, 1984, 136.
- 10 L.S. Prasad, R.S. Ding, H.-Q. Wang, E.G. Bradford, and L.D. Kispert, *Chem. Phys. Lett.*, 1988, **151**, 443.
- 11 L.A. Eriksson, L. Sjöqvist, S. Lunell, M. Shiotani, M. Usui and A. Lund, *J. Am. Chem. Soc.*, 1993, **115**, 3244.
- 12 L. Sjöqvist, M. Shiotani and A. Lund, *Chem. Phys.*, 1990, **141**, 417.
- 13 M. Shiotani, N. Isamoto, M. Hayashi, T. Fångström and S. Lunell, *J. Am. Chem. Soc.*, 2000, **122**, 12281.
- 14 A. Hasegawa, M.C.R. Symons and M. Shiotani, *J. Chem. Soc., Perkin Trans. 2*, 1989, 657.
- 15 Y. Kubozono, H. Ujita, M. Okada, M. Ata, Y. Matsuda and Y. Gondo, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2442.
- 16 D.V. Avila, A.G. Davies, E.R. Li and K.M. Ng, *J. Chem. Soc., Perkin Trans. 2*, 1993, 355.
- 17 F.A. Neugebauer, B. Funk and H.A. Staab, *Tetrahedron Lett.*, 1994, **35**, 4755.
- 18 F. Gerson, G. Gescheidt, J. Knöbel, W.B. Martin, L. Neumann and E. Vogel, *J. Am. Chem. Soc.*, 1992, **114**, 7107.
- 19 F.R. Hewgill, F. Legge and R.A. Webb, *Aust. J. Chem.*, 1993, **46**, 1605.
- 20 J. Eloranta and M. Vuolle, *Mag. Reson. Chem.*, 1998, **36**, 98.
- 21 A. Hasegawa, Y. Itagaki and M. Shiotani, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1625.
- 22 A.G. Davies and K.M. Ng, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2599.
- 23 M.R. Bryce, A.K. Lay, A. Chesney, A.S. Batsanov, J.A.K. Howard, U. Buser, F. Gerson and P. Merstetter, *J. Chem. Soc., Perkin Trans. 2*, 1999, 755.
- 24 C.J. Rhodes, H. Agirbas, M. Lindgren and O.N. Antzutkin, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2135.
- 25 G. Gescheidt, A. Lamprecht, C. Rüdhardt, and M. Schmittel, *Helv. Chim. Acta*, 1991, **74**, 2094.
- 26 F. Gerson, M. Scholz, H.-J. Hansen, and P. Uebelhart, *J. Chem. Soc., Perkin Trans. 2*, 1995, 215.
- 27 L. Ebersson, M.P. Hartshorn and O. Persson, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1735.
- 28 D.V. Avila, A.G. Davies and M.L. Girbal, *Tetrahedron*, 1990, **46**, 1999.
- 29 A.R. Wartini, J. Valenzuela, H.A. Staab and F.A. Neugebauer, *Eur. J. Org. Chem.*, 1998, 139.
- 30 K. Ishiguro, M. Ikeda and Y. Sawaki, *J. Org. Chem.*, 1992, **57**, 3057.
- 31 A.G. Davies, L. Julia and S.N. Yazdi, *J. Chem. Soc., Perkin Trans. 2*, 1989, 239.
- 32 M. Matsushita, T. Momose, T. Kato and T. Shida, *Chem. Phys. Lett.*, 1989, **161**, 461.
- 33 K. Matsumoto, H. Katsura, J. Yamauchi, T. Uchida, K. Aoyama and T. Machiguchi, *Bull. Soc. Chim. Fr.*, 1996, **133**, 891.
- 34 U. Spreitzer, M. Scholz, G. Gescheidt and J. Daub, *Liebigs Ann. Chem.*, 1996, 2069.
- 35 T.M. Barclay, A.W. Cordes, J.D. Goddard, R.C. Mawhinney, R.T. Oakley, K.E. Preuss and R.W. Reed, *J. Am. Chem. Soc.*, 1997, **119**, 12136.
- 36 S.F. Nelsen, H. Chang, J.J. Wolff and J. Adamus, *J. Am. Chem. Soc.*, 1993, **115**, 12276.
- 37 S.F. Nelsen, Y. Kim, F.A. Neugebauer, C. Krieger, R. Siegel and M. Kaftory, *J. Org. Chem.*, 1991, **56**, 1045.
- 38 G. Gronchi and P. Tordo, *Res. Chem. Intermed.*, 1993, **19**, 733.
- 39 K. Komaguchi, M. Shiotani, M. Ishikawa and K. Sasaki, *Chem. Phys. Lett.*, 1992, **200**, 580.
- 40 C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca and E. Espinosa, *J. Org. Chem.*, 1994, **59**, 3307.
- 41 F. Gerson, A. Lamprecht and M. Fourmigué, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1409.
- 42 A. Terahara, H. Ohya-Nishiguchi, N. Hirota, H. Awaji, T. Kawase, S. Yoneda, T. Sugimoto and Z.-i. Yoshida, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1760.
- 43 L. Ebersson, M.P. Hartshorn and O. Persson, *J. Chem. Soc., Perkin Trans. 2*, 1997, 195.
- 44 W. Lau, J.C. Huffman and J.K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 5515.
- 45 A.G. Davies and D.C. McGuchan, *Organometallics*, 1991, **10**, 329.
- 46 D.V. Avila, A.G. Davies, M.L. Girbal and K.M. Ng, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1693.
- 47 W. Lau and J.K. Kochi, *J. Org. Chem.*, 1986, **51**, 1801.
- 48 I.H. Elson and J.K. Kochi, *J. Am. Chem. Soc.*, 1973, **95**, 5060.
- 49 W. Lau and J.K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 6720.
- 50 L. Ebersson, M.P. Hartshorn and O. Persson, *J. Chem. Soc., Chem. Commun.*, 1995, 1131.
- 51 L. Ebersson, M.P. Hartshorn, O. Persson and F. Radnor, *J. Chem. Soc., Chem. Commun.*, 1996, 215.
- 52 L. Ebersson, M. P. Hartshorn, F. Radnor and O. Persson, *J. Chem. Soc., Chem. Commun.*, 1996, 215.
- 53 A.G. Davies and C.J. Shields, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1001.
- 54 J.L. Courtneidge, A.G. Davies, C.J. Shields and S.N. Yazdi, *J. Chem. Soc., Perkin Trans. 2*, 1988, 799.
- 55 H. Hart, A. Teuerstein and M.A. Babin, *J. Am. Chem. Soc.*, 1981, **103**, 903.
- 56 R. Rathore, C. Zhu, S.V. Lindeman and J.K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1837.
- 57 H. Sang and H. Wang, *Mag. Reson. Chem.*, 1992, **30**, 143.
- 58 H. Bock, B. L. Chenards, P. Rittmeyer and U. Stein, *Z. Naturforsch.*, 1988, **43B**, 117.
- 59 C. Alemán, E. Brillas, A.G. Davies, L. Fajarí, D. Giró, L. Juliá, J.J. Pérez and J. Rius, *J. Org. Chem.*, 1993, **58**, 3091.
- 60 M.C.R.L.R. Lazana, M.L.T.M.B. Franco and B.J. Herold, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1305.
- 61 L. Cavara, F. Gerson, D.O. Cowan and K. Lerstrup, *Helv. Chim. Acta*, 1986, **69**, 141.
- 62 J.L. Courtneidge, A.G. Davies, E. Luszytk and J. Luszytk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 155.
- 63 C.J. Cooksey, J.L. Courtneidge, A.G. Davies, J.C. Evans, P.S. Gregory and C.C. Rowlands, *J. Chem. Soc., Perkin Trans. 2*, 1988, 807.
- 64 H. Bock and P. Rittmeyer, *Z. Naturforsch.*, 1988, **43B**, 419.
- 65 H. Bock, P. Rittmeyer and U. Stein, *Chem. Ber.*, 1986, **119**, 3766.
- 66 O. Graalman, M. Hesse, U. Klingebiel, W. Clegg, M. Haase and G.M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 621.
- 67 Q.B. Broxterman, H. Hogeveen and D.M. Kok, *Tetrahedron Lett.*, 1981, **22**, 173.
- 68 L. Ebersson, M.P. Hartshorn, F. Radner and J.O. Svenson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1719.
- 69 J. Calvert, L. Ebersson, M.P. Hartshorn and J.O. Svenson, *J. Chem. Soc., Perkin Trans. 2*, 1995, 645.
- 70 L. Ebersson, M.P. Hartshorn, F. Radner and O. Persson, *J. Chem. Soc., Perkin Trans. 2*, 1998, 59.
- 71 Y. Kita, H. Tohma, K. Hatanaka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai and S. Oka, *J. Am. Chem. Soc.*, 1994, **116**, 3684.
- 72 B. Kirste, P. Tian, G. Kossmehl, G. Engelmann and W. Jugelt, *Magn. Resonance Chem.*, 1995, **33**, 70.
- 73 W. Schmidt and E. Steckhan, *Chem. Ber.*, 1980, **113**, 577.
- 74 R. Bachmann, F. Gerson, P. Merstetter and E. Vogel, *Helv. Chim. Acta*, 1996, **79**, 1627.
- 75 A.R. Wartini, H.A. Staab and F.A. Neugebauer, *Eur. J. Org. Chem.*, 1998, 1161.
- 76 T. Bally, C. Carra, S. Matzinger, L. Truttmann, F. Gerson, R. Schmidlin, M. S. Platz and A. Admasu, *J. Am. Chem. Soc.*, 1999, **121**, 7011.
- 77 A. Terahara, H. Ohya-Nishiguchi, N. Hirota and A. Oku, *J. Phys. Chem.*, 1986, **90**, 1564.
- 78 D.A. Fielder, M. Koppol and A.M. Bond, *J. Electrochem. Soc.*, 1988, **142**, 862.
- 79 M. Culcasi, Y. Berchadsky, G. Gronchi and P. Tordo, *J. Org. Chem.*, 1991, **56**, 3537.
- 80 J.L. Grant, V. J. Kramer, R. Ding and L.D. Kispert, *J. Am. Chem. Soc.*, 1988, **110**, 2151.
- 81 G. Gambini, P. Carloni, S. Zamponi, P. Conti, L. Greci and R. Marassi, *J. Chem. Res. (S)*, 1995, 6.

- 82 F. Gerson, G. Gescheidt, S.F. Nelsen, L. A. Paquette, M.F. Teasley and L. Waykole, *J. Am. Chem. Soc.*, 1989, **111**, 5518.
- 83 G. Gescheidt, R. Herges, H. Neumann, J. Heinze, M. Wollenweber, M. Etzkorn and H. Prinzbach, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1016.
- 84 M.C.R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.
- 85 T. Shida, E. Haselbach and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.
- 86 M. Shiotani, M. Lindgren, N. Ohta and T. Ichikawa, *J. Chem. Soc., Perkin Trans. 2*, 1991, 711.
- 87 M. Lindgren, K. Komaguchi, M. Shiotani and K. Sasaki, *J. Phys. Chem.*, 1994, **98**, 8331.
- 88 Y. Itagaki, M. Shiotani, A. Hasegawa and H. Kawazoe, *Bull. Chem. Soc. Jpn*, 1998, **71**, 2547.
- 89 P. Wang, K. Komaguchi and M. Shiotani, *Chem. Phys. Lett.*, 2000, **320**, 623.
- 90 C.J. Rhodes, *J. Chem. Soc., Faraday Trans.1*, 1988, **84**, 3215.
- 91 C.J. Rhodes and H. Agirbas, *J. Chem. Soc., Perkin Trans. 2*, 1992, 397.
- 92 F. Gerson and X.Z. Qin, *Chem. Phys. Lett.*, 1988, **153**, 546.
- 93 U. Eiermann, F.A. Neugebauer, H. Chandra, M.C.R. Symons and J.L. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 1992, 85.
- 94 E. Butcher, C.J. Rhodes, M. Standing, R.S. Davidson and R. Bowser, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1469.
- 95 M.C.R. Symons and R. Janes, *J. Chem. Soc., Faraday Trans.1*, 1987, **83**, 383.
- 96 D.W. Werst, *J. Phys. Chem.*, 1992, **96**, 3640.
- 97 M.J. Almond, A. Raqabah, D.A. Rice, M.C.R. Symons and C.A. Yates, *J. Chem. Soc., Dalton Trans.*, 1992, 1.
- 98 F. Gerson, *Acc. Chem. Res.*, 1994, **27**, 63.
- 99 C.J. Rhodes, *Mol. Eng.*, 1994, **4**, 119.
- 100 G. Harvey, R. Prins, R. Crockett and E. Roduner, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2027.
- 101 F. Gerson, *High Resolution NMR Spectroscopy*, Wiley-Verlag Chemie, 1970.
- 102 R. Batra, B. Giese, M. Spichy, G. Gescheidt and K.N. Houk, *J. Phys. Chem.*, 1996, **100**, 1837.
- 103 C.J. Rhodes, H. Agirbas, H. Shine, A.K.M.M. Hoque and T. Venkatachalam, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2129.
- 104 C.J. Rhodes and H. Agirbas, *J. Organomet. Chem.*, 1989, **378**, 303.
- 105 R. Janes and M.C.R. Symons, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2173.
- 106 M. Lindgren, R. Erickson, N. P. Benetis and O.N. Antzutkin, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2009.
- 107 M.C.R. Symons, H. Muto, K. Toriyama, K. Numone and M. Iwasaki, *J. Chem. Soc., Perkin Trans. 2*, 1986, 2011.
- 108 C.J. Rhodes, H. Morris, H. Agirbas, M. Standing and Y. Zhang, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1375.
- 109 X.-Z. Qin, Q.-c. Meng and F. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6778.
- 110 A. Hasegawa, G.D.G. McConnachie and M.C.R. Symons, *J. Chem. Soc., Faraday Trans.1*, 1984, **80**, 1005.
- 111 C.J. Rhodes and M.C.R. Symons, *J. Chem. Soc., Chem. Commun.*, 1989, 1393.
- 112 R.A. J. Janssen, O. M. Aagaard, M.J.T.F. Cabbolet and B.F.M. de Waal, *J. Phys. Chem.*, 1991, **95**, 9256.
- 113 V.I. Feldman, F. Sukhov, A. Orlov, R. Kadam, Y. Itagaki and A. Lund, *PCCP*, 2000, **2**, 29.
- 114 Y. Itagaki, N.P. Benetis, R.M. Kadam and A.Lund, *PCCP*, 2000, **2**, 2683.
- 115 J.L. Courtneidge, A.G. Davies, T. Clark and D. Wilhelm, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1197.
- 116 F. Barbosa, L. Ebersson, G. Gescheidt, S. Gronowitz, A.-B. Hörnfeldt, L. Juliá and O. Persson, *Acta. Chem. Scand.*, 1998, **52**, 1275.
- 117 M. Shiotani, K. Ohta, Y. Nagata and J. Sohma, *J. Am. Chem. Soc.*, 1985, **107**, 2562.
- 118 J.L. Courtneidge, A.G. Davies, S.M. Tollerfield, J. Rideout and M.C.R. Symons, *J. Chem. Soc., Chem. Commun.*, 1985, 1092.
- 119 T. Bally, S. Bernhard, S. Matzinger, L. Truttmann, Z. Zhu, J.-L. Roulin, A. Marcinek, J. Gebicki, F. Williams, G.-F. Chen, H.D. Roth and T. Herberitz, *Chem. Eur. J.*, 2000, **6**, 849.
- 120 S. Dai, J.T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1990, **112**, 2835.
- 121 V.N. Belevskii, D.A. Tyurin and N.D. Chuvylkin, *High Energy Chem.*, 1998, **32**, 381.
- 122 L. Ebersson and F. Radner, *J. Chem. Soc., Chem. Commun.*, 1991, 1233.
- 123 M. Lehnig, T. Reiche and S. Reiss, *Tetrahedron Lett.*, 1992, **33**, 4149.