Selected Radical Cations:
An E.S.R. Study

A Thesis submitted by

Jan Rideout

for the degree of

Doctor of Philosophy

in the

Faculty of Science

of the

University of Leicester

Department of Chemistry,
The University,
LEICESTER, LE1 7RH.

JULY 1986

UMI Number: U366705

UMI

Dissertation Publishing

ProQuest

STATEMENT

The accompanying thesis submitted for the degree of Ph.D.
entitled "Selected Radical Cations: An E.S.R. Study" is based
on work conducted by the author in the Department of Chemistry
of the University of Leicester mainly during the period betwee
1982 and 1985.

All the work recorded in this thesis is original unless
otherwise acknowledged in the text or by references. None
of the work has been submitted for another degree in this
or any other University.

Date: .11/.7/.86.........   Signed: .J..K.\Dean....

DEDICATION

My deepest thanks to my parents for their unceasing encouragement
in educational matters. I would also like to thank my Supervisor
for his unselfishness in sharing some of his expertise with me.

Thanks also go to Vicky and Ann whose talent in deciphering
scrawl is amazing. My friends in Leicester, too numerous to
mention, also deserve my greatest gratitude for making my social
life so colourful for the 6 years I spent there.

I would like to express my appreciation to the various co-authors
cited upon publications with myself.

Finally, my thanks to Adrian and the 'Granby Grippers' for
introducing me to the delights of weight-lifting.

LIST OF CONTENTS

CHAPTER
1

Introduction

INTRODUCTION

Gamma (γ) ray irradiation of compounds at reduced temperatures has been a source of interest for many years. The effects of high energy radiation have been studied as 'direct', i.e. irradiation of the pure compound or 'indirect', e.g. irradiation of a frozen dilute solution, with the radiation causing ionisation, primarily of the solvent molecules, followed by a transmission of the damage to the solute, which, by the nature of this transfer, localises the process allowing it to continue no further.

It is the 'indirect' damage system which will be considered here, but let me first give a somewhat simplistic idea of how γ-rays interact with matter.

Firstly, γ-rays are electromagnetic radiation of wavelengths typically ranging from 3×10^{-9} cm to 3×10^{-11} cm, that is of energies between approximately 40 keV and 4 MeV.

γ-Rays are emitted by sources such as ^{60}Co, which has a half-life of 5.27 years. Unlike other forms of high energy radiation (α- and β-particles), γ-rays are usually mono-energetic or lie in a narrow band of specifically emitted energies. ^{60}Co, for example, only emits γ-rays at 1.332 MeV and 1.173 MeV, along with its β-particles.

How then, do these highly energetic photons interact with molecules? Again, a difference occurs between γ-irradiation and α- and β-irradiation. γ-Rays produce what is known as the photo-electric effect, whereupon absorption of almost, or all, of the entire energy of the γ-ray is by a single atomic electron, which is then ejected from the molecule with the energy of the photon minus the binding energy of the electron (the ionisation potential).

This ejected electron has excess energy, which it dissipates

gradually along its path, possibly in amounts large enough themselves to ionise molecules. This would cause 'TRACKS' of ionised particles within the system. If an ejected electron has energy greater than 100 eV it is known as a delta (δ)-ray.

When this electron has dissipated enough energy it becomes faced with a number of choices. The electron may become 'trapped' for example in an anion vacancy (a crystal defect) as in alkali halide crystals, or it may become centred on a molecular-sized cavity in a solid. It is for this reason that glasses, e.g. frozen mixtures of CD_3OD/D_2O, give higher yields of trapped electrons than their crystalline counterparts.[1]

Trapped electrons may then become 'solvated'. In a simple model proposed by Symons,[2] one imagines the removal of an anion, such as I^-, from solution and replacement with an electron, without any major change in orientation nor position of the solvating cage of molecules.

This physical trapping competes with electron-capture by solvent molecules if the solvent molecules can react rapidly with an electron.

An ejected electron may also re-combine with an original cation, in doing so producing a vibrationally or electronically excited molecule, which may relax to its ground state or rearrange in one of the methods suggested later.

After electron ejection, the parent molecule is left with a positive hole, therefore we have formed the radical cation of the molecule. Scheme I summarises the reactions of this highly reactive species.

SCHEME I   Processes following electron-loss

Eqn.   I $CFCl_3\cdot^+ + CFCl_3 \longrightarrow CFCl_3 + CFCl_3\cdot^+$

      II $C_2H_6\cdot^+ + B \longrightarrow C_2H_5\cdot + HB^+$

     III $RCO_2\cdot \longrightarrow R\cdot + CO_2$

      IV $R_3P\cdot^+ + R_3P \longrightarrow [R_3P\overset{\bullet}{-}PR_3]^+$
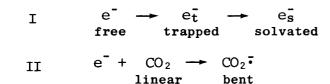
Reaction I in Scheme I implies that, were the irradiated material pure, its radical cation may ionise a neighbour producing a very mobile positive pole. Alternatively, the cation may distort its shape to accommodate its new electron population, e.g. (bond stretching), so raising the energy barrier to electron transfer with a neighbour and trapping the distorted cation.
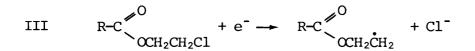
Deprotonation is an alternative 'relaxation' of the cation, as invoked in the explanation of the failure of ethane to produce radical cations [Scheme I, Reaction II], producing instead only neutral ethyl radicals.

Since deprotonation is common, it is of no surprise that radicals may break other bonds to reach energy minima [Scheme I, Reaction III].
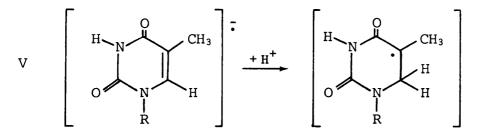
Bond formation is another method exhibited, for example, in the γ-irradiation of trialkyl phosphines[3] [Scheme I, Reaction IV].

SCHEME II   Electron-gain Processes

I

$$e^- \longrightarrow e_t^- \longrightarrow e_s^-$$
free   trapped   solvated

II

$$e^- + CO_2 \longrightarrow CO_2^{-\cdot}$$
linear   bent

III

$$R\text{-}C\overset{O}{\underset{OCH_2CH_2Cl}{}} + e^- \longrightarrow R\text{-}C\overset{O}{\underset{OCH_2\dot{C}H_2}{}} + Cl^-$$

IV $B(OMe)_3^{-\cdot} + B(OMe)_3 \longrightarrow [(MeO)_3B\cdot B(OMe)_3]^-$

V

Scheme II deals with electron-gain processes, beginning with the physical trapping or solvation of the ejected electron (Reaction I).

Argument has continued as to the mechanism by which these trapped electrons may now reach substrate molecules, since they are in solid phase low temperature systems. Miller[4] favours the 'direct tunnelling' of an electron from its trap to a substrate molecule, even over considerable distances. A 'trap-to-trap' mechanism is suggested by Buxton[5] whereby the electron migrates via a short distance 'hopping' process. Symons[2] presents a convincing argument in favour of Buxton's theory but this need not be expanded upon here.

Electron-rich centres may find similar methods of relaxation to those of the cationic centres, for example Reaction II, Scheme II, deals with the shape changes occurring upon addition of the electron using the example of the linear CO_2 becoming CO_2^-, which is bent. Dissociative electron capture is a process whereby, upon addition of the electron to form, potentially, the radical anion, a stable anion separates leaving a neutral radical[6] [Reaction III, Scheme II].

The production of a bond can also occur, as found in the work by Hudson and Williams on $B(OMe)_3$[7] [Reaction IV, Scheme II].

Protonation may occur, as in the case of the thymine anion formed in γ-irradiated aqueous DNA (Deoxyribose Nucleic Acid), to form the 5,6-dihydro-5-thymyl radical '(TH·)', which is responsible for the 8-line spectrum observed by various groups, notably those of Gregoli[8] and Symons[9] [Reaction V, Scheme II].

Any one compound may choose to permit one, or any number of these rearrangements of an electron capture centre. The case of the phosphate esters[10] exhibits this point, with a subtle control of the major rearrangement being accomplished by solvent variation. A further example of the importance of solvent control over rearrangement is seen in the radiation chemistry of $ClCH_2Br$.[11] But it is not my intention
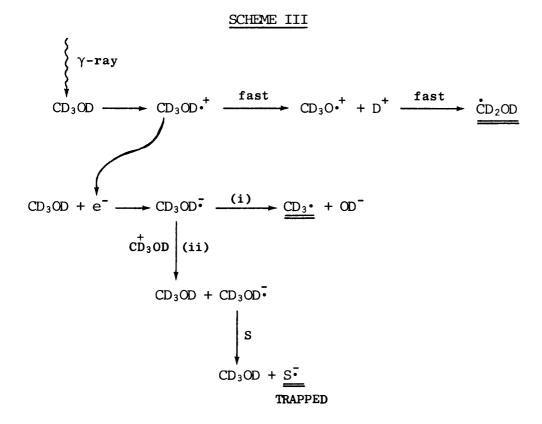
to dwell upon these results here.

Examination of the above processes shows that, by correct choice of matrix, i.e. solvent, the radiolytic pathways occurring in materials may be simplified. Obviously, it is to the advantage of anyone wishing to use ionising radiation if they can, by some process, specifically form electron-gain or electron-loss centres.

Since, as I have previously suggested, the primary effects of irradiation are the production of electron-gain and electron-loss centres, one may consider using the 'indirect damage' idea to produce in a solute, one type of damage centre specifically, and to trap out these centres by freezing the solvent to low temperatures, typically 77 K or even to 4 K. These low temperatures are used to try to prevent the rearrangements occurring, thus allowing the e.s.r. user to extract physical information about the Semi-Occupied Molecular Orbital (SOMO) of the parent radical cation or anion of the solute.

It is by making use of these rearrangements in the solvent radicals, even at low temperatures, that the mobility of the cationic, or anionic, radicals may be prevented. For example, if one wishes to produce the radical anion only of a solute compound, it is desirable to allow transmission of the electron throughout the system, from molecule to molecule, to enable the solute to 'localise' the damage upon itself, whilst preventing the transmission of the positive holes. This is accomplished by using, for example, a CD_3OD/D_2O mixture (Scheme III) as a solvent.

On examination of Scheme III, it is notable that perdeuterated solvents are often used, the need for these is obvious, since under the conditions needed to trap 'S$\cdot^{-}$' radicals, $CD_3\cdot$ and $\dot{C}D_2OD$ are also trapped. This may cause some annoying overlap of signals due to solvent and solute radicals. To overcome, or at least to minimise this problem deuterated solvents are

SCHEME III

$$CD_3OD \xrightarrow{\gamma\text{-ray}} CD_3OD\overset{+}{\bullet} \xrightarrow{\text{fast}} CD_3O\overset{+}{\bullet} + D^+ \xrightarrow{\text{fast}} \underline{\underline{\overset{\bullet}{C}D_2OD}}$$

$$CD_3OD + e^- \longrightarrow CD_3OD\overset{-}{\bullet} \xrightarrow{(i)} \underline{\underline{CD_3\bullet}} + OD^-$$

$$\overset{+}{CD_3OD} \Big\downarrow (ii)$$

$$CD_3OD + CD_3OD\overset{-}{\bullet}$$

$$\Big\downarrow S$$

$$CD_3OD + \underline{\underline{S\overset{-}{\bullet}}}$$

TRAPPED

The gamma radiolysis of methanol, producing the electron plus the electron-loss centre, which immediately deprotonates preventing transmission of the positive hole. The electron-gain centre produces two possibilities, (i) rearrangement preventing transmission and (ii) transmission, eventually to a solute molecule. Reactions (i) and (ii) occur competitively for this matrix.

used. It is also possible to use computer subtraction methods. Other solvent mixtures or solvents used in this way are ethylene glycol $(d^6)/$ D_2O[12] and methyl tetrahydrofuran.[13]

Using this idea we can also produce radical cations specifically, by choice of the correct solvent system. Radical cations, however, have only recently become easily accessible to the e.s.r. spectroscopist, branching readily into most organic functional groupings. Whilst radical anion work has been performed routinely for many years by using the above systems, radical cation work for e.s.r. developed with the discovery of the easy to use inert matrix of trichloromethane (freon).

In the years prior to the discovery of this technique, some solid-state low temperature production of radical cations had been performed, the solvents used in these studies being mainly sulphuric acid or phosphoric acid glasses. The limitations for these solvents are plain but even today they find some usage and this work has produced some interesting cations.[14-19]

With the advent of the freon technique many more cations have been produced, the practical ease of this system to use and its chemical inertness making it popular.

The 'freon' system works by allowing mobility of positive holes while dissociative electron capture (DEC) prevents the transmission of the electron-gain centres (Scheme IV).

SCHEME IV

1) $CFCl_3 \xrightarrow{\gamma} (CFCl_3) \cdot^+ + e^-$

2) $CFCl_3 + e^- \longrightarrow (CFCl_3) \cdot^- \longrightarrow Cl^- + \underline{\underline{CFCl_2 \cdot}}$

3) $(CFCl_3) \cdot^+ + CFCl_3 \longrightarrow CFCl_3 + (CFCl_3) \cdot^+$

4) $(CFCl_3) \cdot^+ + S \longrightarrow CFCl_3 + \underline{\underline{S \cdot^+}}$

This was the type of mechanism proposed by Shida, in his work on the production of the radical cation of pyridine[20] at low temperature.

The choice of this solvent stems from optical work on cations by the same author performed some time earlier.[21] This halogenated solvent had major advantages over those used by Symons and Smith in 1979[22] to produce the first alkane radical cation, that of hexamethyl ethane. The solvents used in these experiments were carbon tetrachloride (CCl_4) and carbon tetrabromide (CBr_4). The advantages of freon are (i) it has no tendency to trap its own parent cation $CFCl_3 \cdot^+$ compared to the formation and trapping of $CCl_4 \cdot^+$ and $CBr_4 \cdot^+$ and (ii) CCl_4 gives $CCl_3 \cdot$ by dissociative electron capture and CBr_4 gives $CBr_3 \cdot$ both of which give

interfering e.s.r. signals in contrast with $CFCl_3$. Fortunately, the radicals $CFCl_3 \cdot^+$ and $CFCl_2 \cdot$ have large anisotropic couplings due to ^{19}F (ca. 543 G)[23] as well as the anisotropic coupling due to ^{37}Cl (47 G). Hence it can be envisaged that with a similar number of radicals of $CFCl_2 \cdot$ and $CCl_3 \cdot$ that the spread of the magnetic field is much larger for $CFCl_2 \cdot$ radicals. Therefore, the change in gradient of the absorption curve is not so severe, implying broader lines with much less amplitude in the first derivative e.s.r. spectrum. The signals due to $CFCl_2 \cdot$ are generally broadened beyond detection in our system.

The solvents used by Symons (CCl_4 and CBr_4) in his early studies, are still useful when a cation has a large hyperfine splitting, e.g. some phosphorus-centred cations,[24] or a large shift from $g = 2$. Carbon tetrachloride is commonly used when there is a suspicion of an inter-action between the solvent fluorine and the solute cation.[25]

General advantages exist in using perhalogenated solvents in that their ionisation potentials are relatively high.[26] It is a prerequisite for Scheme IV, Reaction 4, that the ionisation potential of $CFCl_3$ is greater than that of the solute, making the reaction exothermic and preventing the back-reaction;

$$CFCl_3 + S\cdot^+ \longrightarrow S + CFCl_3\cdot^+$$

hence trapping the solute cation until the melting point of the matrix, i.e. 162 K.[27]

It has, at times, proven advantageous and complementary to use other solvents of the freon type, since hydrogen atom transfer,[28] matrix adduct formation[29,30] and other rearrangements[31] have been observed. These will be discussed at greater length in the following Chapters. Examples of similar solvents are SF_6,[32] C_2F_6[32] and $CFCl_2.CF_2Cl$.[33]

Recently, using this technique, a great deal of work on many functional

groupings has revealed their radical cations. Some functional groupings were proving less straightforward and more reluctant to yield information on their SOMO's. This thesis attempts to communicate the way in which some of these problems were solved and to try to explain some of the surprising results coming from these cations, including the formation of matrix adducts due to chlorine and to fluorine and the aspects involved as to why some solutes bind chlorine and others fluorine, as investigated experimentally and theoretically by Clark.[34]

These 'reluctant' functional groupings include mono-esters,[35,36] lactones,[37] epoxides,[38] organic acids[31] and diesters,[39] some of which have provided the literature with colourful controversy and subtle experiments to settle matters.

The organometallic cations studied here begin to provide a convenient bridge to the, as yet, poorly investigated and still open field of inorganic radical cations. Amongst the few so far studied using these techniques are $SnH_4 \cdot^{+}$ [40] and $N_2O_4 \cdot^{+}$.[41]

Other complementary methods of preparing radical cations for study by e.s.r. are being produced by Knight[42-44] where the trapping of small molecules in inert gas matrices at 4 K is proving informative on such cations as $H_2O \cdot^{+}$, $NH_3 \cdot^{+}$ and $CH_4 \cdot^{+}$.

Some of the groupings previously studied by the 'freon' method are well-covered in the review of the area by Symons.[45] Such groupings are alkenes,[46] alkanes,[47] alkyl halides,[48] ethers,[49] carbonyl compounds,[50] sulphur-centred cations,[51] nitrogen-centred cations,[52] phosphorus-centred cations,[25] organometallics[53] and various sub-groupings of aromatic[54] compounds.

EXPERIMENTAL

One of the greatest advantages of freon as a solvent matrix is that it is so easy to use. The general procedure for all freon samples is basically the same.

Dilute solutions of the substrate in $CFCl_3$ (ca. 0.1% mole fraction) were routinely frozen into polycrystalline lumps by dropping directly into liquid nitrogen. It proved unnecessary to pre-treat these samples in any way prior to irradiation. Alternatively, the samples were frozen in Suprasil tubes, allowance being made for the tube signal.

All chemicals used were the best commercially available and were checked for impurities by NMR and GLC. The $CFCl_3$ used was found to contain an unknown impurity. The signal due to this impurity can be reduced by passing the freon through fine activated γ-alumina (BDH Chemicals Ltd.). Most commonly, these impurity signals were not large enough to be significant in interfering with the solute radical signals.

All glassware used was scrupulously clean and flamed to ensure the absence of any organic materials.

Samples were exposed to ^{60}Co γ-rays at 77 K in a Vickers 'Vickrad' radiation source. The dosage rate was 0.7 Mrad hour and samples were treated with up to 0.7 Mrads.

The e.s.r. spectra were recorded on a Varian E-109 X-band spectrometer and were calibrated by a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe. Diphenylpicrylhydrazyl samples (DPPH) were used as standards.

Samples were annealed by decanting the liquid nitrogen and continuously monitoring the spectral changes as the sample warmed. Upon detection of a significant change the sample was recooled to 77 K and spectra

recorded. This procedure was continued until no further changes occurred and all e.s.r. features lost. To obtain e.s.r. features at various known temperatures, a Varian variable temperature insert was used.

For low temperature work (i.e. down to 4 K), samples were X-irradiated at 4 K, given doses up to 0.5 Mrad (rate = 0.4 Mrad/hour), in an X-ray chamber designed and built by J. A. Brivati in this Department.

The SF_6 samples were prepared in sample tubes according to the method developed by M. Iwasaki.[†] Where a known pressure amount of reagent vapour is allowed into an evacuated gas bulb, then deoxygenated SF_6 up to a pressure of ~1 Atm is allowed into the bulb. The bulb is warmed gently and then the contents transferred to a vacuum line where a tube is attached. The tube is cooled by liquid nitrogen condensing a little of the gaseous matrix. The tube is then sealed and irradiated with γ-rays as described previously.

Several of the deuterated or ^{13}C-substituted compounds used were synthesised by myself, due to their unavailability. These compounds are listed in Table I, together with the references giving their syntheses.

[†] M. Iwasaki, K. Toriyama and K. Nunome, J.A.C.S. <u>103</u>, 3591 (1981).

TABLE I

Compounds Prepared

Reagents		Ref.
$CH_3-C(=O)OCD_3$	$CH_3C(=O)OH$ CD_3OH	S. A. Mumford et al., J. Chem. Soc., 75 (1950)
$CH_3-C(=O)OCHD_2$	$CD_3C(=O)OH$ CD_2HOH	"
Me_2Hg $^{13}CH_3HgCH_3$ $(CD_3)HgCH_3$ $(CD_3)_2Hg$	CH_3I $HgCl_2$ $^{13}CH_3I$ $MeHgCl$ CD_3I $MeHgCl$ CD_3I $HgCl_2$	Gilman et al., J.A.C.S., 52, 3314 (1930)
Et_2Hg	EtI $HgCl_2$	as Me₂Hg
$^tBuSnMe_3$	^tBuLi Me_3SnCl	suggested by Dr. P. Cairns, Organic Chemistry Department [University of Leicester]
$^{13}CH_3SnMe_3$	$^{13}CH_3I$ Me_3SnCl	H. Korsching, Z. Naturforsch., 1, 219 (1946)
$CD_3O-C(=O)-C(=O)-OCD_3$	$CD_3OD + C_2O_4H_2$	Adapted from Synthesis of Diethyl Oxalate, given in Vogel's textbook of Practical Organic Chemistry, 4th. Edn., p.507
2,3-dimethyl oxirane mono-methyl		B. T. Golding et al., J. Chem. Soc., Perkin Trans. 1, 1214 (1973)

REFERENCES

1. M. C. R. Symons, <u>Chem. Soc. Rev.</u>, <u>5</u>, 337 (1976).

2. M. C. R. Symons, <u>Pure & Appl. Chem.</u>, <u>53</u>, 223 (1981).

3. A. R. Lyons and M. C. R. Symons, <u>J. Chem. Soc., Faraday Trans. II</u>, <u>68</u>, 1589 (1972).

4. J. R. Miller and J. V. Beitz, <u>Rad. Res.</u>, <u>6</u>, 301 (1979).

5. G. V. Buxton, <u>Rad. Res.</u>, <u>6</u>, 317 (1979).

6. J. Rideout and M. C. R. Symons, unpublished results.

7. R. L. Hudson and F. Williams, <u>J. Am. Chem. Soc.</u>, <u>99</u>, 1714 (1977).

8. S. Gregoli, M. Olast and A. Bertinchamps, <u>Rad. Res.</u>, <u>65</u>, 202 (1976).

9. P. J. Boon, P. M. Cullis, M. C. R. Symons and B. W. Wren, <u>J. Chem. Soc., Perkin Trans. 2</u>, 1393 (1984).

10. D. J. Nelson and M. C. R. Symons, <u>J. Chem. Soc., Perkin Trans. 2</u>, 286 (1976).

11. S. P. Mishra and M. C. R. Symons, <u>J. Chem. Research (S)</u>, 147, (M), 1660 (1977).

12. M. N. O. Bartlett and M. C. R. Symons, <u>Biochim. Biophys. Acta</u>, <u>744</u>, 110 (1983).

13. M. C. R. Symons, <u>J. Chem. Soc., Chem. Commun.</u>, 408 (1977).

14. M. C. R. Symons, <u>J. Chem. Soc., Perkin Trans. 2</u>, 797 (1973).

15. G. W. Eastland and M. C. R. Symons, <u>J. Chem. Soc., Perkin Trans. 2</u>, 833 (1977).

16. A. Begum, A. R. Lyons and M. C. R. Symons, <u>J. Chem. Soc. (A)</u>, 2290 (1971).

17. H. Reiderer and J. Hüttermann, <u>J. Phys. Chem.</u>, <u>86</u>, 3454 (1982).

18. S. P. Mishra and M. C. R. Symons, <u>J. Chem. Soc., Chem. Comm.</u>, 909 (1975).

19. R. L. Petersen, D. J. Nelson and M. C. R. Symons, <u>J. Chem. Soc., Perkin Trans. 2</u>, 225 (1978).

20. T. Kato and T. Shida, <u>J. Am. Chem. Soc.</u>, <u>101</u>, 6869 (1979).

21. T. Shida and W. Hamill, <u>J. Chem. Phys.</u>, <u>44</u>, 2369 (1966).

22. M. C. R. Symons and I. G. Smith, <u>J. Chem. Research (S)</u>, 392 (1979).

23. M. Iwasaki, <u>J. Chem. Phys.</u>, <u>45</u>, 990 (1966).

24. A. Hasegawa, G. D. G. McConnachie and M. C. R. Symons, <u>J. Chem. Soc., Faraday Trans. I</u>, <u>80</u>, 1005 (1984).

25. J. Rideout and M. C. R. Symons, unpublished results.

26. K. Watanabe, T. Nakayama and M. Lipoky, <u>J. Quant. Spectrosc. Rad. Transf.</u>, <u>2</u>, 369 (1962).

27. P. Bischof, J. A. Hashmall, E. Heilbronner and V. Harnung,
    Helv. Chim. Acta, _52_, 1745 (1945).

28. M. C. R. Symons and P. J. Boon, _Chem. Phys. Lett._, _89_, 516 (1982).

29. D. Becker, K. Plante and M. D. Sevilla, _J. Phys. Chem._, _87_, 1648
    (1983).

30. A. Hasegawa, J. Rideout, G. W. Eastland and M. C. R. Symons,
    J. Chem. Research (S), 258 (1983).

31. M. C. R. Symons, T. A. Claxton and J. Rideout, _J. Chem. Research
    (S)_, 72 (1986).

32. K. Toriyama, K. Nunome and M. Iwasaki, _J. Chem. Phys._, _77_, 5891
    (1982).

33. X.-Z. Qin and F. Williams, _Chem. Phys. Lett._, _112_, 79 (1984).

34. T. Clark, A. Hasegawa and M. C. R. Symons, _Chem. Phys. Lett._,
    in press.

35. D. N. R. Rao, J. Rideout and M. C. R. Symons, _J. Chem. Soc.,
    Perkin Trans. 2_, 1221 (1984);
    M. D. Sevilla, D. Becker, C. L. Sevilla and S. Swarts, _J. Phys.
    Chem._, 1701 (1984).

36. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, _Chem. Phys. Lett._,
    _105_, 587 and 593 (1984);
    M. D. Sevilla _et al._, _Faraday Disc. Chem. Soc._, _78_, 71 (1984).

37. M. D. Sevilla, J. Rideout and M. C. R. Symons, _J. Phys. Chem._,
    _89_, 5251 (1985).

38. J. Rideout, M. C. R. Symons and B. W. Wren, _J. Chem. Soc., Faraday
    Trans. I_, _82_, 167 (1986).

39. J. Rideout and M. C. R. Symons, _J. Chem. Soc., Perkin Trans. 2_,
    in press (1986).

40. A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M. C. R.
    Symons and J. Rideout, _J. Chem. Soc., Dalton Trans._, 1667 (1984).

41. D. N. R. Rao and M. C. R. Symons, _J. Chem. Soc., Dalton Trans._,
    2533 (1984).

42. L. B. Knight, J. M. Bostick, R. W. Woodward and J. Steadman,
    J. Chem. Phys., _78_, 6415 (1983).

43. L. B. Knight and J. Steadman, _J. Chem. Phys._, _77_, 1750 (1983).

44. L. B. Knight and J. Steadman, _J. Chem. Phys._, _78_, 5940 (1983).

45. M. C. R. Symons, _Chem. Soc. Reviews_, _12_, 393 (1984).

46. T. Shida, _J. Chem. Phys._, _73_, 5963 (1980).

47. M. Iwasaki, _J. Chem. Phys._, _77_, 5891 (1982); _ibid._, _79_, 2499
    (1983).

48. M. C. R. Symons, _J. Chem. Soc., Faraday Trans. I_, in press (1986).

49. T. Shida, _J. Phys. Chem._, _85_, 2583 (1981);
    M. C. R. Symons, _J. Chem. Soc., Chem. Comm._, 817 (1982).

50. M. C. R. Symons, _Chem. Phys. Letts._, _89_, 516 (1982); _J. Chem.
    Soc., Perkin Trans. 2_, 1213 (1984).

51. M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 2005 (1977);
    Tet. Letts., 23, 4739 (1982).

52. M. C. R. Symons, *Chem. Phys. Letts.*, 93, 295 (1982).

53. F. Williams, *Organometallics*, 2, 688 (1983).

54. M. Iwasaki, *J. Chem. Soc., Chem. Comm.*, 320 (1983);
    M. C. R. Symons, *J. Chem. Research (S)*, 268, (M), 2746 (1982).

CHAPTER
2

**The Formation of σ^* Adducts
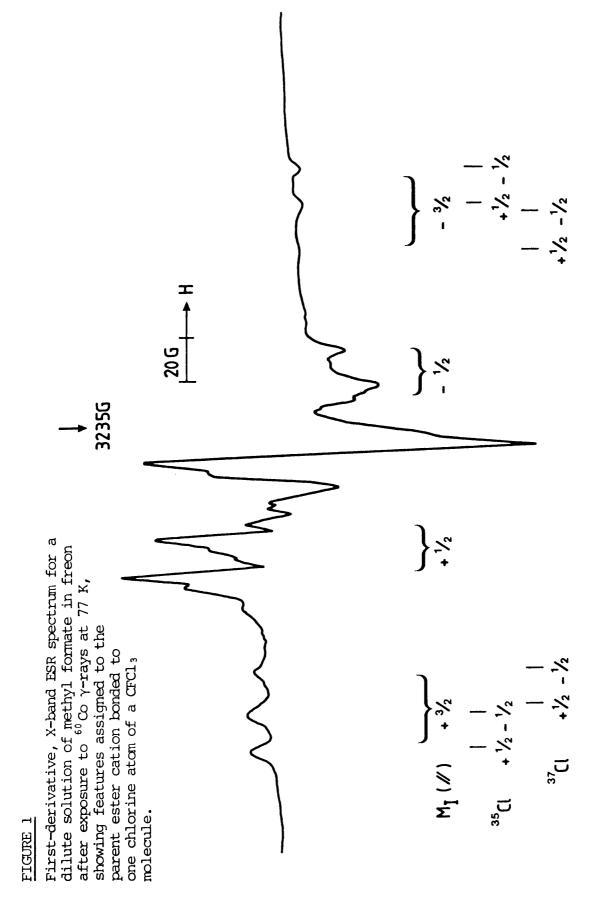with Solvent Molecule Atoms**

INTRODUCTION

The formation of ion to molecule 3 electron, bonds is not a new observation in low temperature radiolytic radical cation formation. Examples with an electron occupying a σ* (sigma antibonding) combination of orbitals between a radical ion and a parent molecule are notably those as found in the gamma radiolysis of trialkylphosphines,[1] other examples are also well documented.[2-4]

Interactions between solutes and solvents have previously been observed by Shida[5,6] in work on electronic spectroscopy. It should, therefore, have come as no surprise to ESR spectroscopists to detect interactions between solvent molecules and solute radical ions in systems using resonance transfer or 'trap-to-trap' mechanism to form those ions.
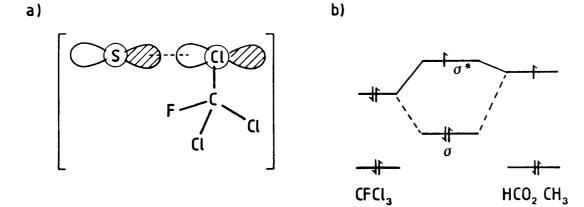
Methyl formate

The study of the radical cations of simple esters is an interesting and extremely complex story, one which will be expanded upon fully in a later chapter. The simplest of all esters, however, produces an entertaining result which will be dealt with here. The spectrum produced by γ-radiolysis of frozen (ca. 77 K), dilute solutions of methyl formate in trichlorofluoromethane (CFCl₃) can be seen in Figure 1. This curious spectrum is obviously not produced simply by the ester radical cation alone. The analysis of this spectrum was assigned by two groups of workers simultaneously,[7,8] as the chlorine adduct of a σ* bond formed between the carbonyl oxygen of the methyl formate and a chlorine bonded to a CFCl₃ molecule (Insert Ia), with the electron loss being shared between the solute and solvent. The changes occurring to this spectrum on thermal annealing (or photolysis) are interesting and are described in the chapter on simple esters (see below). Suffice it

FIGURE 1

First-derivative, X-band ESR spectrum for a dilute solution of methyl formate in freon after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent ester cation bonded to one chlorine atom of a CFCl₃ molecule.

a)   b)

Simple M.O. diagram showing the
formation of a σ* type radical
via adduct formation.

to say that the σ* adduct decomposes by an irreversible breaking of the

σ* bond, suggesting a rearrangement of the resulting solute cation.   It

seems that the initial formation of this σ* adduct occurs in order to

stabilise the SOMO of the cation first formed prior to its rearrange-

ment (see Introductory Chapter).

tert-Butyl Cyanide

A further example of a solute forming a σ* bond to the solvent,

under γ-radiolysis at low temperature, is found by using tert-butyl

cyanide.[10] The t-butyl derivative was chosen in order to minimise the

ionization potential and hence maximise the chance of forming a cation.

In fact, this is the only example of a radical cation of a cyanoalkane

formed in CCl_3F. The spectrum obtained is seen in Figure 2 and is

dominated by the quartet hyperfine features assigned to the isotopes of

^{35}Cl and ^{37}Cl [both have $I = \frac{3}{2}$]. Further hyperfine coupling due to

^{14}N [I = 1] is also seen (a 1:1:1 triplet). This adduct provides the

largest $^{35}Cl_{(//)}$ coupling yet observed (Table 1). The values in Table 1

are for the parallel features, since those for the x and y directions

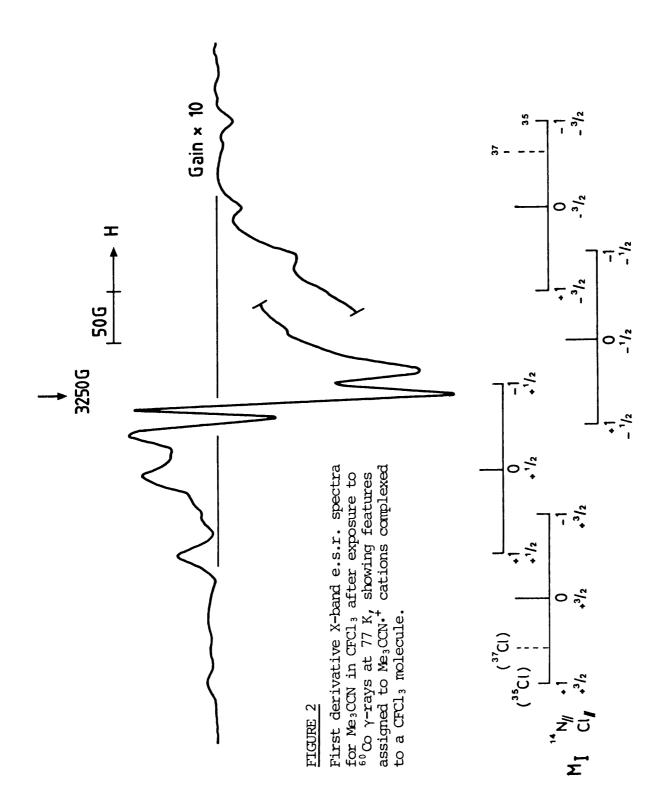are poorly defined. This is usually the case for powder spectra

Gain × 10

$\longrightarrow$ H

50G

3250G

FIGURE 2

First derivative X-band e.s.r. spectra
for Me₃CCN in CFCl₃ after exposure to
⁶⁰Co γ-rays at 77 K, showing features
assigned to Me₃CCN·⁺ cations complexed
to a CFCl₃ molecule.

M_I

$^{14}N_{\parallel}$

$Cl_{\parallel}$

(^{35}Cl)

(^{37}Cl)

37   35

TABLE I

Table of ^{35}Cl parallel hyperfine splittings of adducts formed by various radical cations to the freon matrix

Compound	Nucleus	Hyperfine Coupling Constants/G[a]
Bu^{t}CN	^{35}Cl	125
Methyl formate	"	88
RBr	"	56.9
RCl	"	85
Acetaldehyde	"	~20 G
(Cl$_2$FCCl $\dot{\cdot}$ ClCFCl$_2$)	"	95 G
EtCHO	"	15 G
Cl$_2^-$	"	97 G[b]

a $G = 10^{-4}$ T;
b ~0.5 spin density ~100 G.

dominated by hyperfine coupling to Cl, Br or I.[11,12] The result of
thermal annealing of this adduct produced a spectrum consisting of 10
lines, with poorly defined outer features. The radical responsible for
this spectrum I believe is $Me_3C\cdot$. The lines are rather broad in nature
and I presume there is a small unresolved extra hyperfine interaction.
However, since loss of the CN^+ moiety is unlikely, Scheme I is proposed,

$$
\left[
\begin{array}{c}
Me \\
| \\
Me - C - C \equiv N \xrightarrow{} Cl \\
| \quad\quad\quad | \\
Me \quad\quad\quad C \\
\quad\quad\quad Cl \diagup\!\!\diagdown Cl \\
\quad\quad\quad F
\end{array}
\right]
\xrightarrow{\Delta}
\left[
\begin{array}{c}
Me_3\overset{\bullet}{C} - \!\!\!- (CN) - Cl \\
| \\
C \\
Cl \diagup\!\!\diagdown Cl \\
F
\end{array}
\right]^{+}
$$

that is, transfer of the CN^+ moiety to the solvent molecule while
retaining a small residual coupling to the $Me_3C\cdot$ radical (hence the
broad lines observed). The effects of visible photolysis upon the
adduct are quite different, the formation of $[Me_2C = CH_2]^{+\bullet}$ by the loss
of HCN occurring, the details are therefore unimportant to the subject
of this Chapter and are discussed in detail in Ref. 10.

R-X Alkyl Halides

Various radical cations of alkyl chlorides, bromides and iodides[13]
have been prepared in $CFCl_3$, with the chloro- and bromo- derivatives
providing nicely defined solvent adducts. The iodo- radical cations
are produced only at 4 K and exhibit very weak interactions with the
solvent indeed. The iodides being different due to the larger variation
in ionization potential between RI and CCl_3F, the greater spin-orbit
coupling energy for the cation $[RI\cdot]^+$ causes the large $\underline{g}$-shifts observed
for these cations. This energy needs to be overcome to form the
necessary localised σ and σ^* bonds to the solvent.

With the use of $CFCl_3$ as a solvent, there are two options for adduct
formation by the solute. A σ^* bond may occur to a Cl atom or to a F

atom. Many examples of adduct formation to chlorine have now been recognised, some have already been mentioned specifically, while others include propionaldehyde,[14] acetaldehyde,[14] Me_3PO_4,[15] Me_2S[16] and various lactones.[17]

Adduct formation to fluorine was first suggested to occur for $[C_2F_4\cdot]^+$, by Hasegawa and Symons,[18] who observed an extra hyperfine doublet due to ^{19}F, and has since been observed in the spectra of dimethyl mercury,[19] PPh_3[20] and Me_2Se.[16] It is particularly noteworthy that whilst $Me_2S\cdot^+$ forms a weak adduct with the chlorine ligand, the isostructural cation $Me_2Se\cdot^+$ forms one with the fluorine ligand of $CFCl_3$. Clark et al.[16] have presented a theoretical argument which goes some way to explaining this switch. The formation of adducts is dependent upon (i) the ionization potential (IP) of the solute compared with that of the solvent and (ii) the localised nature of the SOMO.
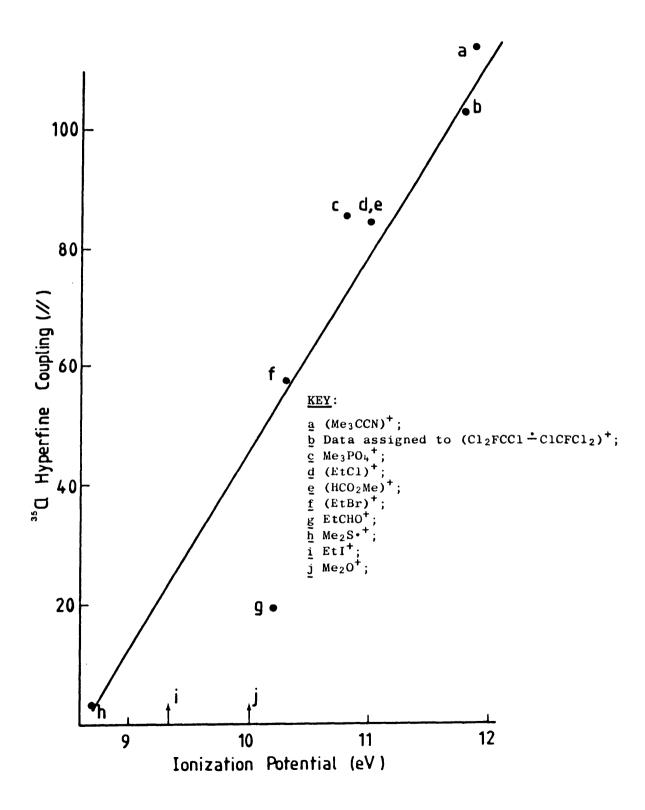
These arguments are based on the qualitative theory of σ^* radicals (3 electron bonds) which implies that the lone-pair orbitals of CCl_3F involved in adduct formation, may be considered as localised on either chlorine or fluorine. The ionization potential of the F-type Highest Occupied Molecular Orbital (HOMO) is approximately 1.1 eV[21] higher than that of the chlorine-type HOMO. The conclusion drawn by these authors is that substrates with a low Δ I.P. (the difference between the I.P. of the solute and the solvent) prefer to interact with chlorine-centred orbitals, whilst those with higher Δ I.P's prefer interactions with fluorine-centred orbitals. The terms low and high are relative to a critical value I.P$^\circ$. The difference between the solute and solvent ionization potentials as calculated by Clark in Ref. 16.

A linear correlation between the ionization potentials of the solutes and the parallel hyperfine coupling due to ^{35}Cl is shown graphically in Figure 3. However, the result for the acetaldehyde cations is well

FIGURE 3

Trends in the parallel hyperfine coupling to ^{35}Cl in
$(S \doteq ClCFCl_2)^+$ complexes as a function of ionization
potential.

KEY:

a $(Me_3CCN)^+$;
b Data assigned to $(Cl_2FCCl \doteq ClCFCl_2)^+$;
c $Me_3PO_4^+$;
d $(EtCl)^+$;
e $(HCO_2Me)^+$;
f $(EtBr)^+$;
g $EtCHO^+$;
h $Me_2S \cdot^+$;
i EtI^+;
j Me_2O^+;

removed from this correlation.

Acetaldehyde

This is an interesting case exhibiting an apparent thermal reversibility of the breaking of the σ^* bond. This reversible loss of the ^{35}Cl hyperfine coupling (Figure 4a and 4b) occurs with virtually no alteration of the isotropic coupling of the aldehydic proton. If the loss of the ^{35}Cl hyperfine were due to the thermolysis of the σ^* bond, an alteration in spin-density and a corresponding alteration in the spectral features would be anticipated.[22] A much more gradual loss of the ^{35}Cl hyperfine occurs in this case; indeed at 120 K weak anisotropic features are still detectable. The only feasible explanation for these observations is that a motional averaging is occurring - in this manner no change of spin-density distribution and hence, spectral alterations, are expected. This, however, requires the isotropic component of the ^{35}Cl hyperfine interaction to be small, which is quite possible.

The radical cation of dimethyl ether produces no adduct with ^{35}Cl or ^{19}F whilst according to its ionization potential of $9.98 \, ev$ be expected to produce a large coupling to ^{35}Cl. This result is surprising since Me_2S forms an adduct to ^{35}Cl and Me_2Se forms an adduct to ^{19}F. Two explanations are proposed:-[16]

[1] The heavy delocalisation of the SOMO over the two methyl groups prevents the required localisation needed to form the σ^*-type bonding.

[2] There is steric resistance to oxygen-chlorine bond formation.

These are acceptable explanations since neither effect is as large for Me_2S.

It is worth considering the importance of adduct formation in the context of the ethylene oxide radical-cation. A small extra splitting
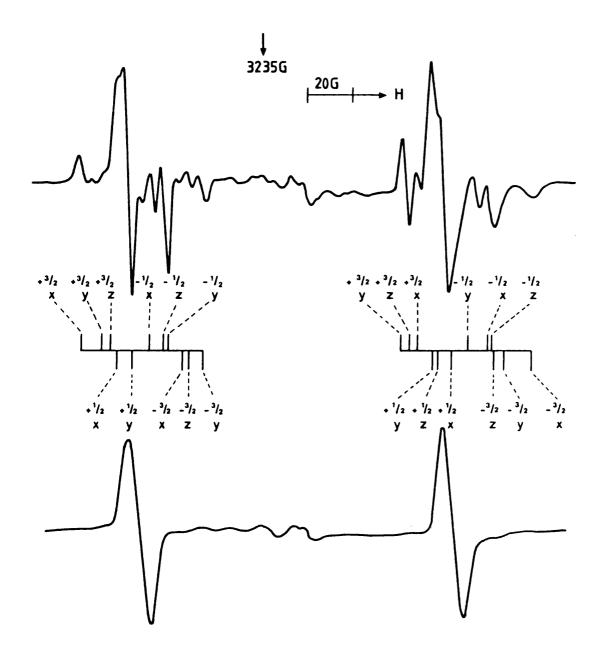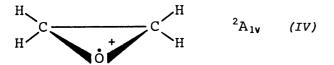
FIGURE 4

First-derivative ESR spectra for acetaldehyde in freon after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to (MeCHO)$^+$ cations (a) at 77 K, (b) at $\approx$ 120 K.

attributable to chlorine is observed,[14] which is reversibly lost on

warming. In the light of the arguments presented here, it seems odd

to propose for this radical, a ring-open structure (III), which must

$$2\overset{\bullet}{HC} \text{-----} \overset{+}{O} \text{-----} \overset{\bullet}{CH_2} \qquad (III) \qquad C_{2v}$$

delocalise the electron density, a factor which, as explained above,

discourages the formation of a σ* complex. The small size of the ^{35}Cl

hyperfine coupling is consistent with the 'thermal reversibility' of

the coupling observed. It seems much more likely to consider the cation

to be ring-closed (IV), as proposed by Symons and Wren,[24] with the

$$\begin{array}{c} H \diagdown \quad\quad\quad\quad\quad /H \\ C \text{-------------} C \\ H \diagup \quad\quad +\quad\quad \diagdown H \\ \quad\quad \overset{\bullet}{O} \end{array} \qquad {}^{2}A_{1v} \qquad (IV)$$

carbon-carbon bond elongated, as shown, localising the SOMO much more.

Consideration of the sizes of the $^{35}Cl_{(//)}$ couplings (Table 1) is

further evidence for the necessity of localisation of the SOMO as a

prerequisite for adduct formation. An estimate of the spin-density on

chlorine can be made by comparison with radicals such as $Cl_2^{\bar{\bullet}}$,

$[EtCl\overset{\bullet}{\text{--}}ClEt]^{+}$[13] and $[FCl_2C\text{-}Cl\overset{\bullet}{\text{--}}ClCCl_2F]^{+}$.[24] In all these cases,

symmetry requires 0.5 spin-density on each chlorine. This result

provides an acceptable reference for estimating the spin-densities on

chlorine in other complexes.

REFERENCES

1. A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. II*, 68, 1589 (1972).

2. F. Williams and E. D. Sprague, *Acc. Chem. Res.*, 15, 408 (1982).

3. E. D. Sprague and F. Williams, *J. Chem. Phys.*, 54, 5425 (1971).

4. L. Knight, *J. Chem. Phys.*, 77, 1750 (1982).

5. T. Shida, *J. Am. Chem. Soc.*, 95, 3473 (1973).

6. T. Shida, *J. Am. Chem. Soc.*, 101, 6869 (1979).

7. M. D. Sevilla, *J. Phys. Chem.*, 87, 1648 (1983).

8. G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons and A. Hasegawa, *J. Chem. Research (S)*, 258 (1983).

9. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, *Chem. Phys. Lett.*, 105, 586 (1984).

10. J. Rideout and M. C. R. Symons, *J. Chem. Research (S)*, 268 (1984).

11. S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1492 (1975).

12. M. C. R. Symons and R. L. Petersen, *J. Chem. Soc., Faraday Trans. II*, 210 (1979).

13. G. W. Eastland, S. P. Maj, M. C. R. Symons, A. Hasegawa, C. Glidewell, M. Hayashi and T. Wakabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1439 (1984).

14. L. D. Snow and F. Williams, *Chem. Phys. Lett.*, 100, 198 (1983).

15. G. D. G. McConnachie and M. C. R. Symons, *J. Chem. Research (S)*, 54 (1985).

16. T. Clark, A. Hasegawa and M. C. R. Symons, *Chem. Phys. Lett.*, in press (1986).

17. J. Rideout, M. C. R. Symons and M. D. Sevilla, *J. Phys. Chem.*, 89, 5251 (1985).

18. A. Hasegawa and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. I*, 79, 93 (1983).

19. J. Rideout and M. C. R. Symons, unpublished results.

20. A. Hasegawa, G. D. G. McConnachie and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. I*, 80, 1005 (1984).

21. (a) H. J. T. Preston and J. J. Kaufman, *Chem. Phys. Lett.*, 50, 157 (1977);
    (b) H. T. Lempka, D. G. Streets, A. W. Potts and W. C. Price, *Trans. Roy. Soc. A*, 268, 59 (1970).

22. L. D. Snow and F. Williams, *Faraday Disc. Chem. Soc.*, 78/2 (1984).

23. M. C. R. Symons, B. W. Wren and J. Rideout, *J. Chem. Soc., Faraday Trans. I*,

24. B. W. Wren and M. C. R. Symons, unpublished results.
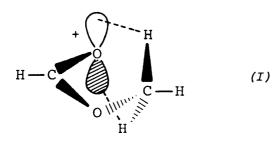
CHAPTER
3

Ester Cations

INTRODUCTION

The radiation chemistry of simple esters has been extensively studied because of its relationship and importance to biological materials, especially lipids.[1,2] Studies have ranged from the gamma radiolysis of the pure materials[3-5] which produce alkyl radicals upon photolysis, with visible or ultra-violet light of the initial radicals, to work on esters trapped in glassy matrices producing, specifically, the radical anion species.[5,6] It is interesting to extend this work to a study of the radical cations of these compounds. This might be achieved using the 'freon technique' recently becoming popular.[7,8,9]

RESULTS

Methyl Formate

The formation of a ^{35}Cl adduct at 77 K is established[10,11] and is reviewed in Chapter 2. When samples exhibiting spectra due to this complex are exposed to visible light or higher temperatures, they produce the spectrum seen in Figure 1. A major triplet with $A(^1H) =$ 23 G and a smaller coupling of 5 G for one proton fits this scheme. This was originally analysed[12,13] as the parent cation of π symmetry with the alcoholic methyl group having limited rotation.

(I)

As shown in Insert I, two protons are seen to have strong couplings and one a very weak coupling. The coupling due to the formyl proton is $A(^1H) = 5G$, fortuitously similar to that of the third proton of the methyl group. Specific deuterations were used to support this analysis
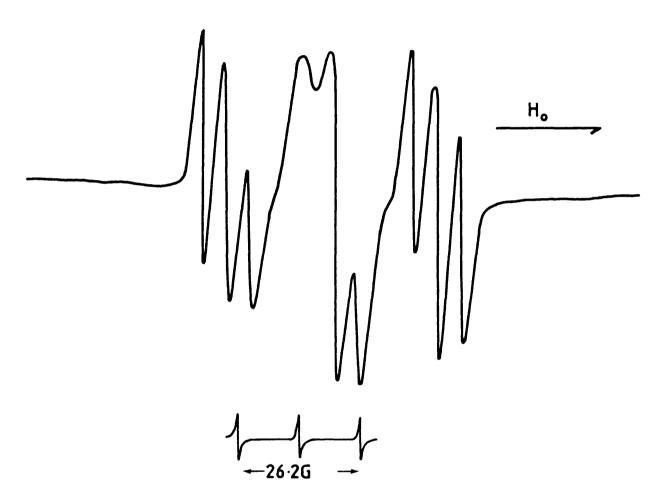
FIGURE 1

ESR spectrum of the methyl formate (HCO_2CH_3) cation in $CFCl_3$. The spectrum shows coupling to all four protons in the radical cation.
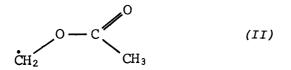
by Sevilla et al.[13]

It is noteworthy that even at relatively high temperatures, no complete averaging of the methyl group occurred. This was explained by use of the idea that an interaction between the protons H_1 and H_2 with the p-orbital on the carbonyl oxygen prevents free rotation. INDO calculations support the π-structure, predicting the observed inequivalence of the methyl protons.

Methyl Acetate

No chlorine-type adduct is observed with methyl acetate. This is probably due to its lower ionisation potential, one of the vital factors in chlorine adduct formation.[14]

Instead, a simple spectrum with $A(^1H) = 22\,G$ for two protons providing the main triplet and a subsidiary coupling of $A(^1H) = 5\,G$ for three protons. Again, this was originally analysed as the π cation exhibiting a limited rotation of the methyl group, as in the case of methyl formate. A collapse of the major triplet when using $CH_3C(O)OCD_3$ supports this analysis. It is also notable that when using more concentrated solutions of this ester, a species more characteristic of radical II was formed by intermolecular hydrogen abstraction.

$$\overset{\bullet}{C}H_2-O-C\overset{\displaystyle O}{\underset{\displaystyle CH_3}{\big<}}$$ (II)
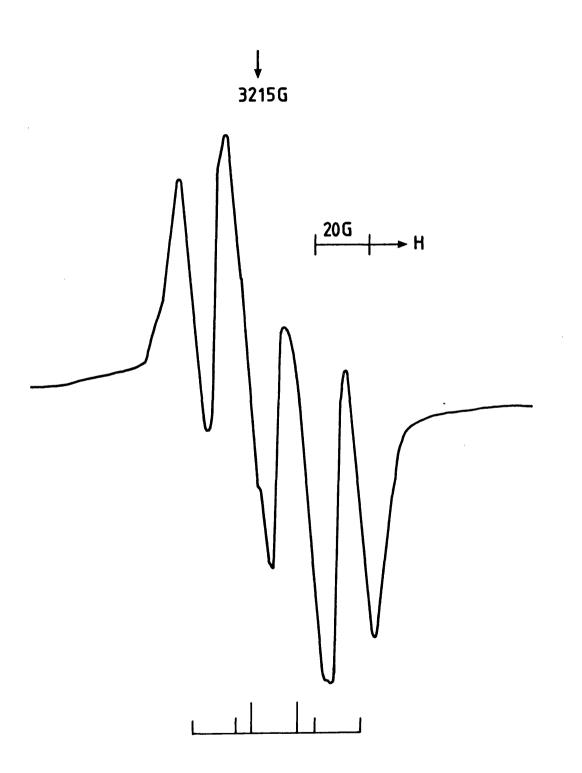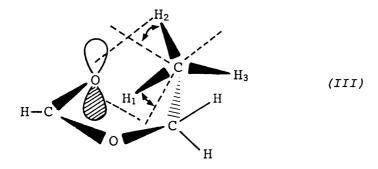
Ethyl Formate

Again, no chlorine adduct was observed at 77 K. Instead, the spectrum observed in Figure 2 was obtained, showing coupling to two protons with $A(^1H) = 22\,G$. These were originally attributed to the two β-protons. Another large proton coupling is evident, with $A(^1H) = 16\,G$. This was attributed to a single proton of the methyl group. Annealing

FIGURE 2

First-derivative X-band e.s.r. spectrum obtained from
a dilute solution of ethyl formate in $CFCl_3$ after
exposure to [60]Co γ-rays at 77 K.

produced a reversible change causing the 16 G doublet to become a 10 G triplet. The results obtained by Sevilla et al. with specific deuterations led to both groups favouring this analysis. At higher temperatures only two of the three methyl protons are seen. It is also of some surprise that these γ-proton couplings are so large. The work of Ellinger[15] and Ingold[16] suggest γ couplings may be large, but require a 'W' plan[17] structure to be so. With the β-proton couplings being 22 G the C-CH$_3$ bond is about 90° from an ideal situation and so the γ-proton couplings should be small. Therefore, a 'through space' interaction must be invoked, as in III.

(III)

Insert III suggests that a single proton (H$_1$) lies near the carbonyl oxygen, forming a weak hydrogen bond to it. With warming (H$_2$) swings into a similar interaction with the other lobe of the p-orbital, causing a torsional oscillation without allowing complete rotation. Hence the coupling to H$_3$ remains small. This analysis is entirely based on the assumption of a π-cation for ethyl formate. Again, original deuterations performed by Sevilla et al.[13] were supportive of this analysis. These are discussed more fully later.

Ethyl Acetate

Ethyl acetate produced similar spectra to the formate. However the two β-protons are no longer equivalent in the low temperature spectra (Table 1). Two couplings were assigned to γ-protons, one large (17 G)

TABLE I

ESR Parameters for Radicals obtained by 77 K ^{60}Co γ-Irradiation
of Dilute Solutions of Simple Esters in CCl_3F

Compound	Nucleus	Temp.	Hyperfine Coupling[a]
Methyl Formate	^{1}H ^{25}Cl$_{(//)}$	77 K	17 G (1H) 84.5 G
	^{1}H ^{1}H	110 K "	23 G (2H) 5 G (2H)
$CH_3C(O)OCH_3$	^{1}H ^{1}H	77 K "	22 G (2H) 5 G (3H)
$CH_3C(O)OCD_3$		77 K	Broad singlet
Ethyl Formate	^{1}H ^{1}H	77 K	22 G (2H) 16 G (1H) 22 G (2H) 10 G (2H)
Ethyl Acetate	^{1}H	77 K	22 G (1H) 31 G (1H) 8 G (1H) 17 G (1H)
t-Butyl Acetate	^{1}H	77 K	14.6 G (8H)
Isopropyl Acetate	^{1}H	77 K	22 G (6H)

[a] $G = 10^{-4}$ T; g_{av} = ca. 2.0026.

and one small (8 G). It was suggested that the extra methyl group must be responsible for having distorted the ethyl formate type structure making it more rigid. This is consistent with the fact that no averaging occurred even up to the softening point of the matrix.
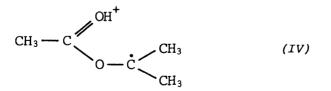
t-Butyl Acetate

At 77 K a well-defined 9-line spectrum with $A(^1H) = 14.6\,G$ (Figure 3) was obtained. The parameters match well with those given by Iwasaki et al.[18] for the isobutene cation. It is proposed that Reaction [1] must occur liberating neutral acetic acid as a by-product. It is

[1]

probably this which provides the driving force for the reaction.

Isopropyl Acetate

A complex spectrum (Figure 4) is found at 77 K, with two species being present. The first is identified as IV, the other being tentatively assigned to the isopropylene cation. This is a tentative

(IV)

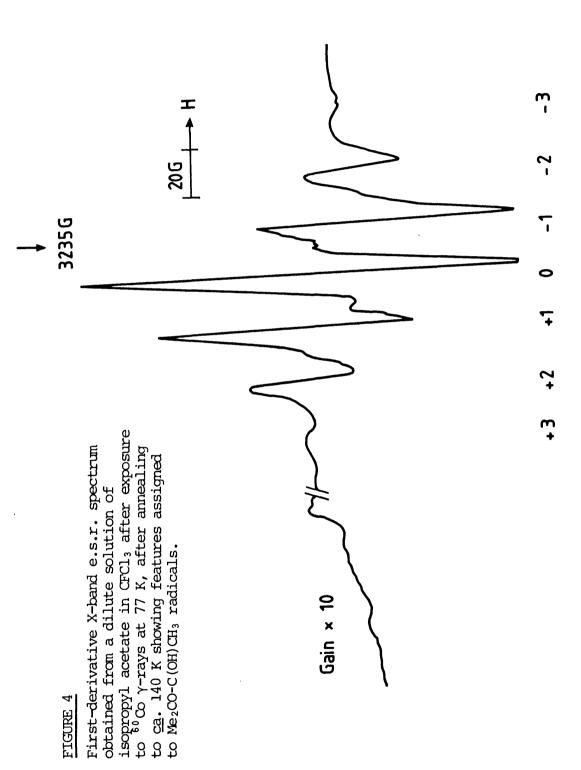assignment since two remarkably different spectra are found in the

3235G

20G

H

FIGURE 3
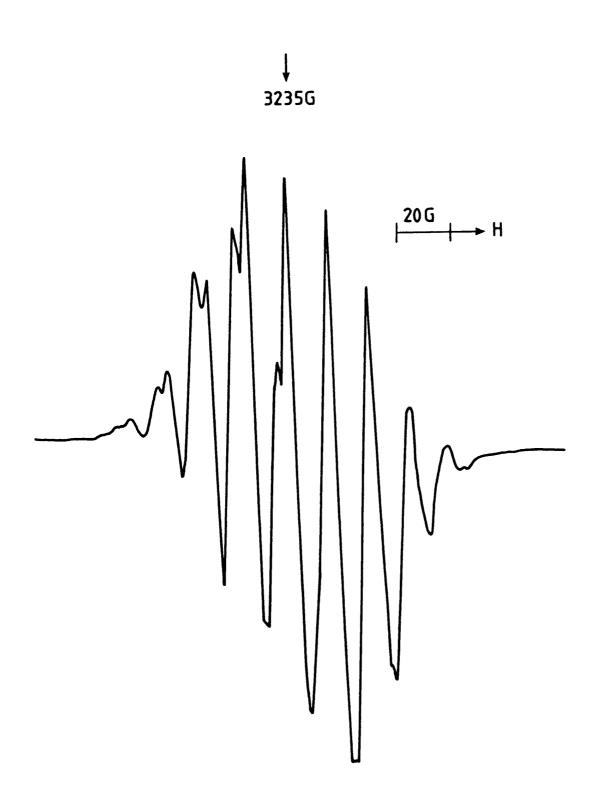
First–derivative X–band e.s.r. spectrum obtained from a dilute solution of t–butyl acetate in $CFCl_3$ after exposure to ^{60}Co γ–rays at 77 K and annealing to ca. 120 K, showing features assigned to the cation, $[H_2C=CMe_2]^{+\bullet}$.
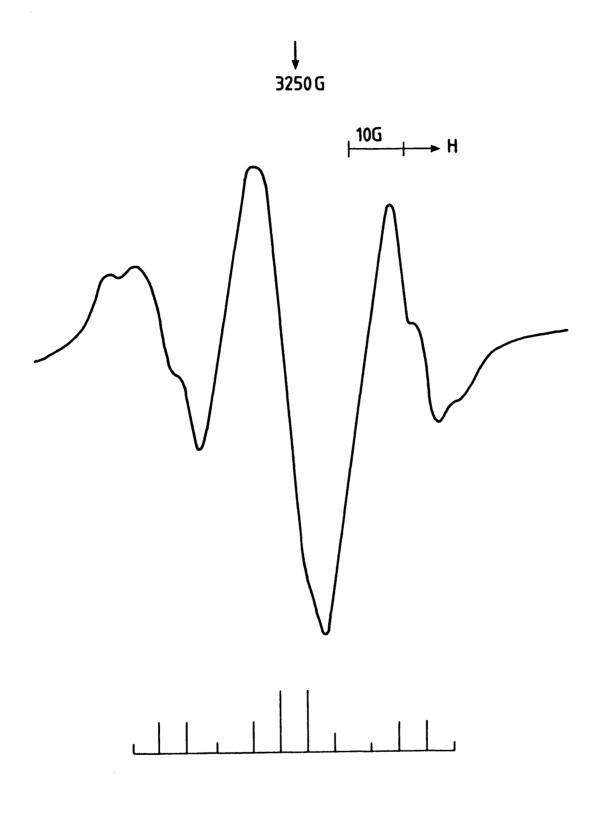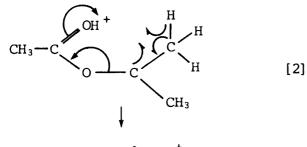
FIGURE 4

First-derivative X-band e.s.r. spectrum
obtained from a dilute solution of
isopropyl acetate in $CFCl_3$ after exposure
to ^{60}Co γ-rays at 77 K, after annealing
to ca. 140 K showing features assigned
to $Me_2CO-C(OH)CH_3$ radicals.

FIGURE 5

First-derivative X-band e.s.r. spectrum obtained from $CH_3CO_2CH_3$ in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $CH_3C(OH)OCH_2$ radical-cations.

literature, produced by different methods.[18] One possible reason for
the different spectra being observed is that there are differing
degrees of twist within the alkene cations. The magnitude of the proton
couplings is strongly dependent upon θ, the degree of twist. As θ
increases, the $p\pi$-$p\pi$ overlap decreases, hence increasing localisation
of both the charge and the unpaired electron. The electron is thought
to localise upon the unsubstituted alkene carbon with the positive
charge preferring the methylated carbon.

The size of θ affects the β-proton coupling according to the $\cos^2\theta$
law.[19] As θ approaches $90°$, so hyperconjugation and hence proton
coupling drops. In this manner when a particular cation is produced
under different circumstances, different spectra might be observed.
'The suggested mechanism for liberation of the alkene cation is given in
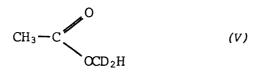Reaction 2.

$$[\text{HCCH}_3 \overset{\bullet}{-} \text{CH}_2]^+ + \text{CH}_3\text{C(O)OH}$$

'The more interesting product, however, is the cation (IV), formed by
intramolecular hydrogen shift. If this is a facile reaction here, it
might have occurred with the methyl and ethyl esters. This was indeed
our original interpretation for these cations, since for example, a
major triplet spectrum is then expected for the methyl formate and
acetates. However, the results for partially deuterated ethyl formate
seemed to rule out this scheme. A good deal of controversy has since
arisen around this point and led us to producing the compound (V) for

study, in the expectation that these results would be definitive (see below).

$$CH_3-C \overset{\displaystyle O}{\underset{\displaystyle OCD_2H}{<}} \qquad (V)$$

DISCUSSION

The identities and analyses given above were questioned by Iwasaki et al. in two publications.[21,22] The main point of argument seems to be whether the species produced are the parent π cations or the proton-shifted π cations favoured by Iwasaki et al. As has been suggested, the proton-shifted radicals were our original analysis also. However, the deuterations performed by Sevilla et al. in the ethyl formate[13] case seemed clear proof of the identity of the species as being the parent cation with a π-structure. The selection by us upon the π cation rather than the rearranged cation VI was made for several reasons. Firstly, the proton coupling seems a little large for two α-protons and, secondly, couplings for the π cation predicted by INDO calculations agreed well with experiment. Thirdly, the anisotropy observed seemed too low for such a centre.[12] It is noteworthy that many radical cations' methyl groups exhibit well-defined fixed conformations rather than free rotation. The spin-density on the acyl carbon is small. INDO calculations[12] suggest a spin-density of -0.42 in the carbon p_z orbital implying a coupling of 8.2 G. This is clearly an over-estimate but establishes the negative sign. Also predicted is the inequivalence of the methyl group protons, the theoretical couplings 23, 20 and 0.4 G being in good agreement with experiment.
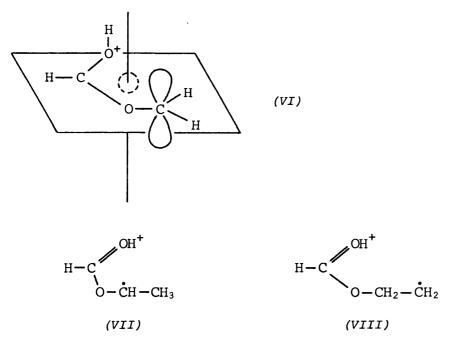
It is interesting that both methyl groups in N,N-dimethyl formamide are freely rotating at 77 K whilst fixed conformations are apparently

observed for the esters if they are π-cations.

Iwasaki et al. chose to favour the production of radical (VI) for methyl formate. Whilst our analyses were heavily based upon the evidence Sevilla et al. had obtained from deuterated ethyl formate [DC(O)OCH₂CD₃]. The non-deuterated radical gave $A(^1H) = 22\,G$ for two protons and two more with $A(^1H) = 10\text{--}11\,G$. The deuterated radicals' spectra exhibited only a 22 G triplet due to two protons. Both Sevilla et al. and ourselves took this as proof that it was the π-cation that was involved.

For the rearranged cation (VII), coupling to only one α-proton is expected with three equivalent β-protons (VI, VII and VIII).

(VI)

(VII)

(VIII)

Radical VIII could fit the data for the protiated radical, two α H's giving 22.5 G and two β H's giving 10-11 G. The deutero analogue (IX) would have been expected to have given an 11 G triplet not the 22 G triplet observed.

This evidence was taken to prove VIII could not be the observed radical. It seemed reasonable to suggest in this light, that the proton

$$
\begin{array}{c}
\overset{+}{\text{OH}} \\
 \\
\text{H}-\text{C} \overset{\displaystyle /\!\!/}{\underset{\displaystyle \backslash}{}} \\
\text{O}-\text{CH}_2-\overset{\bullet}{\text{CD}}_2
\end{array}
\qquad (IX)
$$

transfer species was also not responsible for the methyl derivative spectra.

It occurred to us that the easiest way to prove whether or not a hydrogen shift occurs, was to use $CH_3-C(O)OCD_2H$. The π cation would surely exhibit a 22 G doublet whilst the proton transfer species would appear as a singlet. This is because proton transfer is strongly favoured over deuteron transfer at low temperatures, as observed by Williams.[20] Similarly, the only manner with which the π cation could fit a singlet spectrum, would be for the proton to be at 90° to the plane of the SOMO. This conformation is the reverse of that expected, the lighter isomer should favour the out-of-plane site.[23,24] The single line observed for this species is, therefore, assigned to the proton transfer radical, X, and we conclude firmly that proton transfer occurs for all these esters.

$$
\begin{array}{c}
\overset{+}{\text{O}\,\text{D}} \\
 \\
\text{H}-\text{C} \overset{\displaystyle /\!\!/}{\underset{\displaystyle \backslash}{}} \\
\text{O}-\overset{\bullet}{\text{CD}}_2
\end{array}
\qquad (X)
$$

Indeed, this is the dominating species even at 4 K, implying the proton transfer mechanism occurs largely by a tunnelling mechanism.[18] This result supports the opinion of Sevilla[25] that the species observed by Iwasaki et al.[21,22] at 4 K is the rearranged species and not the parent cation. Sevilla is further supported by results obtained from DCO_2CD_3.[13] The expected solvent adduct is present at 77 K but, upon annealing, the rearrangement noted for $DC(O)OCH_3$ does not occur. The ^{35}Cl adduct is actually far more stable decaying at 150 K compared to 110 K for the protonated radical. Rejecting the species XI, Sevilla et
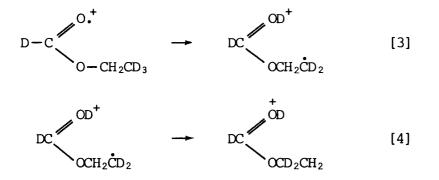
al. prefer XII, by donation of the formyl deuteron to some acceptor.

$$H-C\underset{O-\overset{\bullet}{C}D_2}{\overset{\overset{+}{OD}}{\diagup}} \qquad (XI) \qquad \bullet C\underset{O-CD_3}{\overset{O}{\diagup}} \quad , \quad (XII)$$
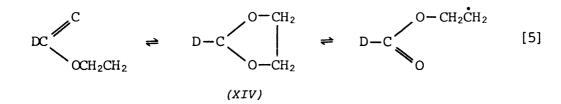
The evidence given for this is based solely upon the g-shift to 2.0017 seen for this radical.

In conclusion, it appears for methyl esters proton transfer is facile for the $\sigma[O_{nb}]$ cation even at low temperatures. For the formate the rearrangement is in competition with solvent adduct formation. Given this general rearrangement for methyl esters and for isopropyl esters, it might be expected that ethyl esters would similarly rearrange. However, it was the results obtained for ethyl formate which misled both Sevilla and ourselves originally. In order to try to clarify this odd occurrence, Sevilla[26] studied $D\overset{O}{C}O CH_2CD_3$ (2,2,2-d_3) and $D\overset{O}{C}O CD_2CH_3$ (l-l-d_2). The same triplet spectrum was obtained for both, at 77 K for 1,1-d_2 and at 140 K for 2,2,2-d_3. The initial spectrum obtained for 2,2,2-d_3 was a 40 G doublet. Reactions [3] and [4] summarize the suggested scheme causing the species suggested to occur for both compounds.
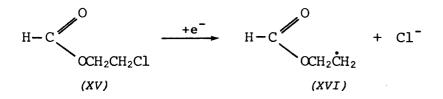
$$D-C\underset{O-CH_2CD_3}{\overset{\overset{+}{O\bullet}}{\diagup}} \quad \longrightarrow \quad DC\underset{OCH_2\overset{\bullet}{C}D_2}{\overset{\overset{+}{OD}}{\diagup}} \qquad [3]$$

$$DC\underset{OCH_2\overset{\bullet}{C}D_2}{\overset{\overset{+}{OD}}{\diagup}} \quad \longrightarrow \quad DC\underset{OCD_2CH_2}{\overset{\overset{+}{OD}}{\diagup}} \qquad [4]$$

A methyl group proton is shifted, the resultant radical XIII [HC(O)H$^+$OCH$_2\overset{\bullet}{C}$H$_2$] is responsible for the triplet of triplets initially found.

Reactions [3] and [4] explain the similarities between spectra for the two compounds H-d_2 and 2,2,2-d_3. It is surprising that a deuteron shift is invoked, when it is known $DC(O)OCD_3$ will not rearrange in this manner.[13] It would surely have been expected that radical XIV should have been formed. If this were so, then Reaction [4] could not occur. The product of Reaction [3] cannot explain the initial 40 G doublet seen at 77 K. Further problems present themselves, for instance the Reaction Scheme [3] and [4] must be effectively irreversible to account for observed results. The other main problem is that the normal cyclic transition state XIV in Reaction [5] cannot be formed due to the presence of the deuteron. This deuteron must shift concurrently with ring formation.

$$
\mathrm{DC}\!\!\begin{array}{c} \diagup C \\ \diagdown OCH_2CH_2 \end{array}
\rightleftharpoons
\mathrm{D-C}\!\!\begin{array}{c} \diagup O-CH_2 \\ \;\;\;| \\ \diagdown O-CH_2 \end{array}
\rightleftharpoons
\mathrm{D-C}\!\!\begin{array}{c} \diagup O-CH_2\overset{\bullet}{C}H_2 \\ \diagdown O \end{array}
\qquad [5]
$$

(XIV)
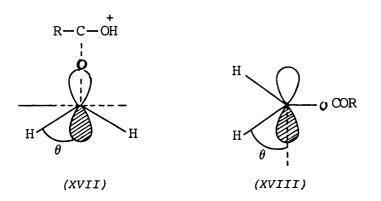
Liquid phase ESR studies have proven Reaction [5] to be facile.[27,28] It appears that although radical XIV has been produced by other methods[29,30] and is stable that it chooses to ring open at room temperature.[27,28] It has been questioned if radical XIV is fully formed or whether the rearrangement is a concerted reaction. Nevertheless, unquestioned is the ease with which Reaction [5] occurs. This evidence in itself supports the idea proposed by Sevilla et al. However, this does not explain the apparent irreversibility for the O-$CD_2\overset{\bullet}{C}H_2$ derivative. The β-proton couplings observed for this type of radical (O-$CH_2\overset{\bullet}{C}H_2$) are given at 16 G and 4 G at 77 K and 10-11 G at higher temperatures. We have performed an experiment in which the un-protonated analogue XVI is formed by electron addition to XV.
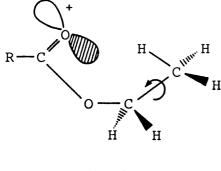
$$H-C\overset{\displaystyle O}{\underset{\displaystyle OCH_2CH_2Cl}{\diagdown}} \qquad \xrightarrow{+e^-} \qquad H-C\overset{\displaystyle O}{\underset{\displaystyle OCH_2\dot{C}H_2}{\diagdown}} \quad + \quad Cl^-$$

(XV)   *(XVI)*

Species XVI exhibits coupling to two equivalent β-protons at about 34 G

each (Figure 6). This species remained stable throughout annealing, the

spectra being unchanged. The species formed from the cation prefers

the structure with $\theta = 60°$ (XVII) whilst species XVI prefers the structure

with $\theta = 30°$ (XVIII).

(XVII)   *(XVIII)*

It is possible that the presence of the OH^+ group causes removal of

any conformational preference. It is more likely that structure XIX

is formed bringing a proton into close proximity with the carbonyl

oxygen.

(XIX)

It remains a question as to why, if this is the case, should the radical

$-OCH_2\dot{C}D_2$ exhibit a large coupling to one β-proton initially.

It seems the only conclusion which can, at present, be drawn is,
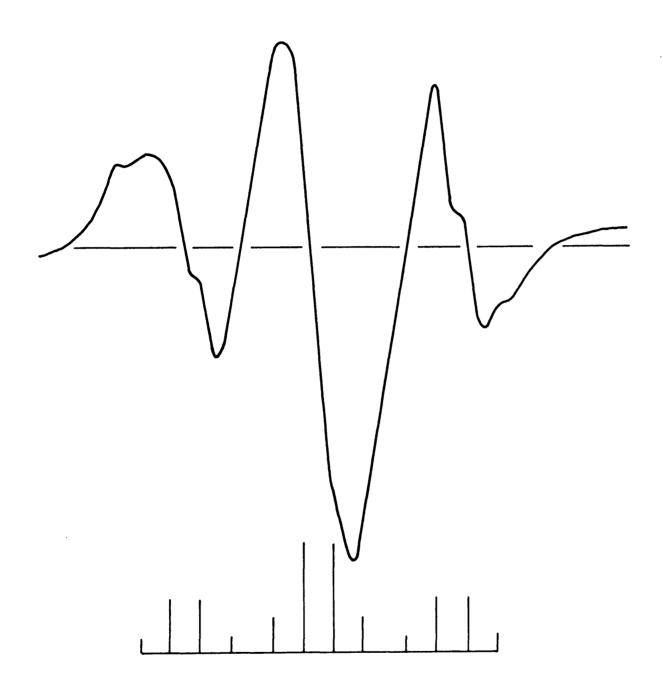
FIGURE 6

First-derivative X-band e.s.r. spectrum obtained from $CH_3CO_2CH_2CH_2Cl$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $CH_3CO_2CH_2\dot{C}H_2$ radicals.

proton transfer competes with solvent adduct formation when possible. Otherwise, the proton transfer species is observed at 77 K given no further facile breakdown occurs.

Sevilla et al.[25] have extended this study on esters concluding for n-propyl formate and acetate that the proton transfer mechanism occurs at 77 K. Isobutyl formate and acetate exhibit spectra very similar to those given by t-butyl acetate. Some evidence exists for a solvent adduct being the initial product of γ-radiolysis of solutions of the formate.[25]

Neopentyl formate gave results indicative of the parent cation.[25] Hyperfine coupling is observed to three equivalent protons giving $A(^1H) = 33\,G$. The broad 4-line spectrum is assigned to the SOMO localised upon the alkyl group. The coupling arising to only 3 of 11 possible protons implying a SOMO similar to the σ cation attributed to neopentane[31] where only 3 of 12 possible protons are observed. Upon warming the spectrum collapsed into a 23 G triplet with marked aniso-tropy. At ca. 150 K the spectrum became 9 lines yielding 8 protons at 15 G, consistent with data obtained from the isobutene radical cation. This mode of breakdown, Sevilla et al. conclude, is typical of mass spectra interpretations for neopentyl esters.

REFERENCES

1. W. W. Nawar, _J. Agric. Food Chem._, 26, 21 (1978).

2. M. G. Simic, G. Merrit Jr. and I. A. Taub, _Fatty Acids_, Ed. E. H. Pryde, The American Oil Chemist Soc., Chapter 23 (1979).

3. R. L. Hudson and F. Williams, _J. Phys. Chem._, 82, 967 (1978).

4. Y. Nakajima, S. Sato and S. Shida, _Bull. Chem. Soc. Japan_, 42, 2132 (1969).

5. P. B. Ayscough and J. P. Oversby, _J. Chem. Soc., Faraday Trans. I_, 1153 (1972).

6. M. D. Sevilla, K. M. Morehouse and S. Swarts, _J. Phys. Chem._, 85, 923 (1981).

7. T. Kato and T. Shida, _Chem. Phys. Lett._, 68, 106 (1979).

8. M. C. R. Symons and I. G. Smith, _J. Chem. Res. (S)_, 382 (1979).

9. J. T. Wang and F. Williams, _J. Phys. Chem._, 84, 3156 (1980).

10. M. D. Sevilla, K. Plante and D. Becker, _J. Phys. Chem._, 87, 1648 (1983).

11. A. Hasegawa, J. Rideout, G. W. Eastland and M. C. R. Symons, _J. Chem. Res. (S)_, 258 (1983).

12. D. N. R. Rao, J. Rideout and M. C. R. Symons, _J. Chem. Soc., Perkin Trans. 2_, 1221 (1984).

13. D. Becker, M. D. Sevilla, C. L. Sevilla and S. Swarts, _J. Phys. Chem._, 88, 1701 (1984).

14. T. Clark, A. Hasegawa and M. C. R. Symons, _Chem. Phys. Lett._, in press.

15. Y. Ellinger, R. Subra, B. Levy, P. Millie and G. Berthier, _J. Chem. Phys._, 62, 10 (1975).

16. K. U. Ingold and J. C. Watson, _J.A.C.S._, 104, 616 (1982).

17. G. A. Russell in Radical Ions, Eds. E. J. Kaiser and L. Kevan, _Interscience NY_, pp.87-150 (1968).

18. M. Iwasaki, _J. Chem. Phys._, 77, 5891 (1982).

19. M. C. R. Symons, _Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy_, Van Nostrand Reinhold Co. Ltd., Wokingham/ Berkshire (1978).

20. F. Williams and E. D. Sprague, _Acc. Chem. Res._, 15, 408 (1982).

21. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, _Chem. Phys. Lett._, 105, 586 (1984).

22. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, _Chem. Phys. Lett._, 105, 592 (1984).

23. D. A. Forsyth, P. Lucas and R. M. Burk, _J.A.C.S._, 104, 240 (1982).

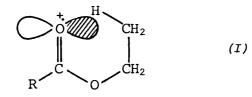24. V. J. Shiner, B. L. Murr and G. Heinemann, _J.A.C.S._, 85, 2413 (1963).

25. M. D. Sevilla, D. Becker, C. L. Sevilla, K. Plante and S. Swarts, Faraday Discuss. Chem. Soc. No. 78, pp.71 (1984).

26. M. D. Sevilla, D. Becker, C. L. Sevilla and S. Swarts, J. Phys. Chem., 89, 633 (1985).

27. A. L. J. Beckwith and C. B. Thomas, J. Chem. Soc., Perkin Trans. 2, 861 (1973).

28. M. J. Perkins and B. P. Roberts, J. Chem. Soc., Perkin Trans. 2, 77 (1975).

29. A. L. Beckwith and P. K. Tindal, J.A.C.S., 97, 7537 (1969).

30. S. Saebø, A. L. Beckwith and L. Radom, J.A.C.S., 106, 5119 (1984).

31. M. Iwasaki, K. Toriyama and K. Nunome, J.A.C.S., 103, 3591 (1981).

CHAPTER
4

Lactone Cations

INTRODUCTION

As can be seen in the previous Chapter concerning simple esters, the ester grouping fails to provide an ester-centred SOMO when irradiated in freon. The 'freon' method[1-4] is now commonly used for specific cation production. As an extension of this work, it was decided to use cyclic esters, or lactones, to try to prevent the proton transfer common to the esters.[5,6] This might be achieved by constraining the structure so as to hold the alkyl group away from the carbonyl oxygen, so preventing the formation of the favourable cyclic transition state as in I.

(I)

It is also of interest to see if any tendency occurs for the ring to open, or to form chloro adducts similar to that formed by methyl formate[7,8] at 77 K. It is first necessary to present the nomenclature of these cyclic compounds; α-lactones being 3-membered rings, β-lactones 4-membered rings, γ-lactones 5-membered rings, and so on.

Alpha Lactones

Unfortunately, due to the reactive nature of these compounds it proved impossible to include these in this study. α-Lactones polymerise spontaneously at 173 K[9] giving polyesters (Reaction II).

(II)

Beta lactones and larger ring sizes are perfectly stable under the conditions used here. Since the intramolecular H-atom transfer obtained for the ester cations is also found in their mass spectra,[10]

it seemed pertinent to investigate the proposed methods of breakdown for the lactones in their mass spectra. The common rearrangements[11] are to release alkyl groups as seen in III.

$$\left[R\overset{O}{\diagdown}\diagup\diagdown O \right]^{+\cdot} \longrightarrow {}^{+}\diagup\diagdown O + R^{\cdot} \qquad (III)$$

It is of interest to look for such alkyl radicals produced in the γ-radiolysis of the solutions of these lactones in CCl_3F. The results observed included ring opening solvent adduct formation and H-atom transfer, but we obtained no evidence for reaction III. It remains only to present each compound individually.

β Propiolactone

A quartet of lines of binomial intensities 1:3:3:1 were observed. Therefore, three equivalent protons of $A(^1H)$ = 22 G are implied. H-atom transfer is precluded from having occurred by this datum. However, more than one reasonable structure could be responsible for the results. When warmed to 150 K the spectrum changed reversibly to one comprising a triplet $[A(^1H) = 24$ G] assigned to two protons, with observable couplings to further protons which sum to 21 G. The central lines are notably broadened, the broadening being assigned to motional averaging, since upon recooling to 77 K the spectrum reverts to its original form. The specifically deuterated analogue (IV) was prepared by Swartz et al.[12] in an attempt to clarify the results. The results obtained at 77 K for γ-irradiated solutions of IV produced a proton hyperfine coupling of 22 G due to two protons.

Two possible ring-opened structures could be responsible for this spectrum and are shown in V. Structure A produced by cleaving the C–O bond produces the $R\overset{+}{C}O$ grouping which is isoelectronic with the highly

$$D_2C \text{———} O$$

(IV)

A $DO\overset{\bullet}{C}DCH_2CO^+$

B $\overset{\bullet}{C}H_2CD_2OCO^+$

(V)

stable RCN moiety. However, it requires two β-protons to be equivalent

at 22 G, which is unlikely for such a radical. Considerations of the

results for the protonated compound would lead to the expectation,

for A, of an 'alpha proton type' anisotropy occurring in the spectrum.

This is not obviously present. The structure B produces the $RO\overset{+}{C}O$ unit

isoelectronic with ROCN, again conferring a notable driving force for

the rearrangement. Radical B better explains all the results giving

expectations for four proton couplings with the two equivalent α-protons

producing 22 G, which is reasonable for an $R-\overset{\bullet}{C}H_2$ type radical.
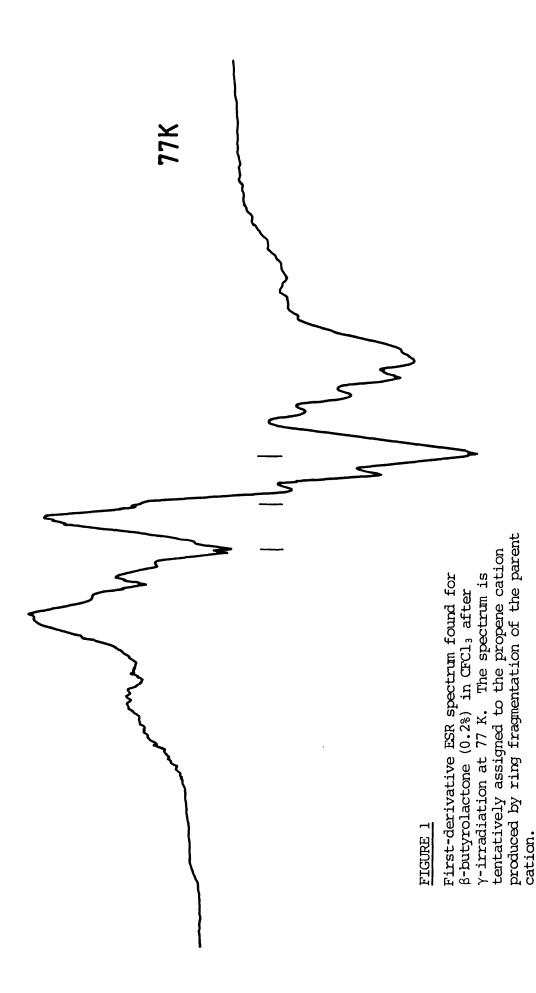
β Butyrolactone

The spectrum detected is seen in Figure 1(a), with observable hyper-

fine couplings at 77 K, of 24 G due to four equivalent protons. Two

inequivalent protons produce splittings of 9 G and 4 G. As for β-

propiolactone, the data are inconsistent with expectation for the proton

transfer radical. The most likely candidates are radicals VI, VII and

VIII.

$H\overset{+}{O}\overset{\bullet}{C}(CH_3)CH_2CO$ $\cdot CH_2CH(CH_3)O\overset{+}{C}O$ $CH_2\overset{+}{-}\overset{\bullet}{C}HCH_3$

(VI)   (VII)   (VIII)

Radical VII would not be expected to produce a major pentet arrangement.

However, the central three lines are more intense than predicted for

four equivalent protons and it is possible that a radical of the type

of VII makes some contribution. This requires that there be two break-

down mechanisms open to the unstable first-formed cation radical. The

77K

<u>FIGURE 1</u>

First-derivative ESR spectrum found for
β-butyrolactone (0.2%) in $CFCl_3$ after
γ-irradiation at 77 K. The spectrum is
tentatively assigned to the propene cation
produced by ring fragmentation of the parent
cation.

fine structure detected is due to two further protons. For structure

VI the $\overset{+}{O}H$ group proton must be responsible for the hyperfine coupling

of ca. 4 G. This is large but not impossible for such a proton.

However, alternative VIII should also be considered. Shiotani et al.[13]

has produced a set of data for the propene radical cation which is in

reasonable agreement with our observed data. The loss of a stable

molecule of carbon dioxide is the driving force for the rearrangement

IX.

$$\left[\begin{array}{c} \text{(structure with CH}_3\text{, O, O)} \end{array} \right]^{\bullet +} \longrightarrow CO_2 + \text{C}\overset{\bullet}{=}\text{C}\overset{+}{\diagup}\underset{CH_3}{\diagdown} \qquad (IX)$$

The tendency for these four-membered rings to open is evidently

far higher than the tendency toward the proton transfer favoured by

esters. Furthermore, the driving force must be great since solvent

adducts of the parent cations were not detected, despite their

prevalence in some cases. It is interesting to note that cyclobutan-

one[14,15] also ring opens, giving a $\overset{\bullet}{C}H_2$-R type radical whereas the higher

cyclic ketone cations retain their ring structures.

Similarly, in contrast to the β-lactone results, the spectra for

γ-butyrolactone, δ-valerolactone and ε-caprolactone recorded at 77 K,

were all dominated by features typical of solvent adducts.[7,8,16] Each

lactone cation exhibiting a major quartet (Table 1) due to the ^{35}Cl

parallel features. Figure 2 for γ-butyrolactone, is a typical example

of the spectra obtained. A good correlation is observed between increase

in ring size and the magnitude of the ^{35}Cl parallel hyperfine coupling.

This ties in well with the decreasing ionisation potential of the solute

molecules with increasing ring size. Ionisation potential is a factor

known to be important in adduct formation,[17] as described in Chapter 2

TABLE I

Structures and ESR Parameters for Lactone Radicals formed in Irradiated CFCl₃ Solutions

Parent	Complex Cation Parameters (77 K)	Suggested Major Decomposition Radical	
		Structure [a]	Hyperfine Couplings/Temp.
(structure) propiolactone	not formed	$\cdot CH_2CH_2OCO^+$	22 G (3H) 77 K 24 G (2H), 10.5 (2H, avg.) 148 K
(structure) propiolactone-d₂	not formed	$\cdot CH_2CD_2OCO^+$	22 G (2H), 3 G (D) 77 K
(structure) β-butyrolactone	not formed	$CH_2 \overset{+\cdot}{-} CHCH_3$	25 G (4H), 9 G (1H), 4 G (1H) 77 K
(structure) γ-butyrolactone	$A_{//}(^{35}Cl) = 73 \text{ G}$ [b] $\underline{g}_{//}(^{35}Cl) = 2.002$	(structure, OH^+)	42 G (2H), 22 G (1H) 145 K

TABLE I (Continued) ....

Parent	Complex Cation Parameters (77 K)	Suggested Major Decomposition Radical	
		Structure [a]	Hyperfine Couplings/Temp.
γ-valerolactone	?		21 G (4H), 40 G (1H) 77 K
δ-valerolactone	$A_{//}(^{35}Cl) = 72$ G $g_{//}(^{35}Cl) = 2.002$		22 G (1H), 4H (132G total – 32 G avg.) 145 K
ε-caprolactone	$A_{//}(^{35}Cl) = 62$ G $g_{//}(^{35}Cl) = 2.003$		44 G (1H), 21 G (2H) 145 K

a While the radical shown fits the observed data best, for several cases other possibilities exist which cannot be eliminated by our data. See the text for a discussion of these other species;

b For this case, the hyperfine structure due to Cl-37 was resolved and the splitting found (61 G) agrees with that expected from the gyromagnetic ratio.

FIGURE 2
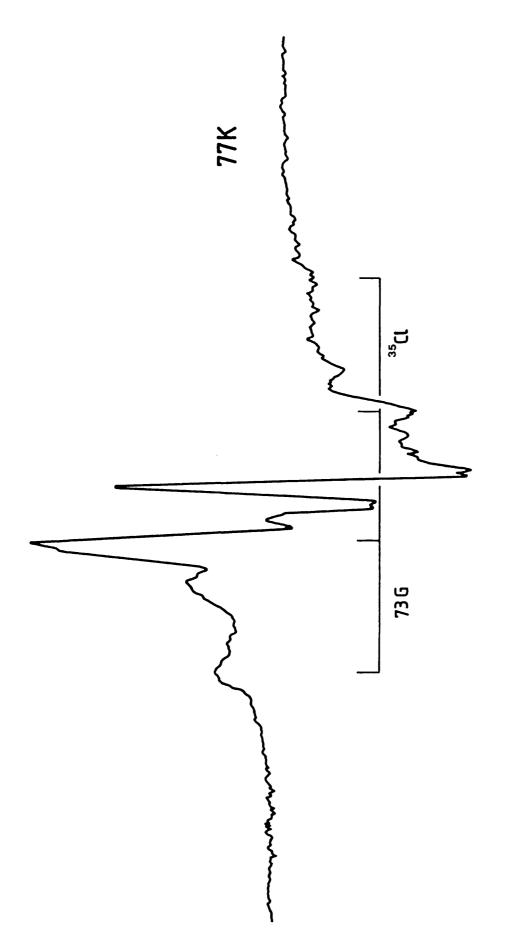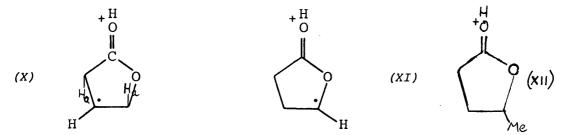
First-derivative ESR spectra found at 77 K after γ-irradiation of CFCl₃ solutions containing 0.2% γ-butyrolactone. The spectra clearly show a large coupling due to one ^{35}Cl nucleus and are considered excellent evidence for complex formation between the solvent and the lactone cation.

of this thesis.

Pulse annealing or photobleaching with visible light, of samples containing this adduct, causes the scission of the σ-bond. The free solute radicals then rearrange by various H-atom transfer mechanisms.

γ Butyrolactone

The spectrum in Figure 3 is assigned to radical X rather than XI. The large splitting of ca. 42 G is expected for the β-protons of the cyclic structure.

(X) (XI) (XII)
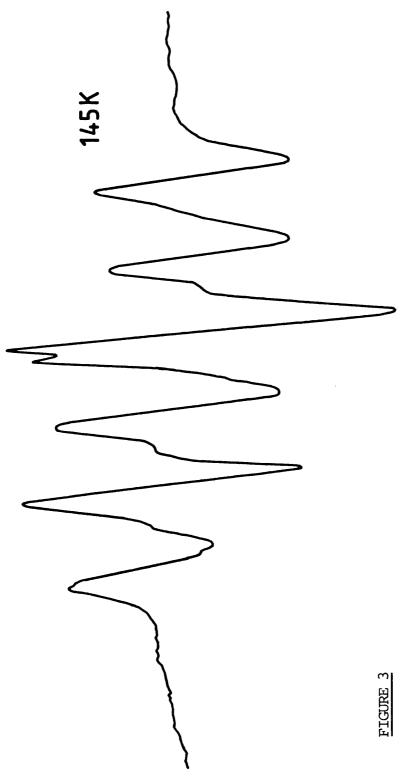
Radical X is preferred to radical XI because the alpha proton coupling of radical XI would be expected to be reduced to ca. 20 G because of delocalisation onto the ring oxygen. Since the alpha proton coupling observed is 22 G, structure X is more favourable.

The large β-proton couplings are probably due to the axial protons (H$_a$) in X . This leaves the other two β-protons with negligible couplings undetectable in the broad line spectra observed.

γ Valerolactone

At 77 K, the spectrum due to the ^{35}Cl adduct overlaps that attributed to the proton transfer radical. This prevents accurate analysis of the size of the ^{35}Cl parallel coupling. On treatment with visible light, the chlorine features were lost. The remaining features were analysed in terms of coupling to three equivalent protons (21 G) and two others giving couplings of 40 G and 21 G. These results suggest radical XII.

The alternative ring-opened structure (XIII) is expected to produce

145K

FIGURE 3

First-derivative ESR spectra found after
thermal decomposition of the complex cation
of γ-butyrolactone in Fig. 2 by annealing to
the temperatures shown in the Figure.
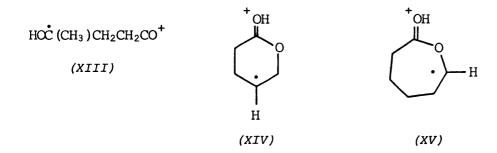
β-proton couplings much smaller than the couplings observed, and comparable with those for the propiolactone 'ring open' radicals reported earlier (24 G).

δ Valerolactone

The spectra for δ-valerolactone were akin to those of alkyl radicals[18] giving large β-proton couplings. Hence we again postulate intramolecular H-atom transfer. The β-proton couplings are ill-defined but sum to $\sum_{\beta H} = 132\,G$ which gives an _average_ of 34 G, which is reasonable for radical XIV. The remaining 22 G splitting is assigned to the single α-proton of this radical.

ε Caprolactone

ε-Caprolactone provides an interesting contrast to the δ-valerolactone, since in this case the transferred hydrogen atom probably comes from the methylene group adjacent to the ring oxygen (XV). This assignment is based on the reduced α-proton coupling and the slightly smaller β-proton couplings (Table 1).

$$HO\overset{\bullet}{C}(CH_3)CH_2CH_2CO^+$$

(XIII)

(XIV)

_(XV)_

In order to be more certain of these assignments, it would be necessary to perform careful specific deuterations at various sites in each case. The enormous expense and time-consuming nature of the preparative work needed, ruled out this approach.

It would perhaps be of interest to ensure that γ or δ-protons are not responsible for some of the observed hyperfine interactions. Large

splittings for such remote protons have been observed for radical cations. For example, a splitting of 27.5 G was assigned to the δ-protons of the cyclohexanone cation.[19] This large coupling implies a specific molecular stereochemistry often referred to as the "W plan structure".[15,20-22] These conformations are less likely with the lactones since they do not adopt the 'chair' geometry adopted by cyclohexanone.

Sevilla and coworkers[12] have performed some geometry optimized molecular orbital calculations in order to find the minimum energy geometries of the lactone radical cations. The results obtained imply that the carbonyl carbon - ring oxygen bond shortens and hence strengthens upon electron loss. For β-propiolactone, this favours radical V(B) in accord with our conclusions. Similarly, ring-opening for other β-lactones is favoured. The spin-densities are calculated to be largely localised on the 'non-bonding' oxygen p-orbitals of the parent cations. This promotes the formation of a σ ^{35}Cl adduct.[17] Since this is not detected, it is reasonable to suggest the cations must have rearranged.

It is interesting to note the fact that larger ring lactones form Cl-adducts primarily, before resorting to proton transfer rearrangements at higher temperatures.

Compare this with the proton transfer that occurs for many esters at 77 K. Especially, perhaps, the case of ethyl formate[6] which produces the Cl-adduct at 4 K and the proton transfer radical upon warming to 77 K. The prevention, in the lactones, of the formation of structure I seems to increase the stability of the adducts.

For the lower lactones, it appears the overriding emphasis is based upon the necessity to release the ring strain. This is reflected in the immediate appearance at 77 K of the ring-opened structure.

I conclude that the facile hydrogen atom transfer exhibited by normal esters is indeed inhibited in the lactones. Nevertheless, parent cations are still not detected. For the β-lactones, ring-strain promotes ring-opening, whilst for the larger ring lactones the cations are initially stabilised by complex formation with solvent, but hydrogen-atom transfer does eventually occur at higher temperatures.

REFERENCES

1. T. Shida and T. Kato, Chem. Phys. Lett., 68, 106 (1979).

2. M. C. R. Symons and I. G. Smith, J. Chem. Res. (S), 382 (1979).

3. J. T. Wang and F. Williams, J. Phys. Chem., 84, 3156 (1980).

4. K. Toriyama, K. Nunome and M. Iwasaki, J. Phys. Chem., 85, 2149 (1981).

5. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, Chem. Phys. Lett., 105, 586 (1984).

6. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, Chem. Phys. Lett., 105, 592 (1984).

7. D. Becker, K. Plante, M. D. Sevilla, J. Phys. Chem., 87, 1648 (1983).

8. G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons and A. Hasegawa, J. Chem. Res. (S), 258 (1983).

9. Sutherland, Vol. 2, pp.907 in Comprehensive Organic Chemistry, Barton and Ollis.

10. F. W. McLafferty, Anal. Chem., 31, 82 (1959).

11. Sutherland, Vol. 2, pp.907 in Comprehensive Organic Chemistry, Barton and Ollis.

12. M. D. Sevilla, S. Swarts, J. Rideout and M. C. R. Symons, J. Phys. Chem., 1985, submitted.

13. M. Shiotani, V. Nagata and J. Sohma, J. Phys. Chem., 88, 4078 (1984).

14. L. D. Snow and F. Williams, J. Chem. Soc., Chem. Comm., 1090 (1983).

15. P. J. Boon, M. C. R. Symons, K. Ushida and T. Shida, J. Chem. Soc., Perkin Trans. 2, 1213 (1984).

16. J. Rideout and M. C. R. Symons, J. Chem. Res. (S), 268 (1984).

17. T. Clark, A. Hasegawa and M. C. R. Symons, Chem. Phys. Lett., in press (1985).

18. a) B. W. Wren and M. C. R. Symons, unpublished results;
    b) T. Claxton, J. Rideout and M. C. R. Symons, in press (1985).

19. L. D. Snow and F. Williams, Faraday Disc. Chem. Soc., 78, 1 (1984).

20. G. A. Russel in Radical Ions (ed. E. T. Kaiser and L. Kevan), New York, p.87 (1968).

21. Y. Ellinger, A. Rassat, R. Subra and G. Berthier, J.A.C.S., 90, 1499 (1968).

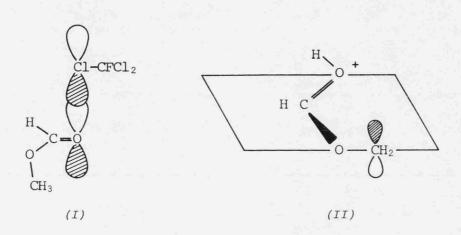22. K. U. Ingold and J. C. Walton, J.A.C.S., 104, 616 (1982).
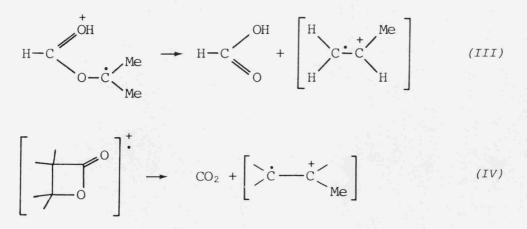
CHAPTER
5

Di-ester Cations

INTRODUCTION

Despite an extensive amount of work being done by various groups of workers,[1-4] the ester functional grouping has proven particularly reluctant to provide any information about its parent radical cation. It prefers to undergo various deformations or rearrangements, for example, methyl formate forms a σ bond to a single chlorine atom forming a ^{35}Cl adduct (I).[5,6] Otherwise, simple rearrangements occur, such as hydrogen transfers,[3,4] giving radicals such as II.

(I)   (II)

Even when constraints are imposed as in the lactones,[7] similar rearrangements can occur. The simple mono esters and the lactones may alternatively lose a stable molecule rearranging to a more stable radical cation (III and IV).

(III)

(IV)

The only case, to date, of an ester which upon electron loss does not

rearrange, nor form a solvent adduct at 77 K, is neopentyl formate studied by Sevilla.[4] Even this example, though, does not have its SOMO centred within the ester grouping, preferring instead to localise its SOMO mainly to the alkyl grouping. It was this observation which led to the study of the diesters. We concluded that to form an unrearranged ester centred SOMO, it is necessary to reduce the localised electron density. Preferably without any alteration of the nature of the SOMO observed as encountered with neopentyl formate.

The esters studied were oxalic acid dimethyl esters working through to higher dimethyl esters, extending to the similar diethyl esters.

Dimethyl Esters
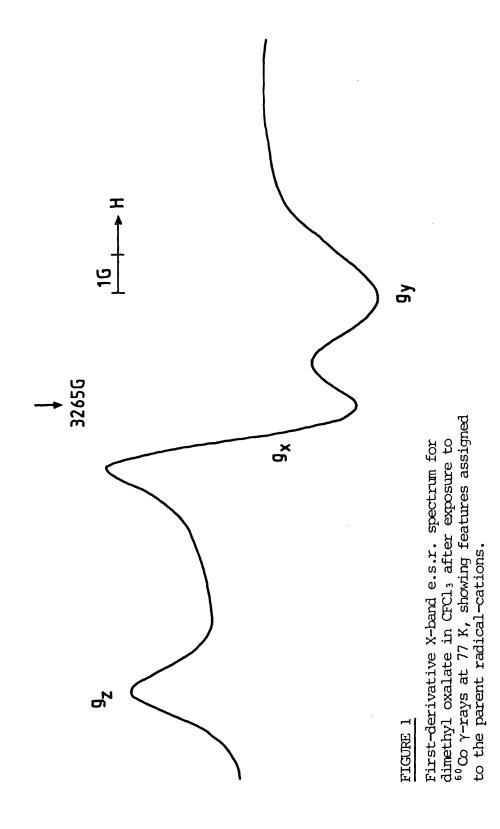
The dimethyl esters gave simple e.s.r. spectra which were readily interpretable.

Dimethyl Oxalate
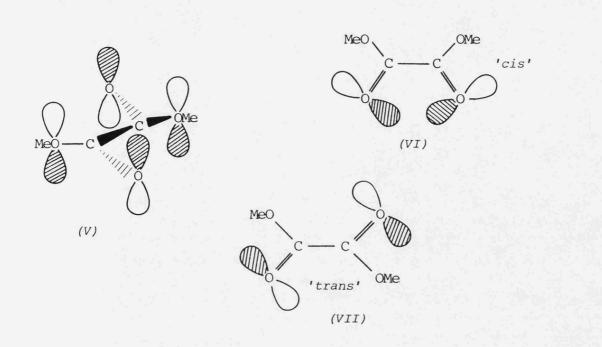
The spectrum obtained at 77 K (Figure 1), is analysed as being a narrow single feature with considerable g-tensor anisotropy. The positive g-shift, implying coupling to a filled orbital energy level.[8] There are clearly no features due to solvent adduct formation. Nor are there any due to the $\overset{\bullet}{C}H_2$-O type radical expected to be formed by proton transfer. The singlet having clear g_x, g_y and g_z features, is assigned to the parent cation of the ester. This implies a considerably stabilised SOMO in comparison to those of simple mono esters and lactones. Three possible molecular structures are available for the cation. The π-type SOMO (V) with the two others being variations (VI and VII) of the in-plane non-bonding orbitals mostly confined to the carbonyl oxygen atoms.

The π-type cation (V), would be expected to have considerable electron

FIGURE 1

First-derivative X-band e.s.r. spectrum for dimethyl oxalate in CFCl₃ after exposure to ⁶⁰Co γ-rays at 77 K, showing features assigned to the parent radical-cations.

(V)

(VI)

(VII)

density on the methoxy oxygen atoms.[3] It would seem reasonable to have expected a significant proton hyperfine coupling to the methyl protons, given this π-type structure. Since no hyperfine splitting is observed, the π-cation option appears less likely.
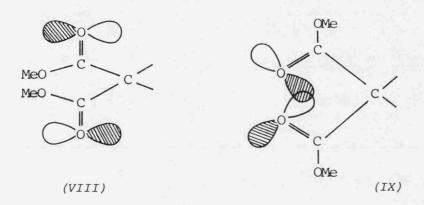
The parent cation is believed to be of the $n_{(C=O)}$ type similar to that observed for aldehydes[9] and ketones.[10] The two structures VI and VII offer the option of a 'cis' or 'trans' conformation. The parent molecule is known to prefer the trans conformation[11] and it is this fact, along with the failure of this cation to produce any visible absorption bands, that lead to structure VII being favoured as the most likely structure for the dimethyl oxalate cation.

Dimethyl Malonate

Samples containing dimethyl malonate, upon irradiation with γ-rays, produced an intense purple colouration. This was readily bleached by visible light.

The e.s.r. signal produced, before visible photolysis, is again a singlet exhibiting a positive g-shift and considerable g-anisotropy.

These results are again attributed to the parent cation of the ester. The π cation is excluded as before, with no proton hyperfine coupling being observed. As before, the two in-plane $\underline{n}(0)$ orbitals are expected to comprise the SOMO. Structures VIII and IX are possible, the 'cis' structure being favoured, because there should be weak but significant bonding, as indicated. This provides an explanation for the intense violet colour, which we assign to the allowed $\sigma_1^2 \sigma_2^1 \rightarrow \sigma_1^1 \sigma_2^2$ transition. The smaller $\underline{g}$-anisotropy observed further supports the 'bonding' scheme suggested for the malonate.

(VIII)   (IX)

Dimethyl Succinate Cations

A strong colouration is observed, as with the dimethyl malonate cations implying a structure analogous to that already suggested. Unlike the malonate cation, the e.s.r. spectrum observed for the succinate exhibits a weak interaction with two equivalent protons, the hyperfine splitting being about 5.5 G for each. The dimethyl d_6 derivative was prepared to ensure that the source of the splitting was not the methyl groups. The narrower lines did produce a structure unseen in the fully protonated compound, which is assigned to a $\underline{g}$-anisotropy effect (Figure 2).

The implication of this is that the six methyl group protons contribute to the line-width and only have very small hyperfine interactions.
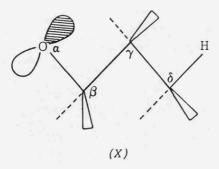
a) 2·5G ⟶ H

3235G

+1 0 -1

b) 2·5G ⟶ H

FIGURE 2
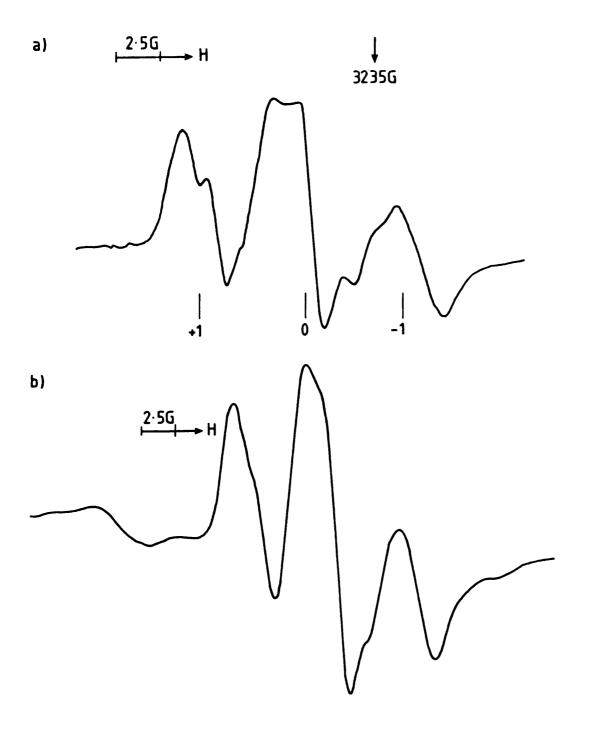
First-derivative X-band e.s.r. spectra for (a) dimethyl succinate ($^2H_6$) and (b) dimethyl succinate ($^1H_6$) in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K. [Spectrum (a) showing features assigned to the parent radical-cations.]

This is seen as further evidence pointing toward the oxygen-oxygen σ-bonded structure proposed, in favour of the π-type cation.

In the cases of the malonate and the succinate, upon thermal annealing, the formation of a triplet spectrum typical of a $\overset{\bullet}{C}H_2O$-R type radical is seen. This is proposed to have come from the proton transfer mechanism common to small mono esters.[3] It seems that the σ bonding interaction stabilises the parent cation with respect to proton transfer, as with the higher lactones.[7] However, the delocalised structure disfavours solvent adduct formation, whilst not finding the necessity to form the solvent adducts seen for them at 77 K.

The absence of any proton hyperfine coupling to the $-CH_2-$ protons of the malonate cation is in good agreement with the results for aldehyde[9] and ketone[10] cations. The methyl proton coupling in the acetone cation was found by ENDOR spectroscopy to be very small.[12] More remote protons in aldehydes and ketones, especially ring structures, are found to exhibit detectable hyperfine couplings, the size of the coupling observed being very dependent upon stereochemistry. The maximum coupling is found for the 'W plan' stereochemistry proposed by Williams[13] for the cyclohexane radical cations (X). The hyperfine splitting of 27.5 G is assigned to the two δ-protons lying close to the plane of the radical.

(X)

For the succinate cation the smaller coupling (5.5 G), is attributed to the delocalisation of the electron through the two carbonyl oxygen

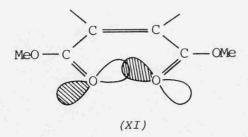atoms. The proximity of the protons to the radical plane may also not
be so favourable.

Visible photolysis of samples exhibiting a colour upon γ-irradiation,
causes a very rapid bleaching to occur along with a simultaneous loss
of the e.s.r. features. A concomitant growth of the anisotropic triplet
due to the $\dot{C}H_2$-O-R type species occurs. This may imply an easier path
to the proton transfer products for photolytically excited states of
the cation.

Dimethyl Maleate and Fumarate

These esters were chosen to investigate the effect of introducing a
π manifold into the backbone of the molecule. We expected this to
encourage the cation to become π rather than n(0). If this did not
occur, the extra rigidity in the olefinic bond would enforce either
cis or trans conformations and so aid in proving the hypothesis of the
'cis' and 'trans' structures suggested for the simple dimethyl ester
cations.

The spectra observed for maleate cations are very similar to those
found with succinate cations except that the observed hyperfine coupling
is 7 G, as shown in Figure 3. The sample is again purple implying
Structure XI which is very similar to that suggested for the malonate.

(XI)

The observed coupling is assigned to the two alkene protons, implying
that they are closer to the radical plane. However, the coupling is
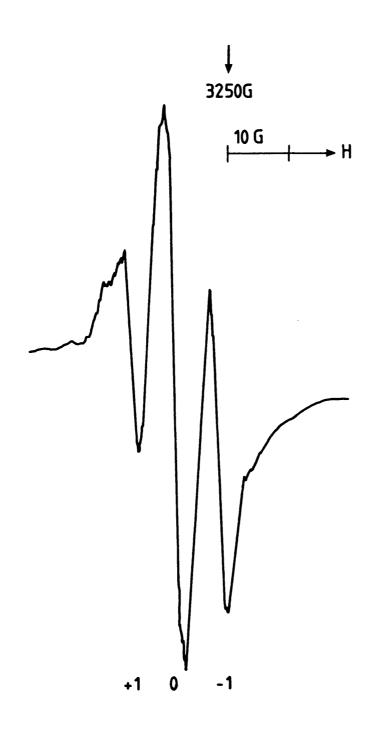still small, presumably because of the delocalisation caused by the σ

-70-

3250G

10 G H

+1   0   -1

FIGURE 3

First-derivative X-band e.s.r. spectrum for dimethyl maleate in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K.

bonding interaction, assisted by the electron withdrawing effect of the methoxy groups.

The results obtained for the dimethyl maleate cations are comparable to the isostructural unmethylated anions (XII) studied by Iwasaki.[14] This work was performed using single crystals of potassium hydrogen maleate.

$$H \quad \diagdown C = C \diagup \quad H$$

(structure XII)   (XII)

It was concluded that the radical with two in-plane oxygen 2p orbitals was the primary product. However, when these crystals were irradiated at room temperature, the radical formed is thought to be π-type, but it was concluded that they were not derived from the original σ-type radical. In further support of the cation work, Iwasaki also suggested considerable oxygen-oxygen σ-bonding. A visible light sensitivity was observed for Iwasaki's σ-radical, as with ours, implying a transition in the visible region, though no reference is made to sample colouration. The observed g-shift (g_{max} = 2.0079) is slightly larger than that found with the cations where g_{max} = 2.007.
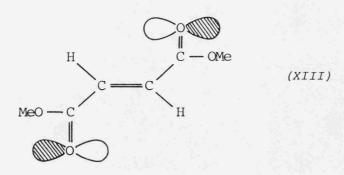
The proton hyperfine coupling observed by Iwasaki is $5\,G \pm 1\,G$ and is only marginally smaller than observed for the radical-cation.[16] Thus the structures for these species must be very similar.

Overall, the variations occurring between the cation work and that of Iwasaki are negligible and readily explained in terms of the systems' differences rather than differences between the species formed.

In direct contrast with the cis olefinic ester, the trans form (fumarate), produced an uncoloured sample upon irradiation. The e.s.r. spectra were typical of a proton transfer species $\overset{\bullet}{C}H_2$-OR, with an aniso-

tropic triplet spectrum with $A(^1H) = 22G$. It appears, as in XIII, that the delocalisation occurring for the maleate is prevented from occurring for the fumarate and that this leads to a more reactive cation.
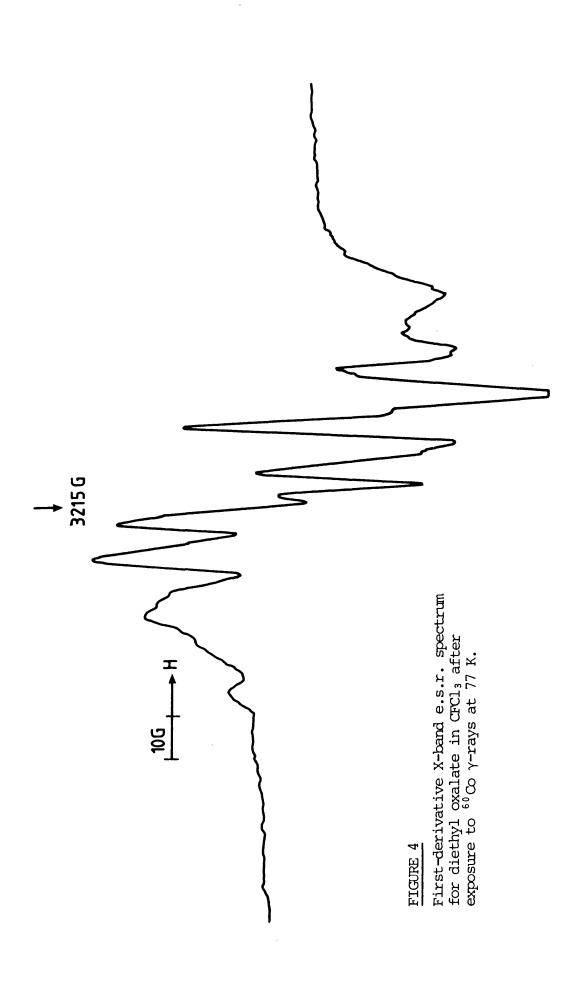

(XIII)

Diethyl Esters

Whereas the dimethyl esters provided simple, easily interpreted spectra with relatively clear-cut analyses, the diethyl derivatives did not, producing extremely complex spectra possibly exhibiting more than a single radical species with each.

Diethyl Oxalate

Figure 4 is an example of the spectra produced by this diethyl ester, with a multitude of features appearing, obviously due to extensive proton hyperfine coupling, which have evaded all attempts at analysis. It is considered that these spectra comprise more than one radical species. The parent cation might have been expected to exhibit very similar spectra to those found for dimethyl oxalate, with negligible hyperfine splittings.

The spectra produced on annealing are much simpler, with $A(^1H) = 22G$ for two protons and $A(^1H) = 11G$ for two more. The resemblance between this and the high temperature spectrum found with ethyl acetate[1,2] is remarkable, and so the spectrum is assigned to the $\dot{C}H_2-CH_2OR$ type species. It is possible the original spectra observed at 77 K comprise a mixture of this, $R-O-\dot{C}HCH_3$ and some parent cation.

3215 G

10G

H

FIGURE 4

First-derivative X-band e.s.r. spectrum for diethyl oxalate in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K.

Di-ethyl Malonate

Complex spectra are once again observed, however, the presence of a more intense central signal may imply a parent cation in a more dominant amount.

Higher temperature spectra, common to the $\overset{\bullet}{C}H_2CH_2$-OR spectra, are again observed in abundance.

Diethyl Succinate

A much simpler spectrum was observed with the main features being a 5 G triplet with a noticeable positive g-shift to g = 2.0049 implying the presence of a diethyl ester parent cation. There is also another, unidentified, species at 77 K which is poorly defined. Proton transfer occurs on warming providing typical features, but with other products causing a messy spectrum.

To produce more useful data on the diethyl esters, it would be necessary to use liquid helium and to use methyl-ethyl substituted analogues and various deutero-substituted esters. Due to the expense involved and the time-consuming nature of the preparatory work, these studies were unable to progress any further.

CONCLUSION

Unrearranged ester cations have been produced. Dimethyl ester cations in particular have delocalised structures thereby inhibiting intramolecular hydrogen transfer. The fact that the SOMO's are formed from the $n_{(C=O)}$ orbitals of the carbonyl oxygens, is perhaps further proof that the initial cation of the simple esters have an $n_{(C=O)}$ SOMO and not π as previously suggested.[1-3] This is in agreement with the results of photoelectron spectroscopy obtained for esters.[19]

TABLE

E.s.r. Parameters for some Radical Cations of Diesters

Dimethyl Ester Cation	^{1}H Hyperfine Coupling (G) [a]	g-Values		
		$\underline{x}$	$\underline{y}$	$\underline{z}$
Oxalate		2.0090	2.0046	2.0023
Malonate [b]		2.0045	2.0026	2.0022
Succinate [b]	5.5 (2H)	2.0043	2.0025	2.0022
Maleate	7.0 (2H)	2.0060		2.0030
Fumarate [c]	ca. 19 (2H)		ca. 2.0030	

[a] 1 G = 10^{-4} T;

[b] Rearranged to give $H_2\dot{C}OR$-type radical at ca. 140 K;

[c] Only the rearranged radical, $H_2\dot{C}OR$, detected at 77 K.

REFERENCES

1. D. N. R. Rao, J. Rideout and M. C. R. Symons, J. Chem. Soc.,
   Perkin Trans. II,

2. M. D. Sevilla, D. Becker, C. L. Sevilla and S. Swarts, J. Phys.
   Chem., 88, 1701 (1984).

3. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, Chem. Phys. Lett.,
   105, 586 (1984).

4. D. Becker, K. Plante, M. D. Sevilla, C. L. Sevilla and S. Swarts,
   Faraday Disc. Chem. Soc., 78 (1984).

5. G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons and
   A. Hasegawa, J. Chem. Research (S), 258 (1983).

6. D. Becker, K. Plante and M. D. Sevilla, J. Phys. Chem., 87, 1648
   (1983).

7. M. D. Sevilla, S. Swarts, J. Rideout and M. C. R. Symons, J. Phys.
   Chem., submitted (1985).

8. M. C. R. Symons, Chemical and Biochemical Aspects of Electron
   Spin Resonance Spectroscopy, Van Nostrand Reinhold Co. Ltd.,
   Wokingham/Berkshire, Chapter 2 (1978).

9. P. J. Boon, M. C. R. Symons, K. Ushida and T. Shida, J. Chem.
   Soc., Perkin Trans. 2, 1213 (1984).

10. L. D. Snow and F. Williams, Faraday Disc. Chem. Soc., 78/1 (1984).

11. 'Tables of Interatomic Distances and Configurations in
    Molecules and Ions', special publication No. 11 (The Chemical
    Society, London 1958) (1965).

12. P. J. Boon, L. Harris, M. Olm, J. L. Wyatt and M. C. R. Symons,
    Chem. Phys. Lett., 106, 408 (1984).

13. L. D. Snow and F. Williams, J. Chem. Soc., Chem. Commun., 1090
    (1983).

14. K. Toriyama, M. Iwasaki, S. Noda and B. Eda, J.A.C.S., 93, 6415
    (1971).

15. K. Toriyama and M. Iwasaki, J. Chem. Phys., 55, 2181 (1970).

16. M. C. R. Symons and J. Rideout, in press (1985).

17. F. W. McLafferty, Anal. Chem., 31, 82 (1959).

18. M. C. R. Symons and J. Rideout, J. Chem. Soc., Perkin Trans. 2,
    in press (1985).

19. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata,
    'Handbook of HeI Photoelectron Spectra of Fundamental Molecules',
    Japan Sci. Soc. Press, 94, 5592 (1972).

CHAPTER
6

Carboxylic Acid Cations

INTRODUCTION

The radiolysis, in freon matrices, of compounds containing most functional groupings has been performed.[1] A variety of molecules containing carbonyl oxygen have been studied. Aldehydes[2] and ketones[3] providing interesting studies and a whole host of esters providing controversial analyses (see Chapter 3).[4-7] The cations of carboxylic acids have not previously been detected by e.s.r. techniques, despite a great deal of work. Various techniques have been used, including γ-irradiation of pure materials[8] and of glassy solutions.[9]

Radiolysis of the pure materials at 77 K is expected to give electron-gain and -loss products. The electron-gain products are often labelled as the 'parent anions', it is more likely that the paramagnetic species observed is of the type shown in Insert I. This species is produced from protonation of the parent anion.[8]
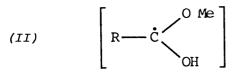
$$(I) \qquad \left[R - \overset{\cdot}{C} \diagup_{\diagdown OH}^{OH} \right]$$

The electron-loss centres provide no species which can unambiguously be identified as the 'parent cation'. The breakdown products (R· from RCO_2H^+) have been observed in the case of CD_3CO_2H, $EtCO_2H$ and higher homologues.[9] Strangely, ·CH_3 radicals were not found in irradiated acetic acid. It is claimed only the 'parent anions' are observed.[9] The implications of this are that methyl radicals react selectively with themselves. Or that they react with CH_3CO_2H, giving an unobserved radical. It is a final possibility that methyl radicals react giving a radical species which gives a spectrum very similar to that of the electron capture product.

The first two possibilities are insupportable. The third is possible

should the methyl group add preferentially to the carbonyl oxygen atom to give II.

(II)

$$\left[R\!-\!\overset{\bullet}{C}\overset{\displaystyle O\ Me}{\underset{\displaystyle OH}{\diagdown}} \right]$$
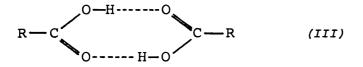
These radicals might exhibit features almost indistinguishable from those attributable to radical I.

Radiolysis of formic acid apparently gives two primary radicals, one is clearly the electron-gain centre $H\overset{\bullet}{C}(OH)_2$.[9] The other exhibits a small proton coupling of $\underline{ca.}$ 12 G, possibly due to $O\overset{\bullet}{C}OH$ radicals.

$(RCO_2H)_2$:   R = alkyl

It is well known that carboxylic acids are associated in condensed phases and frequently in the gas phase.[10,11] They preferentially form complex dimers (III) in inert solvents such as $CFCl_3$. No tendency to dissociate is shown at low temperatures.

Hence the results obtained are for the effects of γ-irradiation upon these dimers.

$$R\!-\!C\overset{\displaystyle O\!-\!H\cdots\cdots O}{\underset{\displaystyle O\cdots\cdots H\!-\!O}{\diagup\diagdown}}C\!-\!R \qquad (III)$$

The results obtained are shown in Table 1. As a whole they are not particularly exciting, producing mainly alkyl radicals from the proposed method of breakdown, shown in Eqn. I.

$$R\!-\!C\overset{O\!-\!H\cdots\cdots O}{\underset{O\cdots\cdots H\!-\!O}{\diagup\diagdown}}C\!-\!R \;\longrightarrow\; R\cdot \;+\; \overset{O}{\underset{O}{\overset{\|}{C}\;}}\!\!\!\!{}_{\|} \;+\; \overset{H\!-\!O}{\underset{H\!-\!O}{+\;\diagdown\diagup}}C\!-\!R \qquad \ldots\ldots\ [1]$$

The existence of dimers in solution is also known to occur for alcohols in freon[12] which prefer to breakdown as in Eqn. 2.

$$R \!-\! \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \!-\! O \overset{H}{\underset{H}{\diagdown\!\!\diagup}} O \!-\! \underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}} \!-\! R \quad \xrightarrow{(-e^-)} \quad R_2\overset{\bullet}{C}OH \;+\; R_2CHOH_2{}^+ \qquad \ldots . [2]$$

[HCO₂H]₂

In contrast to the higher homologues, no hydrogen atoms were detected upon irradiation. The e.s.r. features comprised an asymmetric doublet shown in Fig. 1. The singlet feature (β) is always present but is probably due to another species. The hyperfine splittings are shown in Table 2, along with the g-values. In order to ascertain which of the protons was responsible for the doublet observed, [HCO₂D] was prepared and its dimers studied. Only a slight narrowing of the main features was observed. Also, perdeutero formic acid was obtained [DCO₂D]. The features found are shown in Fig. 2, proving that it is one of the C–H protons of the dimer which causes the splitting. Extensive g-value variation causes the asymmetry observed (Table 2). The central 'singlet' grew with loss of the doublet upon annealing. This proved to be a poorly defined triplet for (HCO₂H)₂ and a narrow singlet for (DCO₂D)₂.

DISCUSSION

There are several possibilities for the identity of the doublet species. Since at no point were hydrogen atoms detected, a probable species is IV.

$$(IV) \qquad H \!-\! \overset{\bullet}{C} \overset{\textstyle\diagup O}{\underset{\textstyle\diagdown O}{}}$$

Which is formed as in Eqn. 3.

TABLE 1

Acid Dimers Irradiated at 77 K as Dilute Solutions in $CFCl_3$
and the Radicals Identified

Acid	Radical Formed
$(CH_3CO_2H)_2$	$\overset{\bullet}{C}H_3$
$(CH_3CH_2CO_2H)_2$	$CH_3\overset{\bullet}{C}H_2$
$(CH_3CH_2CH_2CO_2H)_2$	$CH_3CH_2\overset{\bullet}{C}H_2$
$[(CH_3)_3-C-CO_2H]_2$	$(CH_3)\overset{\bullet}{C}$
$(CF_3CO_2H)_2$	$CF_3\bullet$

TABLE 2

The Spectral Parameters obtained from the proposed Cation
Radicals of Formic and Per-deutero Formic Acids

	Proposed Radicals Formed	Proton Hyperfine Coupling			g-values		
		A_x	A_y	A_z	g_x	g_y	g_z
$(HCO_2H)_2$	$HCO_2H^{\ddagger}$	88	87	92	2.016	2.007	2.003
(DCO_2D)	$DCO_2D\bullet^+$	13.5	13.5	14.6			

FIGURE 1
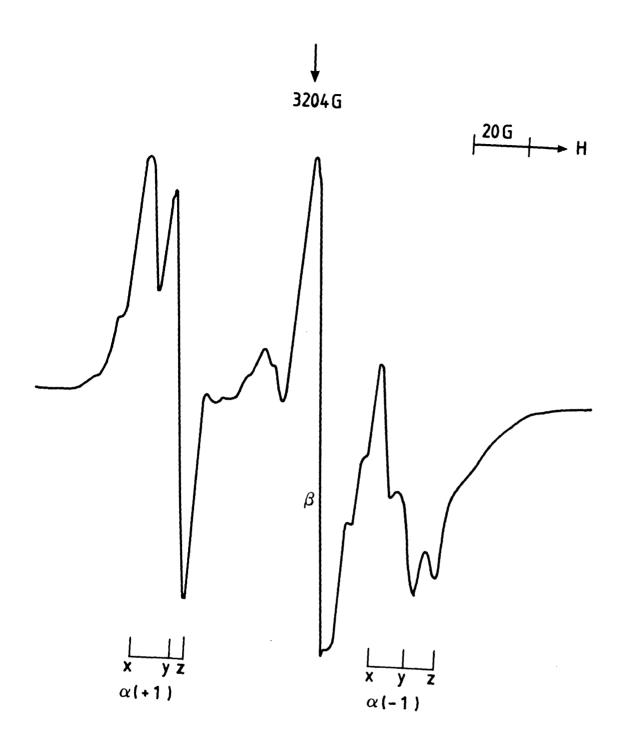
First-derivative ESR spectrum for the formic acid dimer in dilute solution in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[HCO_2H] \cdot^+$ cations (α).

FIGURE 2
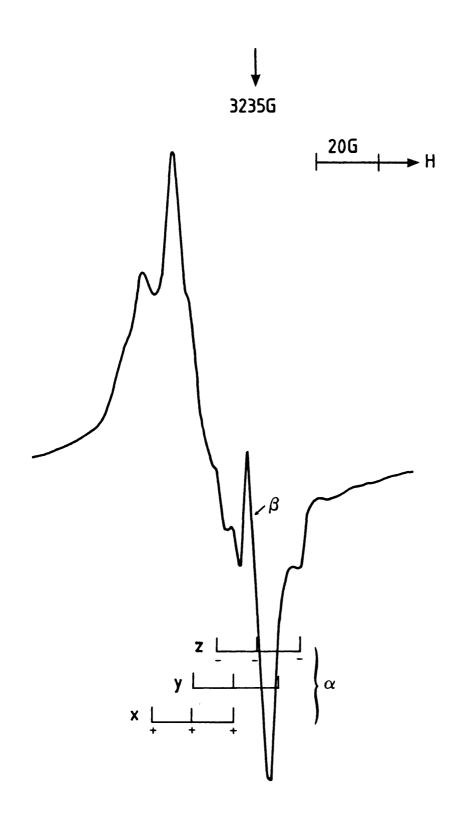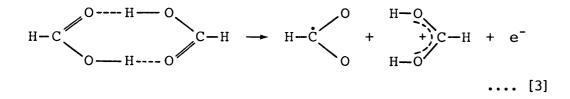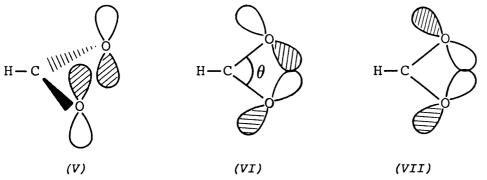
First-derivative ESR spectrum for per-deutero formic acid dimer in dilute solution in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[DCO_2D]^{\cdot+}$ cations (α).

$$
\text{H-C}\begin{array}{c}\text{O}\cdots\text{H}\text{---}\text{O}\\[2pt]\text{O}\text{---}\text{H}\cdots\text{O}\end{array}\text{C-H} \longrightarrow \text{H-}\dot{\text{C}}\begin{array}{c}\text{O}\\[2pt]\text{O}\end{array} + \begin{array}{c}\text{H-O}\\[2pt]\text{H-O}\end{array}\overset{+}{\text{C}}\text{-H} + e^-
$$

$$\dots \quad [3]$$
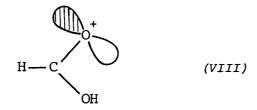
The SOMO for (IV) is largely confined to the two oxygen atoms. There is a variety of possible combinations of 2p-orbitals, each with comparable energy. A clear selection between them (V, VI and VII) is not obvious.

(V) *(VI)* *(VII)*

Calculations performed by Claxton[13] suggest that the ground state is π-type (V) for all reasonable values of the $O\text{-}\hat{C}\text{-}O$ angle. The energy minimum is approached when θ is close to 120°. However, the isotropic ^1H coupling was found to be about 10 G and independent of θ. Little difference was found when one of the two oxygen atoms was treated as forming a double bond to C and the other a single bond. This situation is possible if selective environmental interactions were occurring. The radical $H\dot{C}O_2$ is therefore only a candidate for the central species. However, other radicals of the type $R\dot{C}O_2$ have a greater g-value variation[14] than that observed for the central species.

An alternative candidate for the doublet species is the $n_o(C=O)$ structure VIII for the parent cation. This is the type of structure expected for the cations of esters and organic acids as judged by photoelectron spectroscopy.[9]

(VIII)

It is certain that aldehyde cations are of this type, producing an isotropic splitting of ca. 140 G^2 from the aldehydic proton. The ester cations have been discussed in Chapters 3, 4 and 5 of this thesis. It is concluded that the H-C proton of methyl formate cations has a much reduced coupling because of extensive bonding of the molecule to a solvent chlorine.[15,16] Other simple esters choose other methods of rearrangement, so precluding the drawing of any comparisons.
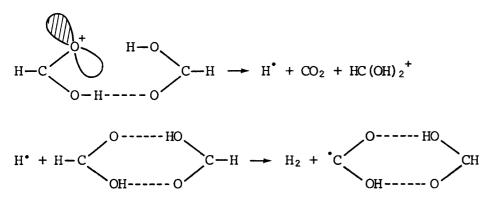
A large proton coupling constant is only expected if the unpaired electron is in an orbital of σ symmetry. Calculations performed by Claxton[13] predict that, if θ < 120, the SOMO should have σ symmetry. This falls well below the energy of the corresponding π-orbital. Problems were encountered with calculations where θ > 120 but it is most unlikely that the σ and π levels should invert for any reasonable value of θ.

The proton coupling is believed to come from electron donation from the C-H σ-bonding orbital to oxygen. Replacing the alkyl group of the aldehyde with the OH of the acid is expected to reduce this donation and, hence, the hyperfine coupling. Therefore, the observed value of about 90 G seems reasonable for the $(HCO_2H)^+$ cation. The separation in energy between the $n_O(C=O)$ and filled π levels is expected to be small. Consequently, for a field applied parallel to the C-O bond direction, a considerable positive g-shift is expected, as observed experimentally.

We consider that from this evidence the doublet species is due to the parent cation $HCO_2H \cdot^+$.

A broad feature obtained upon annealing may be $\cdot CO_2^-$. Formed as

Eqn. 4.

$$H-C \underset{O-H-----O}{\overset{\overset{+}{O}}{<}} \quad \overset{H-O}{\underset{}{>}} C-H \longrightarrow H^\bullet + CO_2 + HC(OH)_2^+$$

$$H^\bullet + H-C \underset{OH-----O}{\overset{O------HO}{<}} C-H \longrightarrow H_2 + {}^\bullet C \underset{OH-----O}{\overset{O------HO}{<}} CH$$

In the liquid phase $O\overset{\bullet}{C}OH$ radicals exhibit very small proton hyperfine

couplings (0.9 G).[17] Therefore it is also impossible to discount

this radical as being responsible for the broad singlet.

REFERENCES

1. M. C. R. Symons, _Chem. Soc. Reviews_ 12, 393 (1984).

2. P. J. Boon and M. C. R. Symons, _Chem. Phys. Letts._ 89, 516 (1982).

3. L. D. Snow and F. Williams, _J.C.S. Chem. Comm._ 1090 (1983).

4. D. N. R. Rao, J. Rideout and M. C. R. Symons, _J. Chem. Soc., Perkin Trans. 2_ 1221 (1984).

5. D. Becker, M. D. Sevilla, C. L. Sevilla and S. Swarts, _J. Phys. Chem._ 88, 1701 (1984).

6. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, _Chem. Phys. Letts._ 105, 586 (1984).

7. M. Iwasaki, H. Muto, K. Toriyama and K. Nunome, _Chem. Phys. Letts._ 105, 592 (1984).

8. R. W. Holmberg, _J. Chem. Phys._ 51, 3255 (1969).

9. P. B. Ayscough and J. P. Oversby, _Trans. Faraday Soc._ 67, 1365 (1971).

10. D. A. Sweigart and D. W. Turner, _J. Am. Chem. Soc._ 94, 5592 (1972).

11. F. H. MacDougall, _J. Am. Chem. Soc._ 58, 2585 (1936).

12. M. C. R. Symons and B. W. Wren, unpublished results.

13. T. A. Claxton, M. C. R. Symons and J. Rideout, _J. Chem. Res. (S)_ (1985) in press.

14. H. C. Box, 'Radiation Effects', Academic Press, New York, p.144 (1977).

15. G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons and A. Hasegawa, _J. Chem. Res. (S)_ 258 (1983).

16. M. D. Sevilla, _J. Phys. Chem._ 87, 1648 (1983).

17. R. O. C. Norman and P. R. West, _J. Chem. Soc. (B)_ 389 (1969).

CHAPTER
7

Oxirane Cations

INTRODUCTION

Ether radical cations have now been widely studied in freon matrices.[1,2] Both acyclic and cyclic ethers have been studied, with their characteristics well noted. Results produced for acyclic ethers have been generally accepted. Similarly, results for cyclic ethers, including oxetane[3] and higher cyclic ethers, remain uncontested. In contrast, the results obtained for oxirane or ethylene oxide are a source of great discussion. This indecision has led to the study included here,[18] along with the studies of various related compounds, in an attempt to produce a conclusion.

Ethylene oxide is a three-membered cyclic ether. The e.s.r. results for the cation led Symons and Wren[4] to favour a ring-closed oxygen-centred, non-bonding type structure. Snow and Williams[3] contested this analysis, favouring the ring-open π carbon-centred radical.

RESULTS

Ethylene Oxide
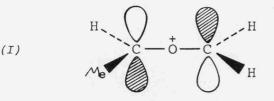
The oxirane parent compound in $CFCl_3$ produced a well-defined quintet having $A(^1H) = 16\,G$. Also observable upon this main quintet is a small fine structure attributed to a ^{35}Cl nucleus from a solvent molecule.[3] This fine structure disappears reversibly upon warming and is analogous to that observed for the acetaldehyde cation.[5] It is noteworthy that the sample is uncoloured, even after prolonged irradiation.

When studied in SF_6 as a solvent matrix, the e.s.r. spectrum observed is almost identical. The fine structure due to ^{35}Cl is, of course, absent, and $A(^1H)$ is slightly smaller at 15.7 G. The most striking difference is the intense orange colouration observed in the less con-stricting SF_6 matrix.

2-Methyl Oxirane

The e.s.r. spectra obtained were extremely complex in nature (Fig. 1a). There seems to be little doubt that the spectra obtained upon annealing to 130 K are due to the ring 'open' species I.

(I)

Samples observed at this temperature exhibited an intense red colouration. Irradiation of samples with X-rays at 4 K produced broad features. Warming to 25-30 K gave a better defined spectrum (Fig. 1b). This is obviously very different to Fig. 1a, the 77 K 'open' structure. It is interesting that the spectrum changes to that in Fig. 1a upon warming, concomitantly with a production of an intense red colouration within the sample. Figure 1b is so broad it might be analysed in several equally plausible ways. It is not felt, however, that this can possibly be just a broadened version of the spectrum in Fig. 1a.

2,3 cis Dimethyl Oxirane

Again the initial 77 K spectrum was very complex (Fig. 2a). It is felt that two species are contributing to this spectrum. The narrower set of lines are irreversibly lost upon warming. When the temperature reaches approximately 90 K, a set of 9 lines is observed with $A(^1H) = 17\,G$ (Fig. 2b). This reverts to 8 lines upon recooling to 77 K (Fig. 2c). The sample is again a pinkish/red colour throughout.

The 8-9 line species is attributed to the ring 'open' cation, proving the α-proton coupling is of the order of 16 G for the 'open' cation. This appears to support the carbon-centred π radical, produced by ring opening, suggested by Snow and Williams[3] for ethylene oxide itself.
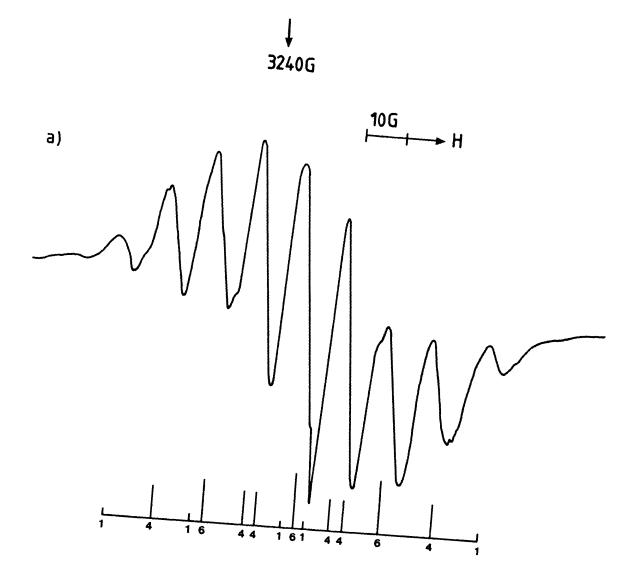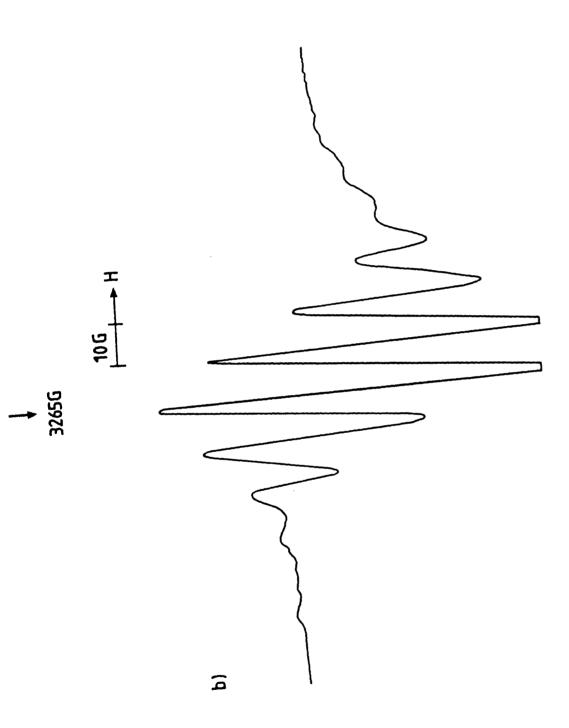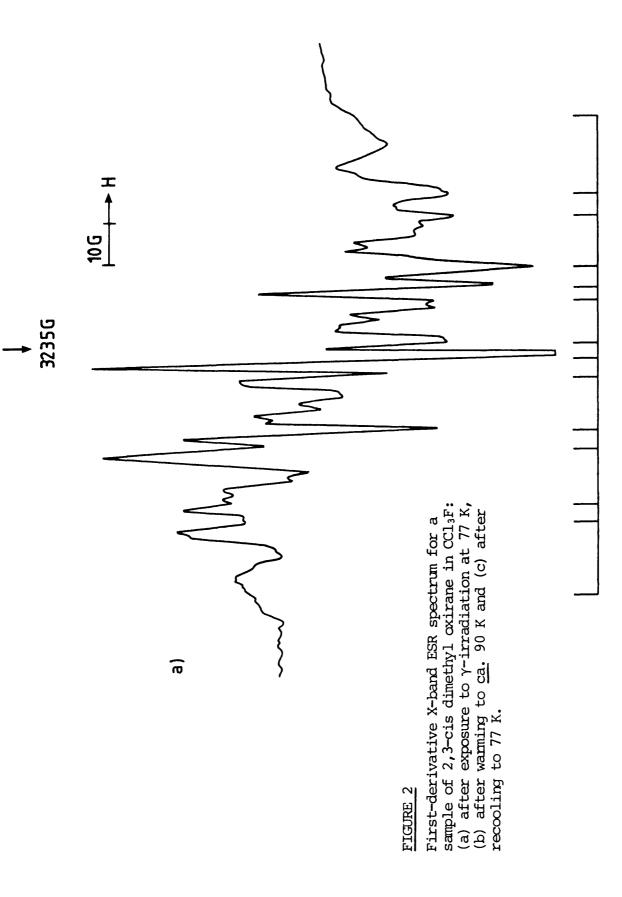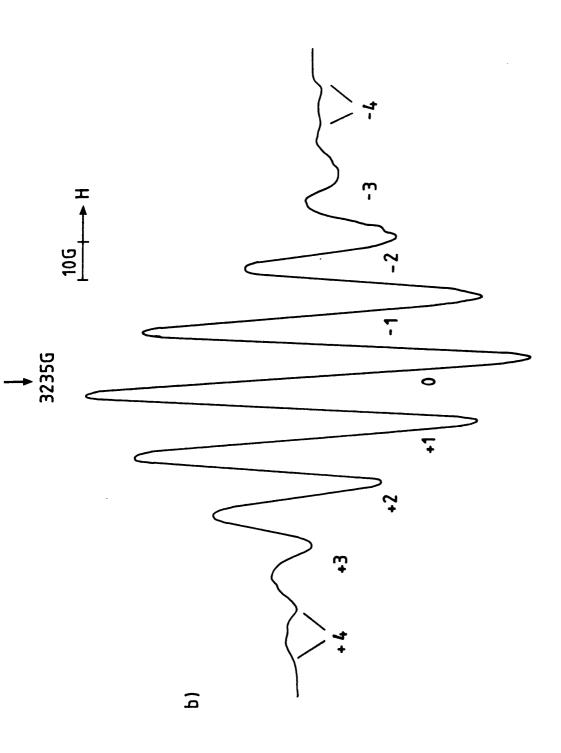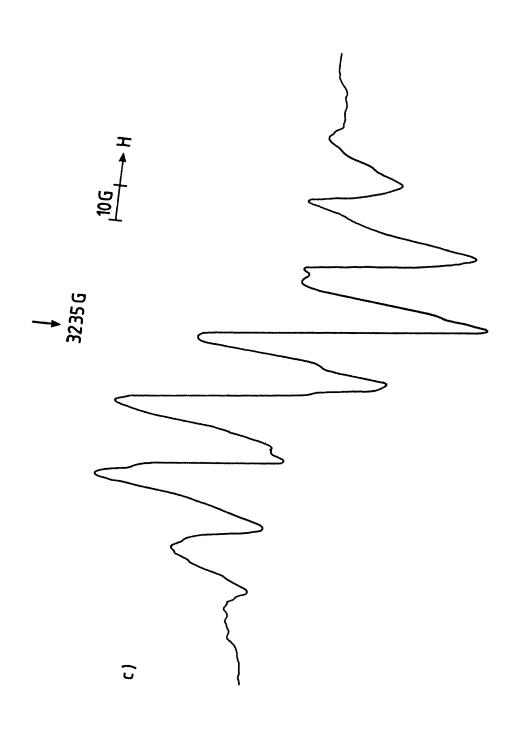
FIGURE 1

a) First-derivative X-band ESR spectrum for a sample of 2-methyl oxirane in CCl$_3$F after exposure to γ-irradiation at 77 K and warming to 130 K;

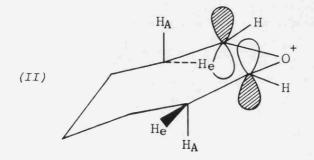b) Spectra obtained at 25 to 30 K following X-irradiation at 4 K.

b)

FIGURE 2

First-derivative X-band ESR spectrum for a
sample of 2,3-cis dimethyl oxirane in CCl$_3$F:
(a) after exposure to γ-irradiation at 77 K,
(b) after warming to ca. 90 K and (c) after
recooling to 77 K.

c)

3235 G

10G

H

These results do not explain the broad features in Fig. 2a. The dimethyl oxirane was then irradiated at 4 K. The resulting sample was again noticeably non-coloured. The e.s.r. features for which were poorly defined, but markedly different from those obtained by irradiation at 77 K. However, annealing the sample to 77 K produced a pink colouration along with spectral changes. The spectrum observed is then identical to Fig. 2a.

Cyclopentene Oxide

Spectra recorded for cyclopentene oxide were well-defined at 130 K (Fig. 3). They can be analysed best, as shown in Fig. 3, as $A(2^1H) = 9\,G$, $A(2^1H) = 15.3\,G$ and $A(2^1H) = 31\,G$. It is clear that the two strongly coupled protons must be the axial protons (H_A in II).

(II)

Using the evidence obtained, upon the typical α-proton couplings, with cis-2,3 dimethyl oxirane it becomes clear the two 9 G couplings are due to the equatorial protons (H_e in II). Given an average β-proton coupling of 15-16 G, the values of 31 G and 9 G fit in nicely for axial and equatorial protons, using the $\cos^2\theta$ law.

In view of these data, the species has been assigned to the ring open form. This is supported by the red-pink colouration of the sample.

3240G

10G

H

FIGURE 3
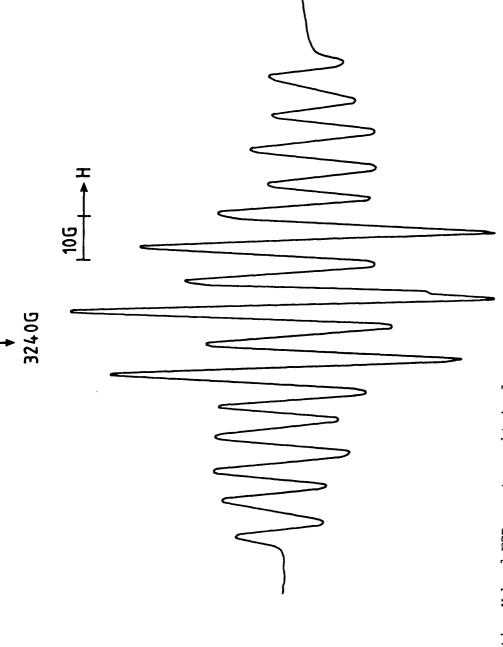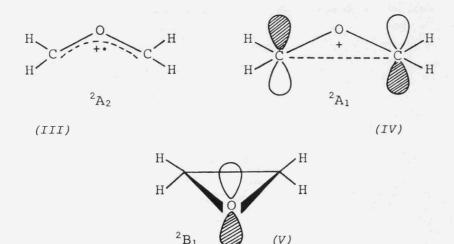
First-derivative X-band ESR spectrum obtained
by exposure to γ-irradiation at 77 K of a
sample of cyclopentene oxide in CCl₃F after
warming to ca. 130 K.

Cyclohexene Oxide

The cyclohexene oxide produced a complex spectrum, showing remarkable temperature sensitivity. It seems that a range of conformational changes must be occurring. The strong colouration of the sample and the general form of the spectra leads us again to conclude that the three-membered ring has 'opened' upon extraction of an electron.

DISCUSSION

A great deal of controversy has arisen as to whether the cation produced by γ-irradiation of ethylene oxide in freon is the ring-opened $^2A_2$ form[3] (III) or the ring-closed $^2A_1$ form[4] (IV). What is without question is that the e.s.r. spectra are not due to the ring-closed $^2B_1$ (V) ground state, since the $A(^1H)$ splitting observed is too low.
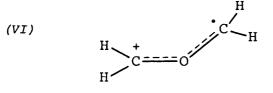
Several groups of workers have applied theoretical calculations for these species.[6,7,8] It is generally agreed that the first-formed cation has the π structure with the $^2B_1$ ground state. However, this must re-arrange to account for the features seen in the e.s.r. spectrum.

Mollere and Wouk[9] favour the $^2A_1$ first excited state as the first-formed species. This $^2B_1 \to ^2A_1$ conversion occurs as a lengthening of the

C–C bond. These theoretical studies support the original analysis

proposed by Symons and Wren.[4] Indeed, higher level calculations by

Clark[7] find the $^2A_1$ structure has effectively planar carbons. Hence,

the observed $A(^1H)$ coupling of 16 G is quite reasonable.

However, theory generally agrees that the most stable structure is

the 'open' form. Argument still continues though over the amount of

allylic stabilisation experienced by this structure. It was originally

believed that an asymmetric structure with one long C–O bond and one

short (VI) was the most stable structure. More recent work has produced

(VI)
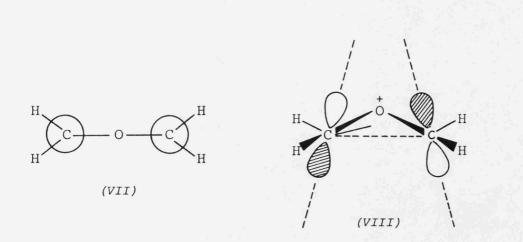
the generally accepted idea that a planar C_{2v} type structure ($^2A_2$) is

favoured.[6,7,8]

The asymmetric structure is ruled out by the e.s.r. results obtained

in the freon matrix. However, a proton hyperfine coupling of 16 G is

expected to be reasonable for a C_{2v} type structure. It seems that the

e.s.r. results establish that the cation of ethylene oxide is ring

opened at 77 K, similar to that suggested by mass spectrometric and

other studies[20,4] in the gas phase.

In further support of this are the results obtained by Williams and

Snow[10] who used ^{13}C-enriched *CH$_2$O*CH$_2$ in freon. The equivalence of

the p-orbitals on the two carbons is ascertained by the strong central

features of the ^{13}C triplet. It is suggested the principal axes of the

two carbon atom p-orbitals are the same.[19] This suggests structure VII

is preferable over structure VIII, where the two p-orbitals do not have
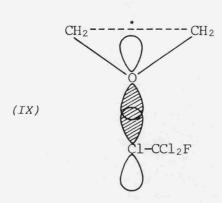
a common principal axis.

(VII)

(VIII)

Despite this apparent confirmation of the 'ring open' structure as the species responsible for the e.s.r. spectra seen at 77 K, we favour the ring-closed structure ($^2A_1$). This is due to the observation of no colouration in the parent oxirane freon samples. Comparatively, the sample of this oxirane in SF_6 produced an intense orange-red colouration at 77 K. Until the $CFCl_3$ solutions had been annealed and irreversible spectral changes had occurred, no colouration was observed.

It is notable that the mono- and di-methyl analogues give colourless samples when irradiated at 4 K. Yet when annealed a red colour grew in, coinciding with changes in e.s.r. spectra. The initial spectra cannot be the $^2B_1$ type cation but may be the $^2A_1$ cation.

Further evidence is drawn from the fact that 2,3-dimethyl oxirane produces two species at 77 K, one is irreversibly lost upon annealing to ca. 100 K. We suggest this unstable species is the $^2A_1$ cation. It is of interest that adduct formation to ^{35}Cl occurs. This is a surprising result since, as suggested in Chapter 2 of this thesis, it is normally only observed when a well-defined σ bond between a highly localised centre and the Cl atom is formed.[11] Neither of the proposed structures seem to fit this requirement. Also, from the correlation of hyperfine splittings with ionisation potential,[11,12] a maximum of 50 G

-99-

is indicated. This is far in excess of that observed (Table I). The only way round these observations is to invoke a Cl-O bond as seen in IX, where the great majority of the SOMO remains upon the C-C bond.

$$CH_2 \text{------} CH_2$$

(IX)

$$Cl-CCl_2F$$

For the open form, any tendency to form a σ bond to one side or the other would distort the radical. The limiting structure is X. A very

(X) $\dot{C}H_2 \text{---} O \text{---} C$ ····|||| H

$$Cl-CCl_2F$$

similar structure has recently been applied to a ring open cyclopropane cation[13] and has been invoked to explain why the SOMO is effectively localised on one CH_2 unit, rather than being equally distributed between the two outer CH_2 units.

It is noteworthy that a dependence of ring-opening on solvent has been detected for the cyclopropane cation. It remains cyclic in $CFCl_3$ but undergoes a ring-opening in the less constricting $CFCl_2-CF_2Cl$.[13]

In conclusion we suggest that while ring-opening is thermodynamically favoured, there is a significant barrier for ring-opening from the $^2A_1$ state and that ring-opening is inhibited in constricting solvents such as $CFCl_3$.

At high temperatures (ca. 160 K), irreversible spectral changes were observed for the parent, ethylene oxide (Fig. 4). The spectra observed
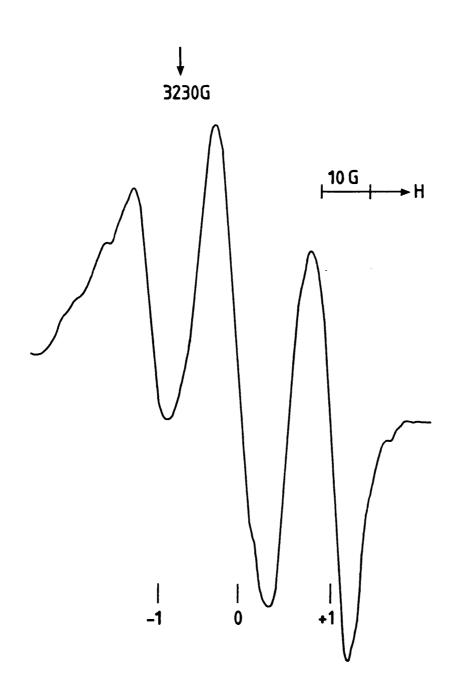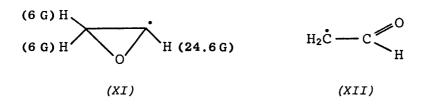
FIGURE 4

First-derivative X-band ESR spectrum for oxirane in CFCl$_3$ after exposure to [60]Co γ-rays at 77 K, followed by annealing to ca. 150 K showing the triplet species discussed.

comprises a binomial triplet of $A(^1H) = 20 G$. This observation can be rationalised in two ways. The first is that a bimolecular reaction between a cation and an oxirane molecule occurs giving XI which rapidly ring opens to XII.

(XI)   (XII)

The radical with structure XII could explain the observed spectra. Radical XI, however, is not expected to ring open rapidly, since it has been studied in the liquid phase at higher temperatures.[14,15,16]

The second explanation is for the cyclic $^2A_1$ structure to undergo ring opening reacting swiftly with a solvent molecule giving structure X. Hence producing the asymmetric triplet observed.

2-Methyl Oxirane

The coupling constants observed for this cation differed from those observed for the 'open' parent cation, 2,3-dimethyl oxirane and tetramethyl oxirane. Therefore a similar structure is unlikely. Instead, an asymmetric structure, where the SOMO is biased towards the CH_2 unit and the positive charge towards the -CHMe unit, is considered. An analysis where a splitting of 12 G for the α-protons of the CH_2 unit, together with 21 G for the single proton upon the CHMe unit, and 21 G each for the methyl group protons, provides a reasonable fit for observed spectra. It seems the methyl group stabilises the carbocation centre, hence the asymmetry. This data is produced from samples studied at 130 K; those at 77 K producing broad features not easily analysed.

Spectra obtained at 30-50 K produced a 6-line spectrum with a 10.5 G splitting. This analyses as 3 protons with $A(^1H) = 10.5$ and one proton

with $A(^1H) = 21\,G$. Without a very highly asymmetric spin distribution, it is hard to analyse these results as a ring-closed $^2A_1$ species, though the lack of colour in these samples until annealing is again taken as evidence of ring-opening mechanism.

2,3-Dimethyl Oxirane

The marked temperature dependence for the spectra of these cations does not assist analysis. The extra features in Fig. 2a seem to analyse as two protons at 16.5 G and two at 21.6 G. Several further features are present which may or may not be related to this species. If the two 16.5 G couplings are assigned to two α-protons, then the sum of the methyl group proton couplings is 43.2 G. Therefore, there is a coupling of 7.2 G to each proton. A hindered rotation of both methyl groups could lead to a set of seven lines, commonly the $M_I = \pm 3$ and 0 lines are narrow, the remainder broad. These results are believed to be due to cyclic $^2A_1$ cation.

CONCLUSION

Though a great deal of evidence has been produced 'proving' that the cations of these oxiranes are ring-opened, I believe the results obtained by us and shown herein are vitally important. The crux of the argument is based upon colours observed upon irradiation (at various temperatures).[18] Haselbach's[17] work shows colours occurring for ring-open forms, yet this fact has been ignored by other groups. No-one, as yet, has attempted to explain the lack of colouration of ethylene oxide in $CFCl_3$, compared with the strongly coloured sample in SF_6, by any means other than that adopted by ourselves.

REFERENCES

1. H. Kubodera, T. Shida and K. Shimokoshi, _J. Phys. Chem._ **85**, 2583 (1981).

2. M. C. R. Symons and B. W. Wren, _Tetrahedron Letts._ **24**, 2315 (1981); M. C. R. Symons and B. W. Wren, _J. Chem. Soc., Chem. Comm._ 817 (1982).

3. L. D. Snow, J. T. Wang and F. Williams, _Chem. Phys. Letts._ **100**, 193 (1983).

4. M. C. R. Symons and B. W. Wren, _J.C.S. Perkin Trans. 2_ 511 (1984).

5. L. D. Snow and F. Williams, _Chem. Phys. Letts._ **100**, 198 (1983).

6. W. J. Bouma, D. Poppinger, S. Saebø, J. K. McLeod and L. Radom, _Chem. Phys. Letts._ **104**, 198 (1984).

7. T. Clark, _J. Chem. Soc., Chem. Comm_ (1984).

8. D. Feller, E. R. Davidson and W. J. Borden, _J.A.C.S._ **106**, 2513 (1984).

9. P. D. Mollere and K. N. Houk, _J.A.C.S._ **99**, 3226 (1977).

10. L. D. Snow and F. Williams, _J.A.C.S._ **107**, 3367 (1985).

11. T. Clark, A. Hasegawa and M. C. R. Symons, _Chem. Phys. Lett_ **79**, 116 (1985).

12. J. Rideout and M. C. R. Symons, _J.C.S. Perkin Trans. 2_ (1986) in press.

13. X. Z. Qin, L. D. Snow and F. Williams, _J.A.C.S._ **106**, 7640 (1984).

14. A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, _J. Chem. Soc. (A)_ 124 (1971).

15. G. Behrens and D. Schulte-Frohlinde, _Agnew. Chem_ **85**, 993 (1973).

16. H. Itzel and H. Fischer, _Helv. Chim. Acta_ **59**, 880 (1976).

17. T. Bally, S. Nitsche and E. Haselbach, _Helv. Chim. Acta_ **67**, 86 (1984).

18. J. Rideout, M. C. R. Symons and B. W. Wren, in press.

19. M. Iwasaki, _Fluorine Chem. Rev._ pp.14-15 (1971).

20. R. R. Corderman, P. R. LeBreton, S. E. Buttrill, Jr., A. D. Williamson and J. L. Beauchamp, _J. Chem. Phys._ **65**, 2929 (1976).

21. W. J. Bouma, J. K. McLeod and L. Radom, _J. Chem. Soc., Chem. Comm._ 724 (1978).

CHAPTER
8

Dialkyl Mercury Cations

INTRODUCTION

Heavy metal compounds are of great biological and environmental[1,2] interest, mainly because of their high toxicity, organometallic derivatives being of special interest, since they may be formed biochemically from less toxic inorganic derivatives.[3,4]

Compounds formed in this way include the monoalkyl mercury(II) compounds, which under more basic conditions,[5] may be converted to the dialkyl mercurials. For example diethyl mercury production is considered to be environmentally important in soils.[6]

These chemicals can find their way into food sources such as fish and vegetables.[7] Since γ-irradiation is becoming an important technique in food sterilisation it seems of interest to investigate the effects of γ-irradiation upon these compounds.

Previous ESR studies have been performed upon γ-irradiated mercury compounds.[8,9] These studies involved the mercury I and II derivatives as either pure compounds or in solution in acidic aqueous media.[8] For example, the γ-radiolysis of pure dimethyl mercury has previously provided evidence for the radical $Me_2Hg^{\cdot -}$.[9] This was characterised by the expected septet of lines from two methyl groups. The radical $H_2\overset{\bullet}{C}\text{-HgCH}_3$ was also detected, its ESR data showing a low spin-density on the mercury atom. No evidence for the parent cationic species was obtained in these studies.

Various inorganic mercury(II) cationic species have been generated, for example studies have been performed on the cations of HgH^{2+}, $HgOH^{2+}$, $HgOEt^{2+}$ and $Hg_2^{+\ 3+}$.[8]

The aim of the present study was to prepare R_2Hg^+ cations, using the freon solvent system, since they have not been identified previously using ESR spectroscopy. The mercurials chosen for study were dimethyl

and diethyl mercury. To supplement this work and to aid interpretation of results the compounds $(CD_3)HgCH_3$ and $(CD_3)_2Hg$ were prepared together with $^{13}CH_3HgCH_3$.

Photoelectron spectroscopic studies of these compounds have been performed previously.[10,11] They show that the first ionization observed is from a molecular orbital with substantial mercury to carbon bonding character. The first ionization potentials for dimethyl mercury and diethyl mercury are recorded in Table I.

TABLE I

Compound	First Ionization Potential
$(Me)_2Hg$	9.3 eV
$(Et)_2Hg$	8.9 eV

RESULTS

Mercury possesses two magnetic isotopes: one is ^{199}Hg which has spin $I = \frac{1}{2}$ and is 16.88% abundant, the other, ^{201}Hg, has spin $I = \frac{3}{2}$ and is 13.24% abundant. The resulting hyperfine couplings to these nuclei may enable the ESR spectroscopist to make calculations which provide useful structural information on the species observed.

Dimethyl Mercury

The ESR spectrum produced by γ-irradiation of dimethyl mercury in $CFCl_3$ at 77 K has clear hyperfine features for ^{199}Hg (Fig. 1a). Those for ^{201}Hg are less clear. A complex pattern of hyperfine interactions to protons is observable on these features. An enlargement of feature B of Fig. 1a is shown in Fig. 2. Unfortunately, there is no immediately obvious, clear interpretation for the observed complexity.

However, two possible structures can be proposed for this cation to
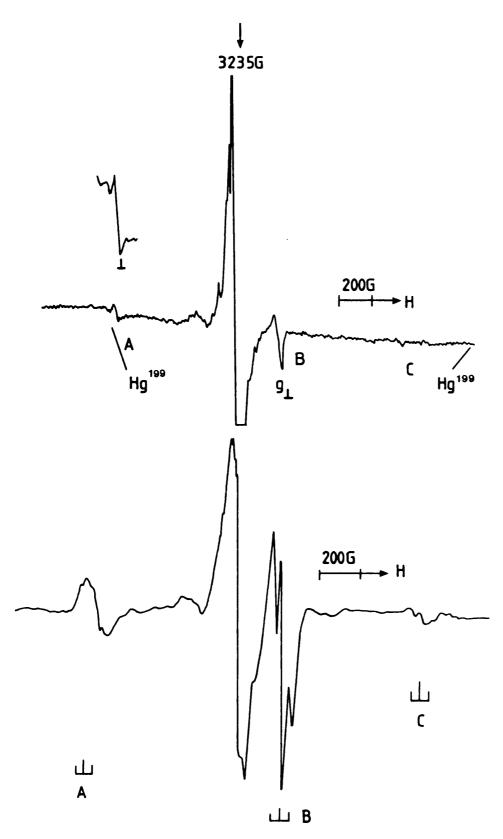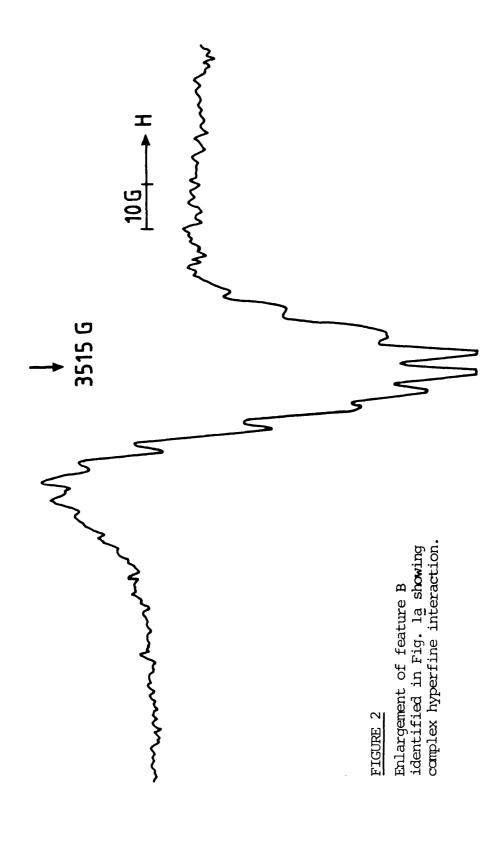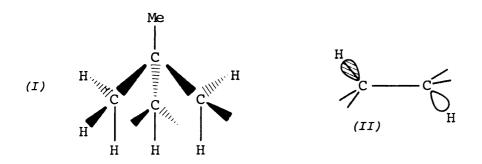
FIGURE 1

a) The e.s.r. spectrum obtained by ^{60}Co γ-irradiation of a
solution of MeHgMe in CFCl$_3$;

b) The e.s.r. spectrum of (EtHgEt)·$^+$.

10G

H

3515 G

FIGURE 2

Enlargement of feature B
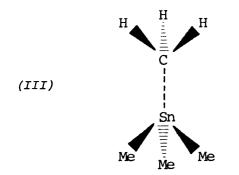identified in Fig. 1a showing
complex hyperfine interaction.

account for the spectrum observed. Fixed orientations for the two

equivalent methyl groups could be responsible. It would be expected

that these groups would rotate freely as the temperature is raised.

Eventually, a seven-line spectrum indicative of 6 equivalent protons

would be expected. This was not observed on annealing up to ca. 160 K.

However, such non-rotating methyl groups have been observed for hydro-

carbon cations.[12] For example, the cations of neopentane[13] and

ethane[12] adopt the SOMO's shown in I and II.

(I)

(II)

The analogy to ethane is quite engaging. The exhibiting of inter-

actions to two strongly coupled protons and four weakly coupled protons

may provide a complex coupling pattern. Equally possible is the

structure with four strongly and two weakly coupled protons.

An alternative structure may be proposed, in which the SOMO is

confined to a single C-Hg bond as the result of a distortion of the

molecule. Structure III can be compared with that obtained for the
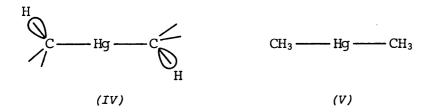
cation of tetramethyl stannane[14,15] (see Chapter 9).

(III)

<u>$(CD_3)_2Hg$ dimethyl mercury (d^6)</u>

In order to simplify the spectrum, the cation of $(CD_3)_2Hg$ was prepared. However, the singlets that were expected were not obtained. Figure 3 shows a definite residual splitting which cannot be assigned to ^2H hyperfine couplings. A possible explanation for this splitting is a weak interaction with the solvent matrix. With $CFCl_3$ it is possible to form interactions to a Cl atom, as found for acetaldehyde[16] (see Chapter 2), or to a F atom, as found for C_2F_4.[17] To be sure which nucleus is responsible, the cation of $(CD_3)_2Hg$ was prepared in carbon tetrachloride (CCl_4).

The resulting spectra revealed the loss of a doublet feature of 10 G, implying the structure observed in Fig. 3 is partly due to a coupling to ^{19}F nuclei. A residual structure remains in CCl_4, and is probably attributable to asymmetry giving $\underline{x}$, $\underline{y}$ and $\underline{z}$ features, or to the presence of extra features due to 'false' turning points (cf. Cu^{2+}).
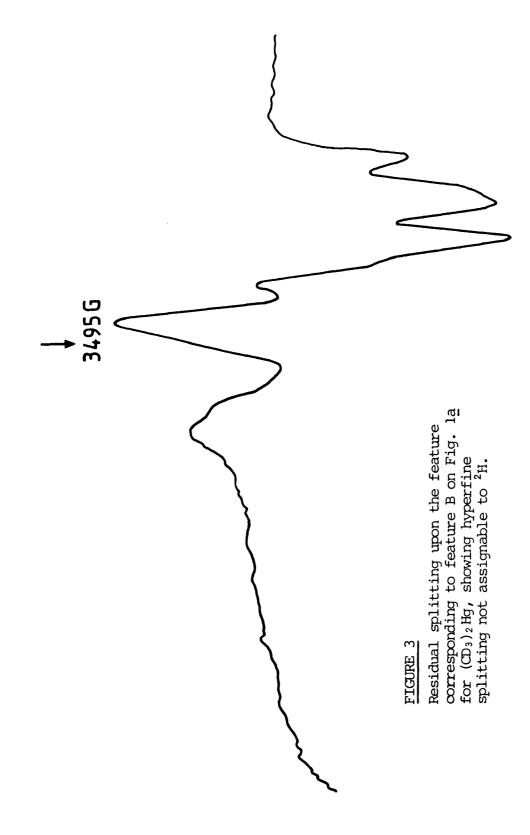
However, even with the results obtained using the perdeuterated dimethyl mercury, it remains difficult to interpret all the features for the $(CH_3)_2Hg$ cation. Hence, it remains impossible to make a clear choice between the symmetric and distorted structures (IV and V).

(IV)   (V)

<u>$^{13}CH_3HgCH_3$</u>

A further attempt to make a choice between IV and V was made, using the mono-^{13}C substituted analogue. Unfortunately, the ^{13}C coupling was found to be too small to resolve.
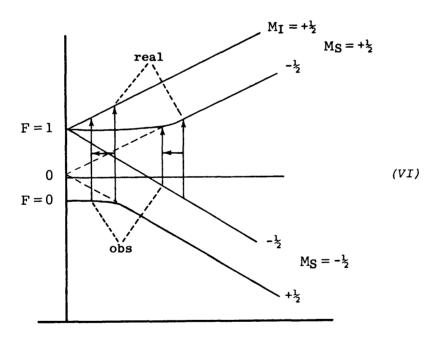
The mercury natural isotopes ^{199}Hg and ^{201}Hg produced large hyperfine

3495 G

FIGURE 3

Residual splitting upon the feature
corresponding to feature B on Fig. 1a
for $(CD_3)_2Hg$, showing hyperfine
splitting not assignable to ^2H.

splittings. $A_\perp {}^{199}Hg$ is approximately 1600 G. If any structural information is to be extracted from the mercury coupling constants, they must be obtained using the full Breit-Rabi expression.[18] The commonly used simple high-field approximations and even the second order expressions are not good enough.
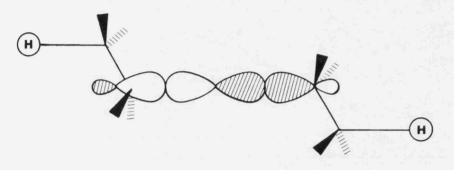
When the observed hyperfine coupling is very large, these are poor approximations. The electron and nuclear spin quantum numbers must be considered as coupled. The effect of this is to shift both absorption bands to low field of the 'normal' positions. This shift is larger for the low field line than for the high field line. The first order hyperfine coupling and g-value are artificially high. Figure VI shows this effect.[19]

(VI)

The true hyperfine couplings and g-values have to be obtained using suitable computer programmes. Unfortunately, this facility is currently unavailable in this Department. Corrections and hence any structural information is, therefore, unobtainable at present.

Diethyl Mercury

Whilst the same problem arises for the mercury couplings, it can be seen (Fig. 1b) that the proton hyperfine interactions are more easily translatable. Feature B in Fig. 1b is attributed to the non-magnetic mercury isotopes. All features A, B and C, exhibit hyperfine coupling to two equivalent protons, the triplet having a splitting of 42 G. This large β-proton coupling of 42 G is suggested to come from two unique strongly coupled protons. The structure VII, analogous to that suggested for the ethane[12] cation, is proposed as being responsible.

CONCLUSIONS

Expectation for a linear 6p' configuration for mercury is that g_z is approximately 2.00 whilst g_x and g_y are less than 2. It therefore seems reasonable to assign feature B (Fig. 1b) to the perpendicular component of the non-magnetic mercury isotopes. Features (A and C), are then the ($M_I = \pm\frac{1}{2}$) components of the ^{199}Hg isotope. The relatively high intensity of the feature A, seems to imply that it is fairly isotropic. Unfortunately, we have not been able to detect the $M_I = -\frac{1}{2}$ parallel component.

Other features observed are tentatively assigned to the ^{201}Hg isotope. Since we are unable to simulate the spectrum using the proper equations, it is impossible to quote values for the tensor components. However, it is clear that $A_\perp$ has a magnitude of approximately 1600 G and that

$|A_{\parallel}| < |A_{\perp}|$. This is an unusual situation, since for most radicals $|A_{\parallel}| > |A_{\perp}|$. It is quite characteristic of the np' type of radical (n = 4, 5 or 6).[20]

If this is correct both $A_{\parallel}$ and $A_{\perp}$ must be negative and, therefore, A_{iso} is large and negative. Unfortunately, the value of 2B cannot be estimated, hence the amount of delocalisation onto the alkyl groups cannot be found by this method. However, the analogy drawn between the structures of the ethane cation and that of diethyl mercury may lead to an estimate of this delocalisation. The observed hyperfine coupling for ethane is 152 G, if no major distortion between these two structures occurs, then 42 ÷ 152 = ·28. In this way an estimate of spin density upon the alkyl groups has been made. This would be expected to be smaller for the dimethyl derivative which exhibits a larger ^{199}Hg coupling. Indeed the results obtained with the ^{13}C substitution are supportive of a small amount of delocalisation onto the alkyl groups, hence the small poorly defined ^{13}C splittings obtained.

In all cases, intense features at g = 2 were found. These showed no similar hyperfine couplings to those observed on the non-magnetic and ^{199}Hg isotope lines. It is therefore concluded that these features are due to an organic impurity, possibly resulting from purification difficulties in the small scale productions of these compounds. It is therefore impossible to clearly establish whether or not alkyl radicals are liberated upon warming as in the case of tetramethyl tin cations.[14,15]

REFERENCES

1. Comp. Organometallic Chemistry, ed. Wilkinson, Pergamon Press, Oxford, Vol. 2, p.980.

2. W. Yule, R. Lansdown, I. B. Miller and M. A. Urbanowicz, Developmental Medicine and Child Neurology, 3, 567 (1981).

3. R. E. DeSunone et al., Biochim. Biophys. Acta, 304, 851 (1978).

4. P. J. Craig and S. F. Morton, J. Organometallic Chem., 145, 79 (1978).

5. 'The Biogeochemistry of Mercury in the Environment', ed. J. O. Nriagu, Elsevier, Amsterdam, p.205 (1978).

6. D. L. Johnson and R. S. Braman, Environmental Sci. Technol., 38, 1003 (1974).

7. Ref. 1, p.1007.

8. R. J. Booth, H. C. Starkie and M. C. R. Symons, J. Chem. Soc. (A), 3198 (1971).

9. B. W. Fullam and M. C. R. Symons, J. Chem. Soc., Dalton Trans., 1086 (1974).

10. T. P. Fehlner, J. Ulman, W. A. Nugent and J. K. Kochi, Inorg. Chem., 15, 2544 (1976).

11. D. K. Creber and G. M. Bancroft, Inorg. Chem., 19, 643 (1980).

12. K. Toriyama, K. Nunome and M. Iwasaki, J. Chem. Phys., 77, 5891 (1982).

13. K. Nunome, K. Toriyama and M. Iwasaki, J. Chem. Phys., 77, 5891 (1982).

14. M. C. R. Symons, J. Chem. Soc., Chem. Comm., 1251 (1981).

15. A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M. C. R. Symons and J. Rideout, J. Chem. Soc., Dalton Trans., 1667 (1984).

16. L. D. Snow and F. Williams, Chem. Phys. Letts., 104, 198 (1984).

17. A. Hasegawa and M. C. R. Symons, J. Chem. Soc., Faraday Trans. I, 79, 93 (1983).

18. G. Breit and I. I. Rabi, Phys. Rev., 38, 2082 (1931).

19. M. C. R. Symons, 'Electron Spin Resonance Spectroscopy', Van Nostrand Reinhold Co. Ltd., Wokingham/Berkshire, 1978.

20. S. V. Nistor, E. Goovaerts, A. Bouwen and D. Schoemaker, Phys. Rev. B, 27, 5797 (1983).

CHAPTER
9

Organo-tin Cations

INTRODUCTION

Some e.s.r. evidence for various tin centred radical cations has been produced after γ-irradiation of various tin alkyls.[1,2] Several groups have made use of the 'freon' technique[3-5] to ensure the production of cationic species. This study was centred upon the simple tin alkyl, tetramethyl tin.[6] Various other tin species have also been studied using this technique, including hexamethyl di-tin,[7] tin tetra-hydride[8] and a series of selected trimethyl tin alkyls.[9] Various points of some of these studies needed more evidence in order to be convincing. A set of stannanes were selected by ourselves in collaboration with the group led by A. Hasegawa in Japan for study. The studies by Hasegawa were centred around SnH_4 and the series Me_nSnH_{4-n} (n = 1, 2 or 3). Whilst our own studies began with Me_4Sn and selected Me_3Sn alkyls and extended to the series Me_nSnCl_{4-n} (n = 1, 2 or 3).

Useful structural information upon the cations formed can be found, since tin has two magnetic isotopes occurring naturally (^{117}Sn and ^{119}Sn). Both exhibit a nuclear spin of ½, hence the observed hyperfine coupling can be used to estimate the spin density upon the Sn atom. ^{13}C substitution was used in the case of Me_4Sn to extract further structural data.

Similar studies using these techniques on Me_4Ge,[10] Me_4Pb[9] and Me_4Si[10] have been produced by other workers.

RESULTS

Tetramethyl tin

As suggested earlier by Symons,[6] the tetrahedral molecule undergoes a distortion upon electron loss. The e.s.r. spectrum observed exhibited a major quartet of 13-14 G from 3 equivalent protons. The

$^{117/119}$Sn coupling is markedly reduced from that observed by Hasegawa for the SnH$_4$ molecule (Table I). This implies a much reduced s-electron density resident upon the central tin atom.

The main quartet of Fig. 1 is assigned to the non-magnetic isotopes of tin. The smaller quartets of A(^{1}H) = 13 G to the high and low field sides of the main features are undoubtedly due to the $^{117/119}$Sn isotopes. The parallel features are not clearly defined, an estimated value having to be used for calculation purposes. Mono ^{13}C-tetramethyl tin was synthesised in order to gain specific information upon the methyl groups. The ^{13}C hyperfine coupling observed is unfortunately small and poorly defined parameters only are available. The study of this compound is extended in this study due to conflicting results obtained by Kochi et al.[9] and Symons,[6] at raised temperatures. The results obtained can be seen in Fig. 2, to support the statement that methyl radicals are released. It is, in fact, well documented that this compound easily liberates methyl radicals.[11-14] It is most likely that the differences achieved by the two groups are due to minor technical differences in sample preparation and treatment.

Trimethyl Ethyl Stannane

This compound was studied by both Kochi et al. and ourselves. The major paramagnetic products at 77 K are ethyl radicals. Kochi et al.[9] also studied trimethyl isopropyl tin, gaining similar results. At 77 K only isopropyl radicals were observed. The results obtained for these compounds support those obtained by other techniques.[14,15]

t-Butyl Trimethyl Tin

Again, this compound was studied both by ourselves and Kochi et al. The spectra observed by both groups are the same but the analyses presented were critically different. The 77 K spectrum is shown in
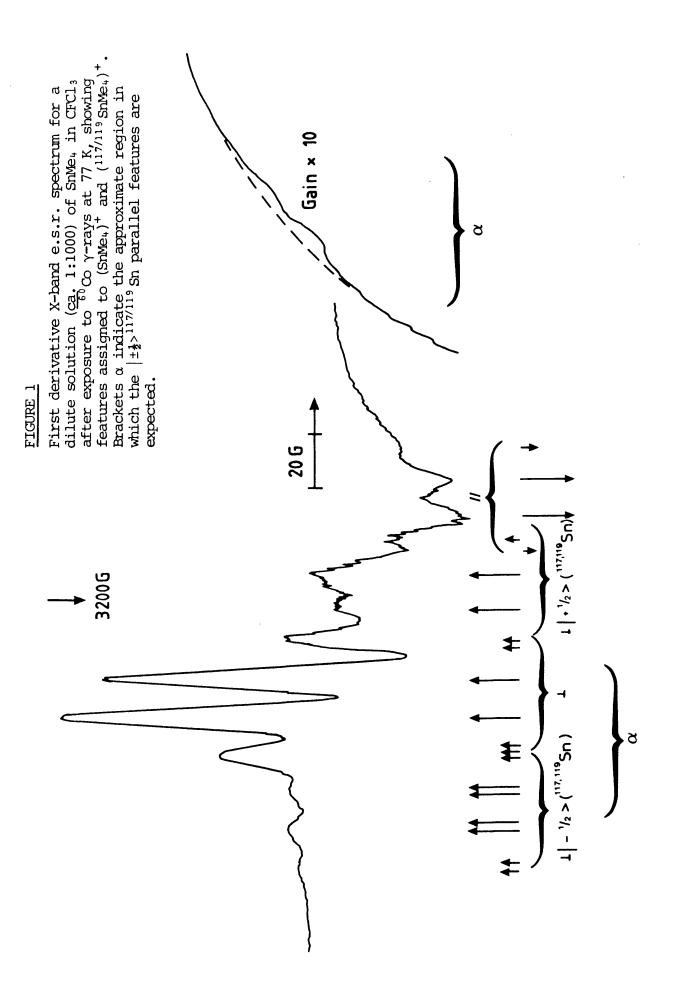
TABLE I

E.s.r. parameters for stannane radical cations

| Radical | $g_\perp{}^a$ | $g_\parallel{}^a$ | Nucleus[b] | Coupling constants[c]/G | | Spin densities[d] | | Structure (stability) |
				$A_\perp$	$A_\parallel$	p_s	p_p	
$SnH_4{}^+$ (I)	2.020	1.991	^{119}Sn	-2370	-3100	0.17	0.93	C_{2v} (unstable)
			^{117}Sn	-2270	-2960	0.17	0.93	
			H(2)	85	85	0.17		
$SnH_4{}^+$ (II)	2.016	1.984	^{119}Sn	-3180	-3650	0.21	0.60	C_{3v} (stable)
			^{117}Sn	-3040	-3490	0.21	0.60	
			H(1)	175	175	0.34		
$SnMe_4{}^+$	2.044	1.999	$^{119}Sn, {}^{117}Sn$	-78	-210	0.01	0.17	C_{3v}
			H(3)	-13.5	-13.5	-0.03		
			^{13}C	53	120	0.067	0.70	

FIGURE 1

First derivative X-band e.s.r. spectrum for a dilute solution (ca. 1:1000) of SnMe₄ in CFCl₃ after exposure to ⁶⁰Co γ-rays at 77 K, showing features assigned to (SnMe₄)⁺ and (¹¹⁷/¹¹⁹SnMe₄)⁺. Brackets α indicate the approximate region in which the |±½⟩¹¹⁷/¹¹⁹ Sn parallel features are expected.
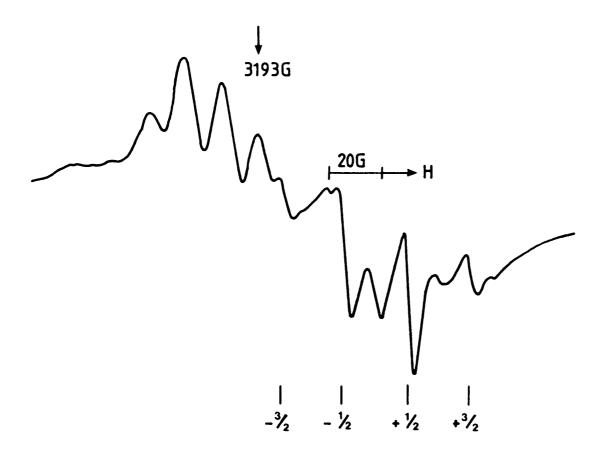
FIGURE 2

Spectrum obtained upon annealing a sample containing Me₄Sn cations.

Fig. 3. Upon annealing the analyses presented by the two groups also differed. We observe •CMe$_3$ radicals being reversibly gained upon annealing. As the signal due to these radicals grows, those features due to the parent cation are lost. On recooling to 77 K, the features indicative of the cation return, with concomitant loss of the spectra due to •CMe$_3$ radicals. The reversible nature of this thermolysis will be discussed later.

Methyl Tin Chloride [Me$_n$SnCl$_{4-n}$ (n = 1, 2 or 3)]

When n = 3 (i.e. the trimethyl derivative) is irradiated in the freon matrix, a 77 K spectrum similar to that produced by SnMe$_4$•$^+$ is found. The proton hyperfine splitting is found to be slightly smaller at 12 G (Table I). Again the production of methyl radicals upon warming is incontestable.

Where n = 2 and 3, methyl radicals are the product obtained directly upon irradiation at 77 K.

DISCUSSION

It is convenient to discuss the results obtained by Hasegawa together with our own. A marked contrast is observed between the isostructural SnH$_4$ and SnMe$_4$ molecules upon extracting an electron. The cations obtained with SnH$_4$ exhibit large Sn isotope couplings (Table I) indicative of a major proportion of the spin-density upon the Sn atom and a high s-character. The SnMe$_4$ exhibits a small tin isotope coupling. Both molecules being tetrahedral are expected to lose an electron from their triply degenerate t$_2$-type orbitals. Jahn-Teller theory calls for the distortions to D$_{2d}$ or C$_{3v}$ symmetry to be initially favoured.

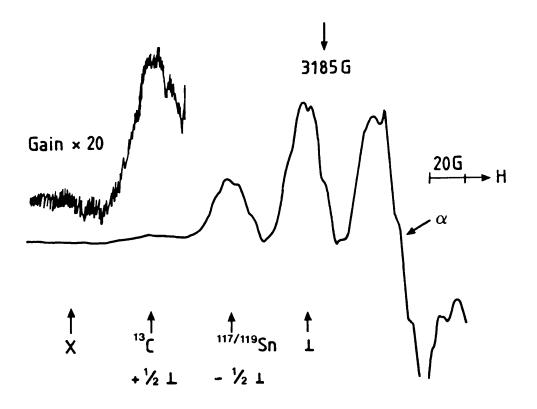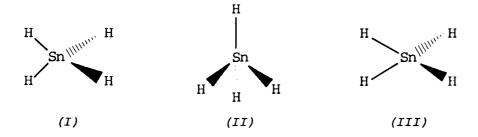It is interesting to observe that structures of C$_{2v}$ (I) and C$_{3v}$ (II)

FIGURE 3

First derivative X-band e.s.r. spectrum
obtained using Bu^{t}SnMe$_3$.

are formed,[16] and that there is no evidence for production of a D_{2d}

(III) type centre (with four equivalent protons for SnH_4^+).
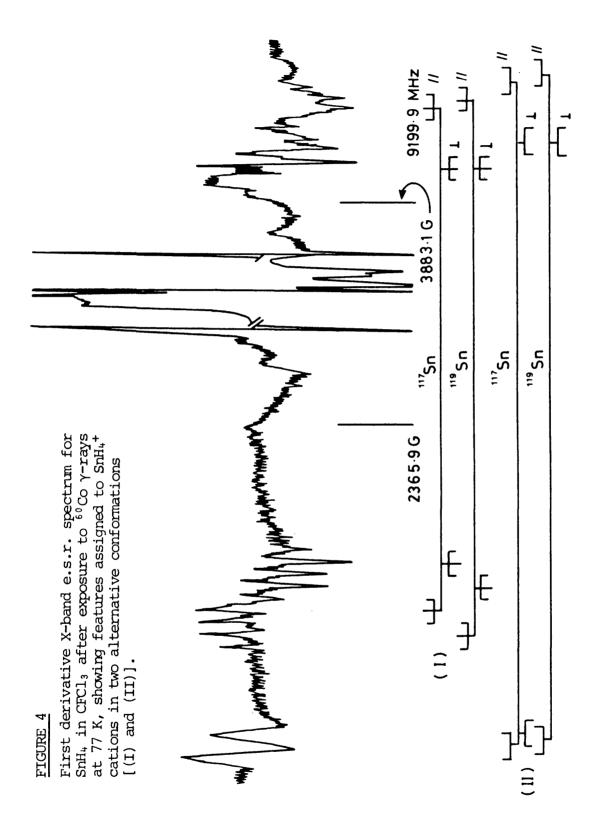

| (I) | (II) | (III) |

Stannane

Figure 4 shows the spectrum observed by Hasegawa upon irradiation

of SnH_4 in CCl_3F. There are clearly two species formed initially.

Despite theory favouring the D_{2d} deformation, only C_{3v} and C_{2v} type

structures are produced. It is suggested that the preference for

tetrahedral molecules to deform to C_{3v} and D_{2d} is applicable to the

initial vibrational pathway toward the lower symmetry forms. The

cations ultimately selecting any reduced symmetry to remove the

orbital degeneracy and so produce an energy minimum.

Structure I is responsible for the signals due to the radical with

two sets of two equivalent protons, one strongly and one weakly coupled.

This structure is analogous to the structure assigned to the cation

radicals of tetramethyl silane[10] and tetramethyl germane.[10]

The C_{3v} type structure (II) has a single strongly-coupled proton.

Of the two structure II is proven to be the more stable, based upon the

conversion upon standing or thermal annealing, of the C_{2v} form into the

C_{3v} form.[16]

It is a general feature of the range of methyl stannanes studied,

except the tetramethyl analogue, that at 77 K initially more than one

species is formed.

FIGURE 4

First derivative X-band e.s.r. spectrum for SnH₄ in CFCl₃ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to SnH₄⁺ cations in two alternative conformations [(I) and (II)].

Methyl Stannane

A large $^{117/119}$Sn coupling is observed exhibiting features assigned to a radical of C_{2v} symmetry. This is the dominant species observed. Another species with a smaller $^{117/119}$Sn hyperfine coupling is also present. The proton hyperfine coupling is unclear and is not assigned to a particular structure.

Dimethyl Stannane

Once more, two species with large $^{117/119}$Sn couplings were detected. That with the lesser coupling being converted to the more stable form upon warming. The more stable form is seen to produce features assigned to two equivalent protons of $A(^1H) = 85\,G$. The structure is probably a C_{2v} type structure, similar to that formed by SnH_4. The second species had only a single strongly coupled proton.
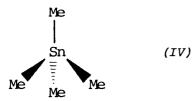
Trimethyl Stannane

Uncharacteristically, this sample produced only a single species with a large $^{117/119}$Sn coupling. No clear proton hyperfine coupling was seen and, hence, no structural assignment can be made.

Tetramethyl Stannane

The tetramethyl tin[6,16] (and lead[9]) cations produce an interesting structural contrast when compared to TMS and tetramethyl germane, favouring a C_{3v} type of structure (IV) with a unique, strongly coupled methyl group. The $^{117/119}$Sn coupling is heavily reduced from that observed in SnH_4 (Table I), implying a much reduced s-character upon the tin. A low 5s (tin) character is present in the SOMO. Hence the Me_3Sn^+ moiety is suggested to be almost flat, together with a lengthening of the unique Me-Sn bond.

The tendency toward a flattening of the Me_3Sn grouping is also seen

Me
|
Sn
Me Me Me

(IV)

in the cation of $(Me_6Sn_2)\cdot^+$, where the SOMO is calculated as being

almost purely 5p.[7]

Given this phenomenon, it is of interest to see whether the unique

methyl group similarly moves toward a flatter structure.

The $^{117/119}$Sn coupling implies the spin-density upon Sn is ca. 18%,

with a little on each of the three minor methyl groups. Therefore,

approximately 75% of the spin-density resides upon the unique methyl

group. Seventy-five per cent of 22.5 G is ca. 16 G, true of a totally

planar methyl group with 75% spin-density. The observed coupling is

actually 13.5 G suggesting near planarity for the methyl group. The

value of 16 G is expected to drop as s-orbital character and hence

bending is introduced. To supplement these arguments, the ^{13}C data

implies ca. 70% $2p_z$ occupancy with about 6.7% 2s character. A p:s

ratio of greater than 10:1 again implies near planarity.

The most pronounced difference between the cations of SnMe₄ and

SnH₄ is the loss of 5s orbital character in the SOMO of the former.

This is caused by the greater elongation of the unique Sn-C bond in the

former. This bond elongation seems to occur in order to allow both the

SnMe₃ and the CH₃ groups to relax to more planar shapes.

t-Butyl Trimethyl Tin

That the spectrum observed in Fig. 3 is due to the parent cation is

unquestioned. Two analyses have been presented: A by Kochi et al.,

B by ourselves.

Analysis A - This gives $A_{\perp}(^{13}C) = 187$ G. The small increase in the tin

isotope coupling and the $\Delta g_\perp$, is caused by an increased spin-density upon tin compared with Me_4Sn. The increase is approximately 25-30%.

If it is taken that $\underline{a}_p^2 \geqslant 0.5$ for carbon, from the $A_\perp$ value, A_{iso} must be greater than or equal to 202 G, implying 18% $\underline{s}$-orbital character. The total spin-density is then 68%, giving a $\underline{p}:\underline{s}$ ratio less than 2.8. These figures imply the Me_3Sn unit becomes planar (as seen for Me_4Sn) whilst the $\cdot CMe_3$ unit is highly pyramidal. The $A(^1H)$ coupling is 7.6 G for the $\cdot CMe_3$ grouping, this is considerably reduced from the +22 G found for free $\cdot CMe_3$ radicals. If this unit were to be assumed to be planar, then the spin-density upon it would have to be as low as 34%, which is unacceptable.
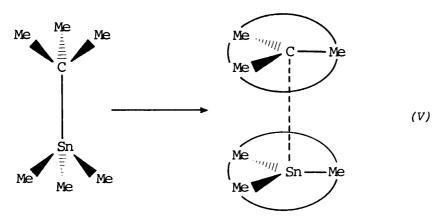
Analysis B - Our interpretation gives the ^{13}C multiplet as a ^{13}C satellite of the $^{117/119}Sn$ isotope feature, rather than a satellite of the main non-magnetic tin isotopes. This analysis calls for the main $Sn/^{13}C$ features to appear fortuitously beneath the main $^{117/119}Sn$ features. This is supported by the lack of any further features outside those observed, as required for the analysis A. Our analysis requires the $^{13}C/^{117/119}Sn$ feature to be almost isotropic to account for its relatively high intensity. Just such a coincidence has been observed for the $[PtH(CN)_4]^{2-}$ complex ions.[17]

If a value of $A_\perp(^{13}C)$ is taken as 90 G with $A_{/\!/} = 140\,G$, A_{iso} is about 107 G. This A_{iso} value corresponds to about 10% $\underline{s}$-orbital character, while 2B is calculated to be 33 G, 54% 2p-orbital character. The total spin-density is then 64% with a $\underline{p}:\underline{s}$ ratio of 5.4. This implies a considerable flattening of the $\cdot CMe_3$ moiety. The $SnMe_3$ moiety is known to flatten. Our interpretation of the data allows the $\cdot CMe_3$ grouping to flatten also.

Upon raising the temperature we find $\cdot CMe_3$ radicals are produced

reversibly. It seems a reversible thermolysis of the $Me_3Sn-(CMe_3)$
bond occurs as V.

(V)

The reversibility of this thermolysis, in contrast with that occurring
for the Me_4Sn cation, is probably related to the size, and hence the
mobility of the 'leaving' alkyl group. It might be expected that
since $\cdot CMe_3$ radicals are more stable than ethyl radicals, bond
dissociation would be easier for the t-butyl derivative. The exact
opposite is actually found, leading to the hypothesis that steric
properties must be important.

As the Sn-C bond stretches, the $SnMe_3$ moiety begins to flatten, as
does the $\cdot CMe_3$ group. Methyl group -methyl group interactions must now
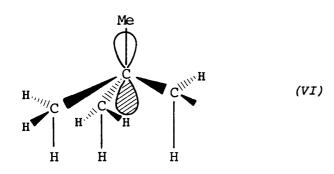occur, resisting further flattening and hence bond dissociation.

Compare this with the (i) Me_3C-Me,[18] (ii) Me_3C-H[18] and (iii)
Me_3C-CMe_3[19] cases. INDO calculations produced by Iwasaki[18] suggest
that the CMe_3 grouping becomes flatter in (i) and (ii) but that in (iii)
it remains pyramidal, as supported by Wang and Williams.[20] The differ-
ence appears to be sterically controlled. Taking a further comparison
to $Me_3Sn-SnMe_3$, where both $SnMe_3$ groups become planar, the phenomenon
is accounted for by considering the extra space caused by the size of
the tin atoms, which relieves methyl-methyl group strain.

CONCLUSION

These results confirm the release of alkyl radicals, which are readily produced when an electron is removed from the molecule, as observed previously in liquid phase mechanistic studies.[15]

It is interesting to compare results obtained for cations of Me_4Sn and Me_4C. Both form a C_{3v} type structure but the former utilises a unique methyl group and the latter produces the SOMO shown in VI.

(VI)

The SOMO[21] exhibits a strong coupling to a single proton from each of 3 methyl groups giving $A(^1H) = 42\,G$ with a negligible contribution from the fourth methyl group. The magnitude of the proton couplings being the distinctive feature with which to separate the two structures.

REFERENCES

1. S. A. Fieldhouse, A. R. Lyons, H. C. Starkie and M. C. R. Symons, J. Chem. Soc., Dalton Trans., 1966 (1974).

2. R. V. Lloyd and T. M. Rogers, J.A.C.S., 95, 2459 (1973).

3. M. C. R. Symons and I. G. Smith, J. Chem. Res. (S), 382 (1979).

4. M. Iwasaki, K. Toriyama and K. Nunome, J.A.C.S., 103, 3591 (1981).

5. T. Kato and T. Shida, J.A.C.S., 101, 6869 (1979).

6. M. C. R. Symons, J. Chem. Soc., Chem. Comm., 1251 (1981).

7. M. C. R. Symons, J. Chem. Soc., Chem. Comm., 869 (1982).

8. A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi and M. C. R. Symons, J. Chem. Soc., Chem. Comm., 1199 (1983).

9. B. W. Walther, F. Williams, W. Lau and J. K. Kochi, Organometallics, 2, 688 (1983).

10. B. W. Walther and F. Williams, J. Chem. Soc., Chem. Comm., 270 (1982).

11. C. L. Wong and J. K. Kochi, J.A.C.S., 101, 5593 (1979).

12. R. J. Klinger and J. K. Kochi, J.A.C.S.,

13. J. K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York (1978), Part III.

14. S. Fukuzumi, K. Mochida and J. K. Kochi, J.A.C.S., 101, 5961 (1979).

15. S. Fukuzumi, K. Mochida and J. K. Kochi, J. Phys. Chem., 84, 2246 (1980).

16. A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M. C. R. Symons and J. Rideout, J. Chem. Soc., Dalton Trans., 1667 (1984).

17. M. C. R. Symons, M. M. Aly and J. L. Wyatt, J. Chem. Soc., Chem. Comm., 176 (1981).

18. K. Toriyama, K. Nunome and M. Iwasaki, J. Chem. Phys., 77, 5891 (1982).

19. J. T. Wang and F. Williams, J. Phys. Chem., 84, 3156 (1980).

20. B. W. Walther and F. Williams, J. Chem. Soc., Chem. Comm., 270 (1982).

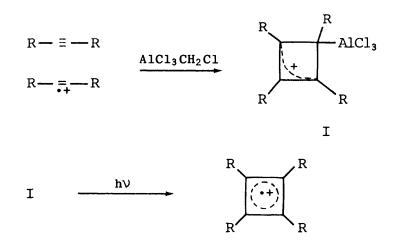21. M. Iwasaki, K. Toriyama and K. Nunome, Radiat. Phys. Chem., 21, 147 (1983).

CHAPTER
10

Acetylenes

INTRODUCTION

The cations of a range of unsaturated hydrocarbons have been prepared by radiolysis in $CFCl_3$ and studied by e.s.r. spectroscopy. The most systematic study is that of Shida and coworkers.[1] Radical cations of dienes have been extensively studied, the cyclobutadienes attracting a great deal of interest. The cyclobutadiene cations have been prepared by the method of Driessen and Hogenveen,[2] using $AlCl_3$ in $CHCl_3$, followed by photolysis to oxidise acetylenes.

$$R—\equiv—R$$

$$R—\underset{\bullet+}{=}—R \qquad \xrightarrow{AlCl_3 CH_2Cl}$$

I

$$I \qquad \xrightarrow{h\nu}$$

Another vital work concerning unsaturated cations is that performed by Shiotani et al.[3] on alkene cations. This work is summarised in the Chapter on simple esters within this thesis and concerns the 'twisting' of alkene cations producing different spectra from the same cation.

However, only one short piece of work has been performed to produce the cation radical of an alkyne. Shiotani claims to have produced the cation of $Me-C \equiv C-Me$ in $(CFCl_2)_2$.[4]

The 'freon system' seemed ideal for this potentially interesting group of cations, where electron loss is expected to occur from one of the two degenerate π-orbitals.[5] It was undertaken to study a range of alkynes, some of which were kindly supplied by Professor A. G. Davies.

RESULTS

All alkynes produced very broad, poorly defined spectra when irradiated at 77 K in $CFCl_3$ matrices. Even X-irradiation at 4 K failed to give any spectra which could usefully be interpreted.

The results obtained upon warming to temperatures ca. 150 K were in complete contrast.

The results for but-2-yne serve as a useful example. The spectrum observed (Fig. 1) consists of a 13-line pattern of binomial intensity, with a hyperfine splitting of 8.7 G due to 12 protons. This species is undoubtedly the tetramethyl cyclobutadiene radical cation, as observed previously by A. G. Davies.[6]
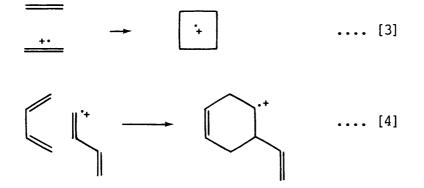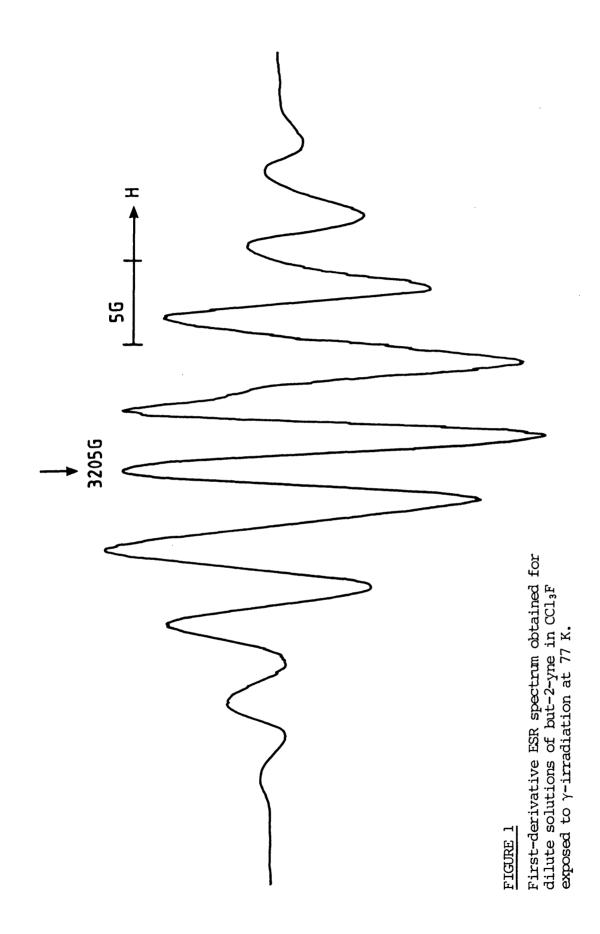

This is a similar cyclisation reaction to that proposed by Ledwith and Bauld[8] in which an alkene or a diene react with an alkene cation to give the cyclobutane or cyclohexene cations respectively.

It seems that the alkyne cation is formed during radiolysis but gives no well-defined e.s.r. spectrum. It migrates through the matrix to react with a parent alkyne molecule. To check this hypothesis, more concen-

FIGURE 1

First-derivative ESR spectrum obtained for
dilute solutions of but-2-yne in CCl₃F
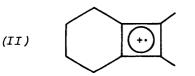exposed to γ-irradiation at 77 K.

trated solutions were used, producing evidence of dimerisation at lower temperatures. Also used were a number of cyclic diynes such as I (2,8-deca diyne).
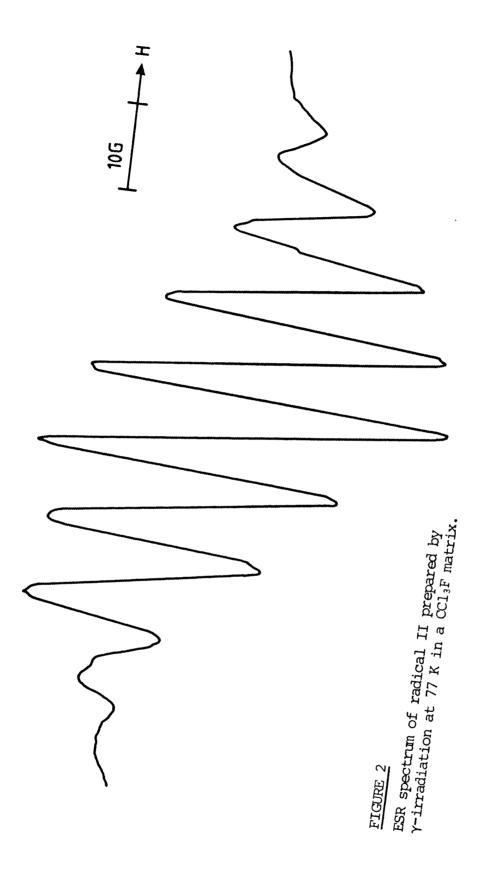

(I)

These molecules produced an effectively high concentration of alkyne, with one alkyne centre always being very near another. Therefore, upon formation of a cation at one, the second alkyne is always close enough to cyclise without the need for higher temperatures aiding diffusion. This is more favourable than using higher concentrations of monoalkynes, since the basic radiation chemistry of the system often changes when the substrate concentration is increased.

Results obtained from the deca 2,8-diyne are typical of those found for the cyclic diynes. Consisting of a set of 11 broad lines of $A(^{1}H)$ 8.8. These results agree well with those found by Davies et al. for the same species[6] in the liquid phase. They are assigned to cation II, spectra for which are shown in Figs. 2 and 3.
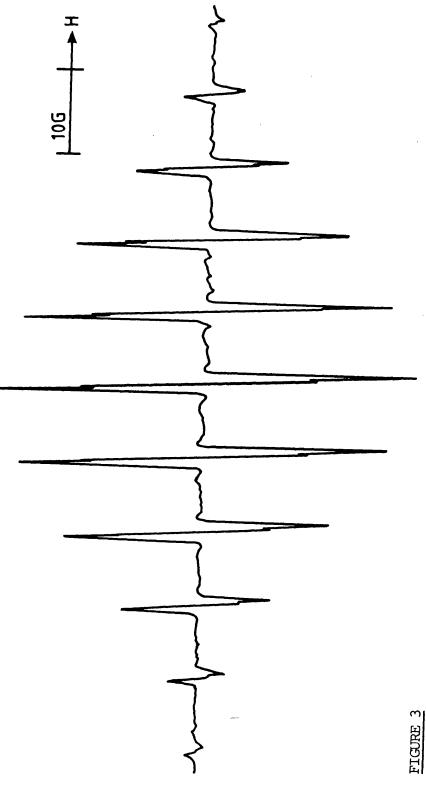

(II)

DISCUSSION

Several alkynes have been studied using this 'freon technique'. The low temperature spectra (down to 4 K) were very broad and inconclusive, although it is almost certain the species responsible are the parent cations. The poor quality of the spectra is probably to do with the expected high g-anisotropy of these species.

FIGURE 2

ESR spectrum of radical II prepared by
γ-irradiation at 77 K in a CCl$_3$F matrix.
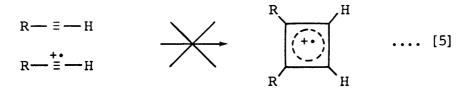
10G

H

FIGURE 3

ESR Spectrum of radical II prepared by the method
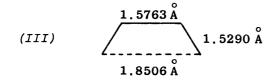of Driessen and Hogenveen in CH_2Cl_2.

Such linear molecules are not expected to distort according to Jahn-Teller theory. Hence the two degenerate π-orbitals do not become significantly perturbed, the two π-type orbitals remaining very close in energy. Hence, the orbital angular momentum is poorly quenched. Therefore, large g-shifts are expected, similar to those occurring in the cases of hydroxyl radicals and O_2 ⁻ radicals.

In the case of but-2-yne and other alkynes, the inability to observe the spectrum of the cations results from the fact that the degeneracy, which might have been expected to have been removed by the fixed orientation of the alkyl groups, leads to the considerable g-anisotropy. These results lead to an interesting question. Is the [2π + 1π] cyclo-addition of an alkyne cation and an alkyne non-synchronous? The answer for the alkene and diene cases has been probed by Bauld et al.[11] for the [2π + 1π] cycloaddition between an alkene cation and an alkene. With the conclusion, drawn from MNDO and MINDO/3 calculations, that this symmetry forbidden cycloaddition occurs in a non-synchronous manner.
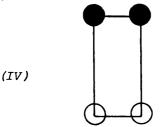
It is curious that both in the results obtained by ourselves and Davies[6,10,11] no terminal alkyne has produced a dimer (Eqn. 5) detected by e.s.r.
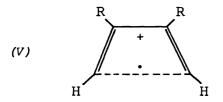

.... [5]

A possible answer lies in the structure proposed by Bauld for the cyclobutane cation radical formed from alkene cation – alkene cyclo-addition. The cyclobutane cation is proposed to have a single long bond III.

1.5763 Å

1.5290 Å

1.8506 Å

It is also suggested the cation of cyclobutane formed in freon has a

$^2B_3$ state with two long and two short bonds, hence forming a rectangular cation IV.[12]

(IV)

Perhaps the different mode of formation is the governing factor here.

If the alkynes were to form in the $[2\pi + 1\pi]$ manner, it is possible a form of the cation could be V, there being greater ring strain in the

R   R

+

·

(V)

H   H

cyclobutadiene than in the cyclobutane. The radical formed from 'terminal' alkynes being less stable than that formed with four alkyl substituents.

It remains to be said, however, that Shiotani[4] has recently reported the detection of the cation of but-2-yne, prepared in $CF_2Cl-CFCl_2$. As yet we have been un able to confirm or refute this assertion.

In conclusion it seems that the spectra obtained for the first formed species of the alkyne solutes must be attributed to the parent cations. As yet the exact analysis of these has eluded us.

TABLE

Acetylenes Irradiated at 77 K in Freon Matrices

Acetylene Derivative	Radical Formed	
	77 K	Anneal
H – C ≡ C – H	Unclear	Unclear
Me – C ≡ C – H	"	"
Me – C ≡ C – Me	"	Dimer
Et – C ≡ C – Et	"	Dimer
^{n}pr – C ≡ C – ^{n}pr	"	Dimer
+ C ≡ C +	"	$\left[\text{dimer structure} \right]^{\cdot +}$ [a]
ph – C ≡ C – Me	[b]	[b]
ph – C ≡ C – ph	[b]	[b]

[a] Results agree closely with those obtained in the liquid phase (Ref. 11);

[b] SOMO seems to be based in aromatic rings not on acetylene.

REFERENCES

1. T. Shida, Y. Egawa and H. Kubodera, _J. Phys. Chem._ **73**, 5963 (1980).

2. P. B. J. Driessen and H. Hogenveen, _J.A.C.S._ 1193 (1978).

3. Y. Nagata, M. Shiotani and J. Sohma, reported at the 22nd. Japanese ESR Symposium, 1983.

4. M. Shiotani, _J.A.C.S._ **107** (1985).

5. H. Beck and B. G. Ramsey, _Agnew. Chem. Internat. Ed._ **12**, 734 (1973).

6. J. L. Courtneidge and A. G. Davies, _J.C.S. Chem. Comm._ 136 (1984).

7. A. Ledwith, _Acc. Chem. Res._ **5**, 133 (1972).

8. D. J. Bellville, D. D. Wirth and N. L. Bauld, _J.A.C.S._ **103**, 718 (1981).

9. P. G. Gassman and D. A. Singleton, _J.A.C.S._ **106**, 7993 (1984).

10. J. L. Courtneidge, A. G. Davies, S. Tollerfield, J. Rideout and M. C. R. Symons, _J.C.S. Chem. Comm._ in press.

11. J. L. Courtneidge, A. G. Davies, E. Lusztyle and J. Lusztyle, _J.C.S. Perkin Trans. 2_ 155 (1984).

12. N. L. Bauld, D. J. Bellville, R. Pabon, R. Chelsky and G. Green, _J.A.C.S._ **105**, 2378 (1982).

13. K. Ohta, H. Nakatsuzi, K. Kubodera and T. Shida, _J. Chem. Phys._ **76**, 271 (1983).

Selected Radical Cations: An E.S.R. Study

Jan Rideout

ABSTRACT

This thesis is concerned with a process which has become commonly used. Producing radical cations specifically for observation at reduced temperatures within the X-band electron spin resonance spectrometer cavity.

Gamma irradiation is used to cause electron addition and electron loss centres in a CCl_3F matrix. These damage centres can be passed to solutes by the processes outlined below:-

$$CCl_3F \xrightarrow{\gamma} CCl_3F^{\cdot +} + e^-$$

$$CCl_3F + e^- \longrightarrow CCl_3F^{\cdot -}$$

$$CCl_3F^{\cdot +} + CCl_3F \longrightarrow CCl_3F + \boxed{CCl_3F^{\cdot +}}$$

$$CCl_3F^{\cdot +} + S \longrightarrow CCl_3F + \boxed{S^{\cdot +} \; Trapped}$$

$$CCl_3F^{\cdot -} \longrightarrow \boxed{CCl_2F^{\cdot} \; Trapped} + Cl^-$$

Various functional groups have been investigated. A variety of groups have been chosen to attempt to show a great many of the effects, which cause a molecule to produce interesting e.s.r. spectra. Effects ranging from the 'solvent adducts' investigated in Chapter 2, to the Breit-Rabi distortions encountered by the cations of dialkyl mercurials.

Attempts have also been made to clarify one or two areas of radical cation chemistry which have caused contention in the current literature. Such areas are those outlined in Chapters 3, 4 and 5 with ester groupings and Chapter 7 with oxirane cations.