Radical Cations in Condensed Phases

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1 Introduction

This Review was inspired by a series of recent e.s.r. studies of radical cations formed by radiolysis of rigid solutions at low temperature. Many novel cations have been prepared by this technique, and much new structural information has been forthcoming. The work is complementary to similar e.s.r. studies of radical anions in rigid solutions, also prepared by ionizing radiation.[1] Curiously, techniques for preparing these anions were developed some years before the development of methods for preparing the cations, whereas in other branches of Chemistry, far more is known about radical cations than radical anions.

Most of this information stems from radical cations generated in the gas phase, the two most significant techniques being mass spectroscopy and photoelectron spectroscopy (PES). The latter technique generates information on the 'hot' cations formed by 'vertical' electron loss, and vibrational features in the spectra give information on the modes involved in relaxation to the ground-state configuration of the cation. In contrast, the condensed-phase studies give information on the long-term ground-states of these cations or their rearranged products.

Very recently there have been exciting new developments in the study of cations in the gas phase, which promise to give very detailed rotational and vibrational spectroscopic information.[2,3] Space limitations are such that I cannot cover the solid-state work adequately if I give room to these other areas. Indeed, they are well covered in a major new book,[2] which does not in fact deal with the topics discussed in the present review.

Gas-phase results, particularly by PES have inspired very extensive theoretical studies of radical cations. In most cases these are necessary for a proper interpretation of the PES spectra. Thus the e.s.r. spectroscopist studying radical cations is entering an already well trodden field. Nevertheless, the detailed information provided by this technique about the SOMO in particular extends and sharpens our knowledge. My major aim is to bring this new information to more general notice.

The preparative procedure with which I am primarily concerned involves the use of ionizing radiation and low-temperature matrixes. To those who are interested in radical cations but unfamiliar with these procedures, let me stress that they are really quite simple tools which are utilised because they do an efficient job.

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[1] M. C. R. Symons, *Pure Appl. Chem.*, 1981, **53**, 223.

[2] 'Molecular Ions: *Spectroscopy, Structure and Chemistry*, ed. T. A. Miller and V. E. Bondybey, North-Holland, Amsterdam, 1983.

[3] M. I. Lester, B. R. Zegarski, and T. A. Miller, *J. Phys. Chem.*, 1983, **87**, 5228.

2 Preparative Procedures

Only relatively stable radical-cations have been studied in the liquid-phase by e.s.r. spectroscopy. These are usually prepared by conventional techniques including redox chemistry, electrolysis, or photolysis. For example, various aromatic cations were prepared in sulphuric acid or related acidic media many years ago.[4-6] Norman, Gilbert, and their co-workers have used the Ti^{III}–H_2O_2 system as a source of $\cdot OH$ radicals which will sometimes extract electrons from good electron donors, either directly or indirectly. The resulting radical-cations may not be detected directly by e.s.r. spectroscopy,[7] but secondary products, such as $(Me_2S)_2{}^+$,[8] formed from $Me_2S\cdot^+$ cations, may be sufficiently stable for e.s.r. study. Similarly, electrolysis has been used most effectively by Roberts and his co-workers to prepare $(R_3P)_2{}^+$ cations, formed from the undetectable $R_3P\cdot^+$ ions.[9] To leave room for recent solid-state developments, I do not dwell on these procedures here.

Two different techniques are used for solid-state studies. One, recently developed by Knight and his co-workers,[10, 11] involves photoionization of the substrate in the gas-phase at the site of deposition on a rare-gas matrix at *ca.* 4 K. The fate of the ejected electrons in these experiments is not clear, but good e.s.r. spectra for a range of radical-cations have been forthcoming. It seems that this procedure is very good for preparing small cations such as H_2O^+, $NH_3{}^+$, and $CH_4{}^+$, but probably less satisfactory for preparing larger cations. It may therefore prove to be complementary to the second technique described below.

The second technique utilises *X*- or γ-rays rather than ultraviolet light, and the solid matrix is irradiated rather than substrate molecules in the gas-phase.

In some cases, it is satisfactory simply to irradiate the pure compounds as crystalline solids. Ideally, this gives electron-loss and electron-gain centres well separated from each other, examples being the formation of $NO_3\cdot$ and $\cdot NO_3{}^{2-}$ from $NO_3{}^-$ in nitrates of $[Mn(CO)_x hal]^+$ and $[Mn(CO)_x hal]$ from $Mn(CO)_5 hal$ crystals.[12] However, in other cases, electron-return dominates, with consequent 'photolysis' as the main source of radicals, and in many others the electron-gain and -loss centres react with neighbouring molecules. Thus the majority of radical cations described below are not detected when the pure substrates are irradiated.

Some years ago, we helped to develop a technique for preparing specific electron-gain or electron-loss centres from ionic substrates using doped salts. Thus, for example, $CaCO_3$ doped with $NO_3{}^-$ ions gave $\cdot NO_3{}^{2-}$ ions,[13] or $CaSO_4$ doped with $PO_4{}^{3-}$ gave $PO_4{}^{2-}$.[14] This technique has the great advantage that single

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[4] S. I. Weissman, E. de Boer, and J. Conradi, *J. Chem. Phys.*, 1956, **26**, 963.

[5] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Am. Chem. Soc.*, 1970, **92**, 412.

[6] R. Hulme and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 446.

[7] B. C. Gilbert, R. O. C. Norman, and P. S. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1980, 647.

[8] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748.

[9] W. B. Gara and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1975, 949.

[10] L. B. Knight, J. M. Bostick, R. W. Woodward, and J. Steadman, *J. Chem. Phys.*, 1983, **78**, 6415.

[11] L. B. Knight and J. Steadman, *J. Chem. Phys.*, 1983, **77**, 1750.

[12] O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 1329.

[13] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 790.

[14] S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc.* (*A*), 1970, 1239.

crystals can be used. It has been extended recently by Morton and Preston and their co-workers,[15,16] and Ammeter *et al.*[17] to the use of $Cr(CO)_6$ single crystals doped with neutral molecules.[15,16] Here neutral rather than charged substrates can be used, but there seems to be some uncertainty as to whether a given solute will form its cation or its anion on irradiation. To what extent this approach can be extended beyond the field of transition-metal carbonyls is not yet clear.

The technique highlighted in this Review, however, is one in which certain solvents, notably fluorotrichloromethane, $CFCl_3$, (freon) are used. The key to understanding their utility lies in equations (1)—(4).

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

$$CF_3Cl_3 + e^- \longrightarrow (CFCl_3)^- \longrightarrow Cl^- + \cdot CFCl_2 \tag{2}$$

$$(CFCl_3)^+ + CFCl_3 \longrightarrow CFCl_3 + (CFCl_3)^+ \tag{3}$$

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

Ejected electrons (1) are rapidly scavenged by the solvent molecules (2), but solvent cations are mobile *via* electron transfer (3) until they meet a solute molecule, S. Provided the ionization potential of S is less than that for $CFCl_3$ (*ca.* 11.9 eV) reaction proceeds. However, as shown later, sometimes there is weak bonding between one solvent molecule and S, the 'hole' being shared between them $(Cl_2FCCl---S)^+$. In a few cases, it has been possible to prepare cations from substrates with ionization potentials >11.9 eV by using solvents such as SF_6 or C_2F_6. However, no-one has yet prepared small protic cations such as H_2O^+ or $CH_4{}^+$ by this method.

Before proceeding to the heart of this Review, which is primarily concerned with the results obtained from freon and related solvents, I should mention another method developed some years' ago, namely the use of sulphuric or phosphoric acids as solvents for the radiolytic generation of radical cations. The basis of the method is summarized in equations (5)—(7).

$$HSO_4{}^- \xrightarrow{\gamma} HSO_4\cdot + e^- \tag{5}$$

$$HSO_4\cdot + S \longrightarrow HSO_4{}^- + S^+ \tag{6}$$

$$\text{or} \quad HSO_4 + SH^+ \longrightarrow H_2SO_4 + S^+ \tag{7}$$

Generally, reaction only occurs on annealing, the HSO_4 radicals being rigidly trapped at 77 K. In some cases, electron transfer occurs (6) and, in others, hydrogen atom transfer seems to be favoured (7).

This technique is of less value than the 'freon' method, and the majority of cations prepared in freon and related solvents do not seem to form in sulphuric (or phosphoric) acid. However, it has the advantage that compounds soluble in these acids are sometimes either insoluble in freon, or dissolve as dimers or as aggregates therein. Since it is essential to have only monomers in solution, this makes the acid media advantageous at times.

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[15] J. A. Howard, J. R. Morton, and K. F. Preston, *Chem. Phys. Lett.*, 1981, **83**, 226.

[16] T. Lionel, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1982, **76**, 234.

[17] J. H. Ammeter, L. Zoller, J. Bachmann, P. Baltzer, E. Gamp, R. Bucher, and E. Deiss, *Helv. Chim. Acta*, 1981, **64**, 1063.

Examples of the successful generation of radical cations in acidic glasses include $R_3N\cdot^+$ from R_3NH^+ ions,[18] $R_3P\cdot^+$ from R_3PH^+ ions,[19,20] uracil cations, probably from the parent molecules,[21] and $(H_2CO)^+$ cations from H_2CO.[22] Also, the π-cations $(RSSR)^+$ are formed in good yield by this procedure,[23] as can be judged from Figure 1, but this is not a good general procedure for preparing radical cations.

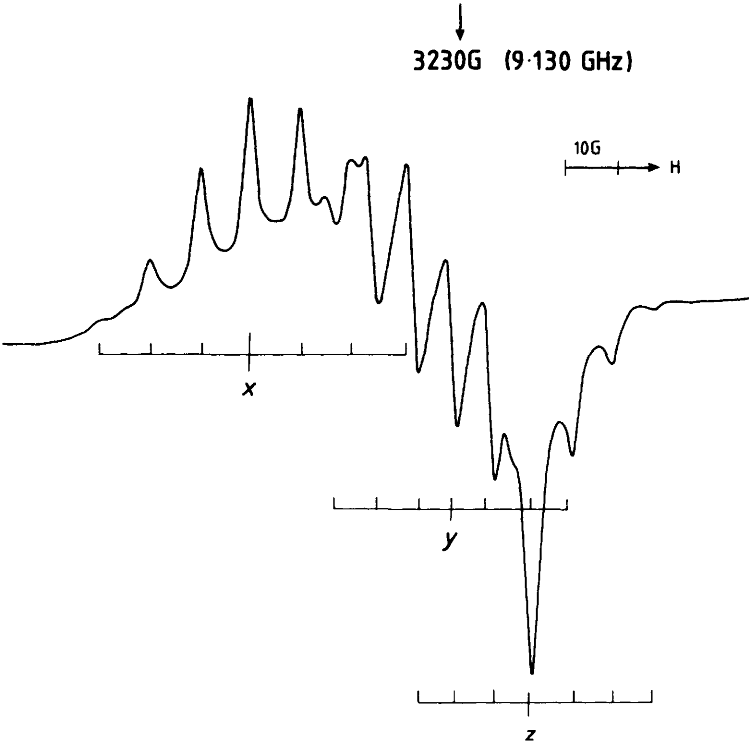

Figure 1 *First derivative X-band e.s.r. spectrum from dimethyl disulphide in* 6M-D_2SO_4-D_2O *after exposure to* ^{60}Co γ*-rays at* 77 K, *and annealing until features for* $SO_4\cdot^-$ *and* $\cdot SO_3^-$ *were lost showing features assigned to* MeS–SMe$^+$ *radicals.* [*From Ref.* 23] *This shows that good radical cation spectra have been obtained in early studies. It also illustrates the complexities of anisotropic solid-state e.s.r. spectra*

In the following sections, some of the results so far obtained are described. Analysis of the e.s.r. spectra is not easy, as can be judged from that in Figure 1, but since there is no room here for detailed explanations, I am afraid that published analyses have to be accepted herein.

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[18] M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1973, 797.

[19] G. W. Eastland and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1977, 833.

[20] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290.

[21] H. Riederer and J. Hüttermann, *J. Phys. Chem.*, 1982, **86**, 3454.

[22] S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1975, 909.

[23] R. L. Petersen, D. J. Nelson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1978, 225.

3 Alkane Cations

The first alkane cation to be studied by e.s.r. spectroscopy was the hexamethylethane cation $(Me_3CCMe_3)^+$.[24] Hexamethylethane was selected for this study with some care, since there had been many previous unsuccessful attempts to study alkane cations by e.s.r. spectroscopy. It was thought that the $C_2H_6{}^+$ cation would probably lose a proton to almost any medium to give $C_2H_5\cdot$, and that such proton loss would normally be rapid even at low temperatures. Also, because the methyl groups are equivalent, the e.s.r. spectrum for $Me_3CCMe_3{}^+$ should be relatively simple in comparison with most other alkane cations. It was predicted that the 'hole' would be considerably confined to the central C–C σ-bond which would therefore stretch, with concomitant partial flattening of the two $-CMe_3$ units, and that ^1H coupling would arise *via* hyperconjugation.

These conclusions have, after some criticism and scepticism, been largely accepted and confirmed. However, although proton loss is indeed facile, especially for $C_2H_6{}^+$,[25] it does not occur readily at very low temperatures in fluorinated solvents. Furthermore, because many of the protons in alkane cations interact very weakly with the unpaired electron, the e.s.r. spectra for alkane cations turn out to be far simpler than had been supposed. Following the publication of our study of $(Me_3CCMe_3)^+$ cations, Iwasaki and his co-workers initiated a very thorough and most perceptive study of a wide range of alkane cations, and it is mainly their work that I describe in the following.[25,26] The results are in marked contrast with those for alkyl radicals, for which, to a first approximation, conventional, localized structures (SOMOs) suffice. They show that the unpaired electrons are delocalized in specific MOs, throughout the molecular frame in the same way as they are in normal π-radicals. This may come as a surprise to those of us who were reared on localized σ-bonds, but has long been predicted by MO theory. However, in many cases, there are a range of possible SOMOs and the choice made in these freon systems is often a subtle one. Probably the original conformation of the molecular precursor dictates the selection, but this is also governed by the most favourable mode of relaxation (bond bending or stretching) which may well be influenced by the surrounding solvent molecules.

The Methane Cation.—Attempts to prepare this by the technique of radiolysis have not succeeded, but Knight and his co-workers have been successful using their photolysis procedure described above.[27] They found that the four protons were apparently equivalent even at *ca.* 4 K [$A(^1H) = 54.8$ G], but for $\cdot CH_2D_2{}^+$ cations the results clearly establish that this is due to rapid averaging; the coupling to the two hydrogens being 121.2 G. Thus the static structure has C_{2v} symmetry, as found for the isoelectronic $\cdot BH_4$ radical,[27a] with two hydrogen atoms participating in the

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[24] I. G. Smith and M. C. R. Symons, *J. Chem. Res. (S)*, 1979, 382; M. C. R. Symons, *Chem. Phys. Lett.* 1980, **69**, 198.

[25] K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, 1982, **77**, 5891.

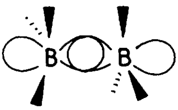
[26] K. Nunome, K. Toriyama, and M. Iwasaki, *J. Chem. Phys.*, 1983, **79**, 2499.

[27] L. B. Knight, J. Steadman, D. Feller, and E. R. Davidson, *J. Am. Chem. Soc.*, 1984, in press.

[27] (*a*) M. C. R. Symons, T. Chen, and C. Glidewell, *J. Chem. Soc., Chem. Commun.*, 1983, 326.

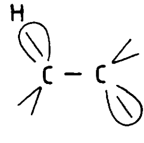
SOMO. This major distortion involves the movement of two hydrogen atoms towards each other, with the unpaired electron (or 'hole') shared between them and the carbon atom, and the movement of the other two hydrogen atoms away from each other within the nodal plane of the electron. It is most interesting that this is still in the fast averaging regime for $\cdot CH_4{}^+$ at *ca.* 4K, but that the isotope effect completely selects one of the distorted structures for $\cdot CH_2D_2{}^+$.

The Ethane Cation.—This cation is isoelectronic with $B_2H_6{}^-$, and these radicals have the choice of two alternative structures, one which is related to the bridged B_2H_6 molecule, with two unique hydrogen atoms, and the other, with all hydrogen atoms equivalent, related to C_2H_6. It is remarkable that the structures have 'inverted', with $B_2H_6{}^-$ having the structure (1)[28,29] and $C_2H_6{}^+$ the structure (2).



$3a_{1g}$

(1)



$4a_g$

(2)

The choice is clearly subtle, and theory has been undecided. Thus, a thorough *ab initio* study suggested that the $3a_{1g}$ structure with a stretched C–C bond, as found for B_2H_6 , should be favoured.[30] Our own *ab initio* calculations on $B_2H_6{}^-$ and $C_2H_6{}^+$ also favoured this distortion.[29] However, the photoelectron spectrum indicated preferential loss from the $1e_g$ orbital.[31] This orbital is degenerate and a Jahn–Teller distortion is expected, lowering the symmetry to C_{2h}, and giving the two orbitals $4a_g$ and $1b_g$. The e.s.r. spectrum, comprising a well defined triplet at 4.2K (Figure 2*a,b*), leaves no doubt that the SOMO is the $4a_g$ orbital and that the Jahn–Teller distortion is fixed. On warming to 77K a seven-line spectrum is formed reversibly (Figure 2*b*). Since free relative rotation of the methyl groups is not expected, Toriyama *et al.* suggest that the distortion, which involves the inward movement of the two in-plane hydrogen atoms (towards the bridging structure), has become dynamic. The fact that the overall splitting remains unchanged shows that the coupling to the remaining four protons is very small indeed. These results have been confirmed using CH_3CD_3 and CD_3CD_3. (There are interesting isotope effects, but these details do not alter the broad conclusions outlined herein.) Ignoring the Jahn–Teller requirement, it is clear that there are two alternative distortions available to the cation – one being primarily a bond-stretching with some flattening of the $-CH_3$ units, and the other being primarily the bending of two

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[28] P. H. Kasai and D. McLeod, *J. Chem. Phys.*, 1969, **51**, 1250.

[29] T. A. Claxton, R. E. Overill, and M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 701.

[30] A. Richartz, R. J. Buenker, P. J. Bruna, and S. D. Peyerimkoff, *Mol. Phys.*, 1977, **33**, 1345.

[31] J. W. Rabalais and A. Katrib, *Mol. Phys.*, 1974, **27**, 923.

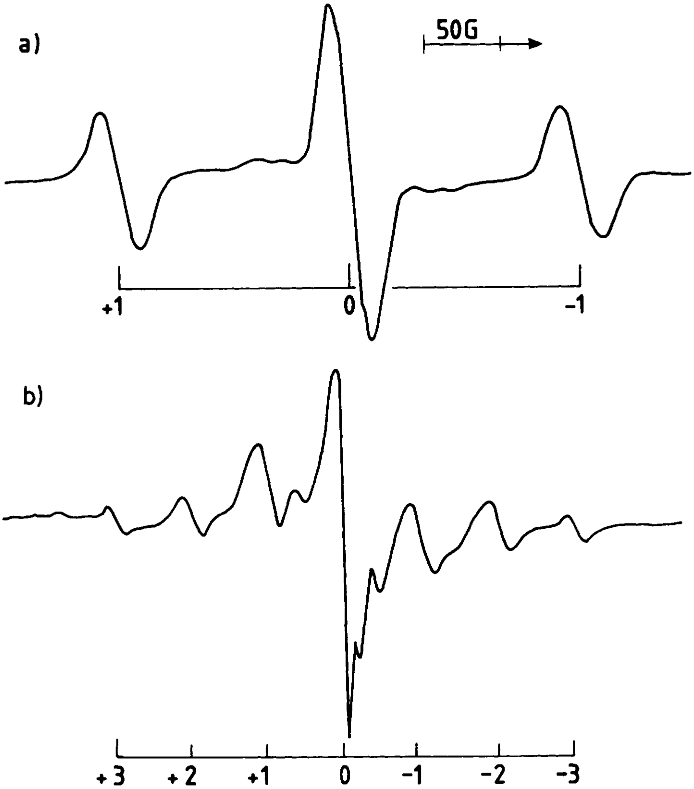
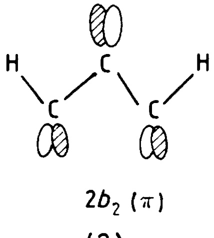


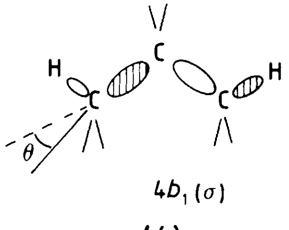
Figure 2 *E.s.r. spectra of* $C_2H_6^+$ *(a) in* SF_6 *irradiated and measured at* 4.2 K; *(b) in* SF_6 *irradiated at* 4.2 K *and measured at* 77 K. *(From Ref.* 25)

bonds, probably also with slight C–H stretching. Just such alternatives have been found in other systems on electron-addition.[1]

The Propane Cation.—Again, there are two predictable structures (3) and (4). The former (3) is in a sense a π-structure, whilst the latter is the expected extension of



(3)

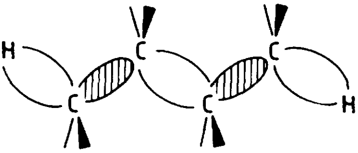


(4)

the $C_2H_6{}^+$ structure. Both have been detected, the π-structure in $CFCl_2CF_2Cl$ and the σ-structure in SF_6. This extraordinary matrix effect is not fully understood as yet.

The $2b_z$ (π) structure is of great interest since it represents a sort of hyperconjugation limit. It can be compared, for example, with the $(R{-}O{-}CH_2O{-}R)^+$ structure considered below, or with the well known cyclohexadienyl structure, with respect to the central CH_2 group. This acquires a high spin-density in all cases, as indicated by the proton hyperfine coupling constants. For the propane cation this is very large for the central CH_2 protons (105.5G) which, as predicted by simple theory is *ca.* twice that for the four outer protons (52.5G).

Other Normal Alkane Cations.—In general, σ-delocalized structures (ethane type) are favoured, the extended structures $H{-}(CH_2)_n{-}H$ having e.s.r. spectra which are dominated by a triplet splitting from the two outermost in-plane protons. A typical orbital is shown in (5) for (n-butane)$^+$. In some cases, outer features were also detected which were assigned to gauche structures and there are again marked solvent effects on their relative concentrations. The reader is referred to the original paper for more details.[25]



(5)

Branched-chain Alkane Cations.—A structural switch occurs for branched-chain alkane cations,[26] the SOMO being localized quite strongly in a stretched C–X bond (X = H or alkyl), as in the alternative structure discussed for $C_2H_6{}^+$. The scales may be tipped by hyperconjugative stabilization which tends to distribute the positive charge amongst several groups. For example, for the cations $(Me_3C{\cdot}H)^+$, $(Me_3C{\cdot}CH_3)^+$ and $(Me_3C{\cdot}CMe_3)^+$ the Me_3C group is thought to flatten considerably, thereby maximizing hyperconjugation and stabilizing the incipient carbocation Me_3C^+. The greater this stabilization, the more the spin-density will move onto the other group. The cation $(Me_3C{\cdot}H)^+$ is remarkable in having the largest proton hyperfine coupling of any known organic radical (251 G). This result shows that there is a remarkably uniform distribution of the electron in this bond. Taking the extensive delocalization onto three of the methyl protons (48.8G) into account, this shows that, within the C–H bond, the electron distribution indeed favours H. The hyperconjugative coupling falls to *ca.* 40G for $(Me_3C{\cdot}CH_3)^+$ which may mean that the valence bond structure $(Me_3C^+ ---{\cdot}CH_3)$ is even more favoured in this case. However, for $(Me_3C{\cdot}CMe_3)^+$ this coupling has fallen to 29G although the spin-density must now be 50% on each Me_3C– group. This can be explained in terms of a reduced flattening of the Me_3C– units caused by steric repulsions between the six methyl groups.

Some interesting trends in the hyperfine coupling constants for *trans* C–H$_\beta$ protons for methylated propane and butane cations are shown in Figure 3,[26] and results for a selection of n- and branched-chain alkane cations are given in Table 1.

Thermal Reactions of Alkane Cations.—One or more bonds are greatly weakened by electron loss, and there is unit positive charge within the radical. The former effect must encourage the breaking of the weakest bonds, especially in those cases in which one bond is mainly involved, as with the branched-chain alkane cations. The latter should favour unimolecular breakdown to give the most stable

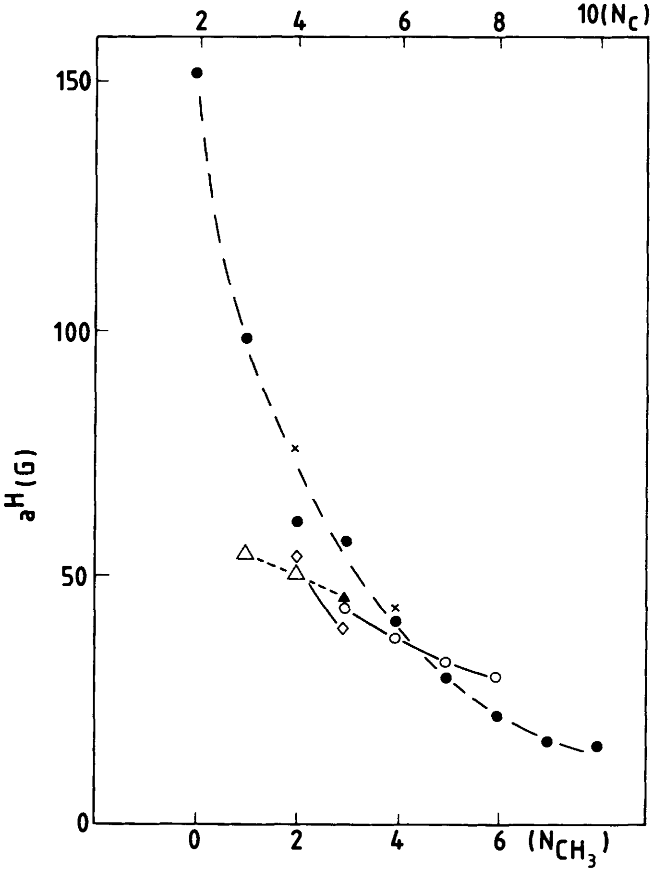


Figure 3 *The dependence of the* trans C–H$_\beta$ *proton coupling constants on the number of* CH$_3$ *groups.* ◇ *methyl-substituted propane radical cations;* ○ *methyl-substituted butane radical cations;* △ *neutral alkyl π radicals;* ● *and* × *the carbon number dependence of the in-plane end* C–H *proton coupling constants in n-alkane radical cations.* (*From Ref.* 26)

Table 1 *The observed hyperfine coupling constants of alkane cations*

Cations	*Matrices*	*Temp.*/K	*H.F. coupling constants*/G
$C_2H_6^+$	SF_6	4	152.5 + 0.5 (2H)
		77	50.3 ± 0.5 (6H)
	C_2F_6	4	153.1 ± 0.5 (2H)
$CH_3CD_3^+$	SF_6	4	140.5 ± 1.0 (1H); 9.0 ± 1.0 (2H) 21.9 ± 0.5 (1D)
$C_2D_6^+$	SF_6	4	23.0 ± 1.0 (2D)
$C_3H_8^+[4b_1]$	SF_6	4	98.0 ± 0.5 (2H)
		77	95.0 ± 0.5 (2H)
$C_3H_8^+[2b_2]$	$CFCl_2CF_2Cl$	4	105.5 ± 1.0 (2H); 52.5 ± 1.0 (4H)
	$CFCl_3$	77	100.0 ± 1.0 (2H); 52.0 ± 1.0 (4H)
$CH_3CD_2CH_3^+[4b_1]$	SF_6	4	98.8 ± 0.5 (2H)
$CD_3CH_2CD_3^+[4b_1]$	SF_6	77	14.8 ± 0.2 (2D)
n-$C_4H_{10}^+$	$CFCl_2CF_2Cl$	77	61.3 ± 0.5 (2H)
	n-C_4F_{10}	77	63.0 ± 0.5 (2H); 8.0 ± 0.2 (4H)
n-$C_6H_{14}^+$	$CFCl_2CF_2Cl$	77	41.0 ± 0.5 (2H)
	$CFCl_3$	77	44.0 ± 0.5 (2H); 4.1 ± 0.2 (8H)
$(CH_3)_3CH^+[11a']$	SF_6	4	58.0 ± 0.5 (2H)
	$CFCl_2CF_2Cl$	4	52.5 ± 1.0 (2H)
	$CFCl_3$	4	55.0 ± 1.0 (2H); 15.0 ± 1.0 (1H)
$(CH_3)_3CH^+[6a_1]$	$CFCl_2CF_2Cl$	77	250.0 ± 1.0 (1H); 47.5 ± 1.0 (3H)
	$CFCl_3$	77	251.2 ± 1.0; (1H); 48.8 ± 1.0 (3H)
$(CH_3)_3CD^+[11a']$	SF_6	4	57.8 ± 0.2 (2H)
	$CFCl_3$	4	54.2 ± 0.5 (2H)
$(CD_3)_3CH^+[11a']$	SF_6	4	unresolved single-line (ΔH_{pp} = 27.0)
	$CFCl_3$	4	8.5 ± 0.5 (2D); 18.0 ± 0.5 (1H)
$(CH_3)_4C^+$	SF_6	4	40.0 ± 1.0 (3H)
	$CFCl_2CF_2Cl$	4	39.8 ± 0.5 (3H)
	$CFCl_3$	4	40.7 + 0.5 (3H)
$(CH_3)_3CC(CH_3)_3^+$	$CFCl_2CF_2Cl$	77	29.0 ± 0.5 (6H)
	$CFCl_3$	77	28.8 ± 0.5 (6H); 3.8 ± 0.2 (12H)

carbocation, or, in the presence of a proton acceptor (B), proton transfer should occur. For example, for $(Me_3C{\cdot}CH_3)^+$ this would lead to (8) or (9). The former is

$$(Me_3C{\cdot}CH_3)^+ \longrightarrow Me_3C^+ + {\cdot}CH_3 \tag{8}$$

$$(Me_3C{\cdot}CH_3)^+ + B \longrightarrow Me_3C\text{–}\dot{C}H_2 + BH^+ \tag{9}$$

not observed. Instead, in the 120—140 K range reaction (10) is detected. I am tempted to suggest that the thermolysis (8) does occur, but that in these solids a

$$(Me_3C{\cdot}CH_3)^+ \longrightarrow (Me_2C{=}CH_2)^+ + CH_4 \tag{10}$$

very efficient cage-back reaction leads to hydrogen abstraction giving the products in (10).

One major reason why these studies of alkane cations have been successful is the very low basicity of molecules such as SF_6 and $CFCl_3$. I suspect that CH_4^+ is so strong an acid that it can protonate these solvent molecules but evidently $C_2H_6^+$ cannot. Nevertheless, an efficient bimolecular proton-transfer can occur, which is presumably transfer to parent alkane molecules (11). Such reactions are well known in the gas-phase, but it is a surprise that alkanes, having no obvious site for

$$RH^+ + RH \longrightarrow R\cdot + RH_2^+ \qquad (11)$$

protonation, are more basic than say $CFCl_3$, for which protonation can be readily formulated! In studies of such proton-transfers the possible rôle of basic impurities such as water must always be borne in mind.

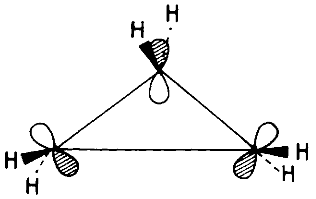
For solvents SF_6 and CF_2Cl–$CFCl_2$, proton transfer (9) occurs before the unimolecular decompositions set in, but for the more rigid $CFCl_3$, these decompositions occur in preference to proton transfer.

Photolysis of Alkane Cations.—It seems probable that most alkane cations have absorption bands in the visible and near i.r. region.[32] Photolysis within these bands for a range of n-alkanes seems to result in the specific formation of but-2-ene cations with the elimination of the corresponding alkane[33] (12). Thus, for example, the n-hexane cation gave the $(2\text{-}C_4H_8)^+$ cation, readily detected by e.s.r.

$$(C_nH_{2n+2})^+ \longrightarrow (2\text{-}C_4H_8)^+ + C_{n-4}H_{2n-6}) \qquad (12)$$

spectroscopy, together, presumably, with ethane. It would be most interesting to follow the course of photolysis of the branched-chain cations for comparative purposes.

Cycloalkane Cations.—Cyclopropane cations have been studied at 77 K by Shida and co-workers[34] and at 4 K by Iwasaki and co-workers.[35] This is another example of a parent cation with a degenerate ground-state which must undergo a Jahn–Teller distortion. The results at 77 K show that this is dynamic, but the hyperfine features were poorly resolved because of the very small average proton coupling. However, at 4 K the distortion is frozen, with two strongly coupled protons (+21 G) and four weakly coupled protons (−12.5 G). The opposite signs are required by the averaging results, and by theory for the $^2A_1$ distortion indicated



(6)

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[32] T. Shida and Y. Takemura, *Radiat. Phys. Chem.*, 1983, **21**, 157.

[33] M. Tabata and A. Lund, *Z. Naturforsch.*, 1983, **38a**, 428.

[34] K. Ohta, H. Nakatsuzi, H. Kubodera, and T. Shida, *Chem. Phys.*, 1983, **76**, 271.

[35] M. Iwasaki, K. Toriyama, and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 1983, 202.

in insert (6). The observed distortion is an elongation of one C–C bond, the SOMO having considerable σ-bond character. The four protons attached to these carbon atoms are in the *p*-orbital nodal surfaces and hence give a negative coupling. Possible alternative distortions, such as $^2B_2$, involving equal stretching of two C–C bonds would give quite different proton coupling constants, according to theory, and can be rejected.

Similar arguments apply to *cyclobutane cations*. Again a distortion must occur, that predicted being the $^2B_3$ state of D_2 symmetry (two stretched C–C bonds giving a rectangular cation). The e.s.r. results show, once again, that this is dynamic at 77 K, the average splitting being 14 G.[34]

For the *cyclopentane cation*, the SOMO is clearly confined to three CH_2 units, with strong coupling to two protons (22.4 G) and weak coupling to the remainder.[34,36] At 77 K the spectrum is a broad 1:2:1 triplet, but the hole moves around the ring rapidly at *ca.* 100 K, all 11 lines being detectable (6.3 G). Thus, the structure is σ rather than π in character, and the ground state is Jahn–Teller distorted. The relatively low values for $A(^1H)$ suggests that the SOMO is largely confined to C–C bonds, presumably in part because 'planar' arrangements favouring delocalization into the C–H orbitals cannot be achieved.

Cyclohexane cations have been widely studied,[34,36,37] the most definitive work being that of Iwasaki and his co-workers.[37] At temperatures ⩾ 140 K the expected Jahn–Teller distortion is dynamic, and six of the twelve protons couple strongly (43 G each). However, at *ca.* 4 K this changes to a set of 13 lines. The results vary somewhat with different matrixes, but they extrapolate to a situation in which there are two strongly coupled protons (103 G) and four equivalent weakly coupled protons (13 G). These results compare well with the values predicted by INDO calculations for the a_g orbital which is the SOMO for the ^2A_g ground state. This orbital is shown in Figure 4 together with the alternative b_g SOMO. There are three equivalent structures having two parallel C–C bonds stretched, and equivalence is achieved when these interconvert rapidly. Further interesting details of this study are also described.[37]

One very interesting feature of these spectra is the large shift in $g_{\parallel}$ (z) (= 2.0111). This shift, which is much greater than is usually observed, was explained in terms of the proximity of the filled b_g level which is coupled by B_z. These results beautifully illustrate the phenomenon of σ-delocalization. I now turn to examples in which more conventional structures can be used, beginning with the alkene cations.

4 Alkene Cations

Although the tetramethyl ethylene cation, $(Me_2C{=}CMe_2)^+$, was studied by e.s.r. spectroscopy many years ago,[38] the only systematic study of alkene cations is that of Shida and his co-workers.[39] However, the most interesting study is of the parent $(C_2H_4)^+$ cation, since the large coupling to four equivalent protons clearly

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[36] M. Tabata and A. Lund, *Chem. Phys.*, 1983, **75**, 379.

[37] K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Soc., Chem. Commun.*, 1984, 143.

[38] R. M. Dessau, *J. Am. Chem. Soc.*, 1970, **92**, 6356.

[39] T. Shida, Y. Egawa, and H. Kubodera, *J. Chem. Phys.*, 1980, **73**, 5963.

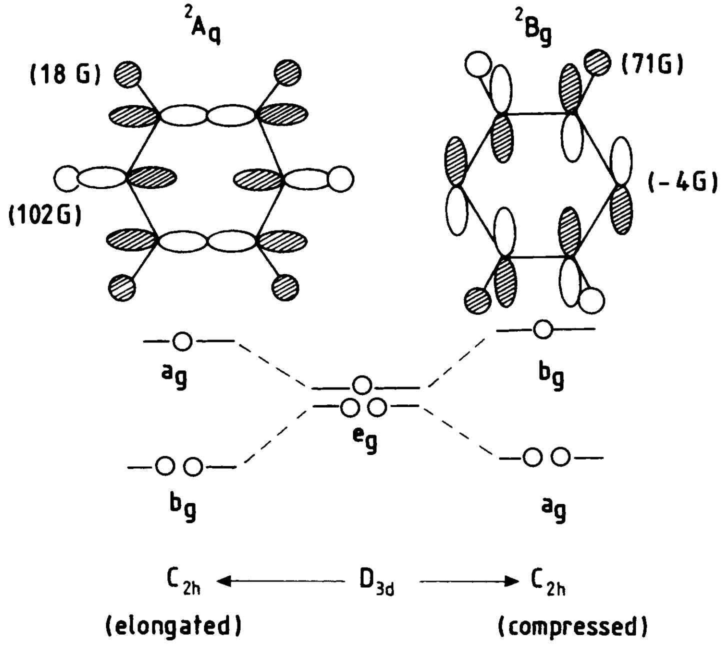

Figure 4 *The SOMOs for the ^2A_g and ^2B_g states of the cyclohexane radical cation*

establishes that this species is twisted.[40] The planar ion is expected to have negative proton couplings in the region of 11 G. However, on twisting, the protons can couple as β-protons as well as α-protons. So the splitting should fall to zero and then become positive, which must be the situation for the large values observed.[40] I cannot say more about the results for $(C_2H_4)^+$ cations since details have not been published. It is interesting to note that in 1947 Mulliken and Roothan predicted a 30° twist for this ion arising because of the hyperconjugative interaction that ensues.[41] Since then there has been considerable controversy about the degree of twisting,[42] and at least one recent calculation has predicted a planar structure.[43]

Results for the methyl-substituted cations were all discussed in terms of planar structures, and seemed to be well accommodated by INDO calculations. They need to be reconsidered now, in terms of possible twisted structures. We have considered the structures of asymmetrically substituted alkene cations and shown that trends in proton coupling constants can be understood in terms of a separation of the charge and the electron. Thus methyl substituents stabilize the 'hole' by electron release so the electron tends to favour the least methylated carbon. For example,

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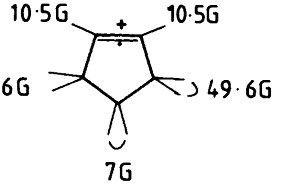
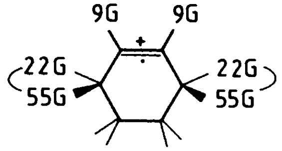
[40] Y. Nagata, M. Shiotani, and J. Sohma, reported at the 22nd Japanese ESR Symposium, 1983.
[41] R. S. Mulliken and C. C. J. Roothan, *Chem. Rev.*, 1947, **41**, 219.
[42] D. J. Bellville and N. L. Bauld, *J. Am. Chem. Soc.*, 1982, **104**, 294.
[43] S. Merry and C. Thomson, *Chem. Phys. Lett.*, 1981, **82**, 373.

for the cation $(H_2C{=}CMe_2)^+$ the valence-bond structure $H_2\dot{C}{-}\overset{+}{C}Me_2$ is favoured. Hence the (H_2C) proton coupling of 14 G is higher, whilst the methyl-proton coupling of 16.5 G is lower, than would be predicted for an even distribution of spin-density.[44]

Cyclic Alkene Cations.—The cation of *cyclopentene* is of interest since, in this case, extensive twisting about the carbon–carbon double bond is unlikely. The results obtained by Tabata and Lund at 110 K are shown in (7).[36] The α-proton coupling of 10.5 G is probably negative, and is in good accord with expectation for a planar cation. Also, for the cyclohexene cation (8) a splitting of (−) 9 G suggests only a small degree of twist.

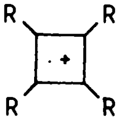


(7)



(8)

Diene Cations.—In the field of diene cations, quite the most interesting development has been the discovery of some persistent cyclobutadiene cations



$R = CH_3$, $MeCH_2$ etc.

(9)

(9).[45,46] The results for cyclohexa-1,4-diene cations are interesting in that there is complete delocalization *via* the two CH_2 groups as evidenced by their large ^1H coupling (67.1 G).[36]

The cation of *cyclopentadiene* is of interest since, at first sight, one might again have expected a large coupling from the bridging methylene protons. However, this is a 3π-electron radical, in contrast with the corresponding radical anion and the well-known cyclohexadienyl radical, which have 5π-electrons. For the 3-electron systems there is a node through the methylene group so these protons cannot participate in the wave-function (10). The results, shown in (10) confirm this conclusion.[39]

So far, there has been no publication dealing with alkyne cations. These are of particular interest in view of the degeneracy of the π-orbitals from which electron

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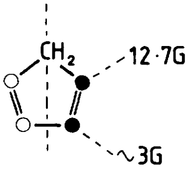
[44] M. C. R. Symons and L. Harris, *J. Chem. Res.*, (*S*) 1982, 268; (M) 1982, 2746.

[45] Q. B. Broxterman, H. Hogeveen, and D. M. Kok, *Tetrahedron Lett.*, 1981, **22**, 173; 1983, **23**, 639.

[46] J. L. Courtneidge, A. G. Davies, and J. E. Parkin, *J. Chem. Soc., Chem. Commun.*, 1983, 1262.

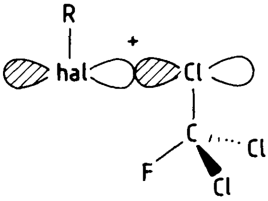


(10)

loss is expected to occur. We have obtained some interesting spectra from MeC≡CMe, but are as yet somewhat uncertain of the correct analysis. However, there is no large *g*-value variation, so it is unlikely that the spectra are due to the undistorted parent cations. The Review continues with various cations having major spin-density on heteroatoms. Carbon-centred radicals with aromatic derivatives are again discussed in Section 14.

5 Alkyl-Halide Cations

Various cations $RCl\cdot^+$, $RBr\cdot^+$ and $RI\cdot^+$ have been prepared in $CFCl_3$,[47] but the results are complicated by the fact that there is weak complexing between these cations and one chlorine atom of a neighbouring $CFCl_3$ molecule (Table 2). We suggest that relatively weak σ^* bonds are formed, as in (11), for example. This



(11)

makes spectroscopic identification easier despite the extra splitting from ^{35}Cl and ^{37}Cl, since the expected degeneracy of the halogen π-orbitals is lifted, and hence the *g*-values are relatively close to 2, and the lines are not greatly broadened. Unfortunately, hyperfine coupling to β-protons is small (*ca.* 10G), whereas it is predicted to be large, at least for one or possibly two protons. This difference reflects the presence of σ bonding, which has been shown in several cases to reduce delocalization within the two components (see Section 11).

Although the chloro- and bromo-cations gave well-defined solvent complexes, no such complex could be detected for iodoalkanes. However, at *ca.* 4K six broad components were detected in the $g = 3.6$ region, and two unresolved broad features were detected at *ca.* $g = 1.2$ and $g = 0.85$. This species is thought to be the parent cation, $RI\cdot^+$ with very weak interaction with solvent molecules. One reason for this

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[47] G. W. Eastland, C. Glidewell, A. Hasegawa, M. Hayashi, S. P. Maj, M. C. R. Symons, and T. Wakabayashi, *J. Chem. Soc.. Faraday Trans. I*, 1984, in press.

Table 2 *E.s.r parameters assigned to alkyl halide cation adducts and dimers*

			g-values			*Hyperfine coupling*[a]	
Host	*Matrix*	*Radical*	$g_{\parallel}$	$g_{\perp}$	*Nucleus*	$A_{\parallel}$	$A_{\perp}$
C_2D_5Br	$CFCl_3$	$[C_2D_5Br \cdots ClCFCl_2]^+$	1.922	2.392	^{79}Br	464	159
					^{81}Br	500	171
					^{35}Cl	57	*ca.* 17
C_2H_5Br	$CFCl_3$	$[C_2H_5Br]_2{}^+$	1.988	*ca.* 2.0	^{79}Br	421	*ca.* 120
					^{81}Br	454	*ca.* 130
C_2H_5Br	CCl_4	$[C_2H_5Br \cdots ClCCl_3]^+$	1.955	2.329	^{79}Br	480	119
					^{81}Br	517	129
					^{35}Cl	68	*ca.* 17
C_2H_5Cl	$CFCl_3$	$[C_2H_5Cl \cdots ClCFCl_2]^+$	2.002	*ca.* 2.0	$^{35}Cl(I)$	110	*ca.* 35
					$^{35}Cl(II)$	85	*ca.* 35
					$^{37}Cl(I)$	92	*ca.* 30
					$^{37}Cl(II)$	71	*ca.* 30
					^{1}H	10	10
C_2H_5Cl	$CFCl_3$	$[C_2H_5Cl]_2{}^+$	2.006	*ca.* 2.0	^{35}Cl	99	*ca.* 35
					^{37}Cl	82	*ca.* 30
C_2H_5Cl	CCl_4	$[C_2H_5Cl \cdots ClCCl_3]^+$	2.003	*ca.* 2.0	$^{35}Cl(I)$	105	*ca.* 35
					$^{35}Cl(II)$	88	*ca.* 35
					$^{37}Cl(I)$	87	*ca.* 30
					$^{37}Cl(II)$	73	*ca.* 30
					^{1}H	7	7
C_2H_5I	$CFCl_3$	$[C_2H_5I]_2{}^+$	1.877	*ca.* 2.1	^{127}I	460	*ca.* 120

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

difference is the greater discrepancy between ionization potentials of RI and $CFCl_3$, and the other is the large spin-orbit coupling energy for $RI\cdot^+$, responsible for the very large *g*-shifts, which needs to be overcome in order to form localized σ- and σ*- bonds to chlorine or fluorine.

At relatively high concentrations, or on annealing, dimer cations $(Rhal\text{–}halR)^+$ were formed. These are also σ* complexes, and are the major electron-loss centres formed on irradiating pure halogenoalkanes.[48] The tendency to form such σ* dimers is very marked for all but first-row radicals provided the SOMO of the electron-loss centre and HOMO of the parent cation are not extensively delocalized.

Much more work has been directed towards oxygen- and sulphur-centred radicals, which are now discussed.

6 Alcohol and Ether Cations

Unfortunately, our attempts to prepare alcohol radical-cations by this procedure have failed. This is because of extensive hydrogen bonding giving dimers or clusters of alcohol molecules in the frozen solutions. Infrared studies show that even in the most dilute solutions suitable for cation studies, there is extensive hydrogen bonding, and on radiolysis reactions of type (13) predominate, only the radicals $R_2\dot{C}OH$ being detected by spectroscopy. It may well be that at least $CH_3\dot{O}H^+$

$$(R_2CHOH)_2 \longrightarrow e^- + R_2\dot{C}OH + R_2CHOH_2{}^+ \qquad (13)$$

will prove to be suitable for study by the matrix-isolation technique developed by Knight and his co-workers.

In contrast, ether cations, never previously detected by e.s.r. spectroscopy, have now been widely studied in freon matrices.[49-51] Some results are summarized in Table 3. The most noteworthy aspect is the magnitude of the β-proton hyperfine coupling. For $Me_2O\cdot^+$ cations, this is *ca.* 43 G. This can be compared with values for $Me_2\dot{C}H$ (*ca.* 26G), $Me_2\dot{N}H^+$ (*ca.* 37G), or $Me_2\dot{N}$ (27.4G). These increases accord well with the simple picture of hyperconjugation involving, primarily, electron donation from the C–H σ-orbitals towards the central atom rather than electron donation from the central atom into the C–H σ*-orbital (see Figure 5). In passing, I call attention to one of the major e.s.r. puzzles of recent years. The radical $Me\dot{O}$, trapped in solid methanol at 4K, exhibits an average proton hyperfine splitting of 52G.[52] This accords with results for ether cations. However, this coupling for MeO• radicals in the gas-phase is calculated to be 23.2G, after correcting for orbital magnetic contributions.[53] Theory cannot be relied upon to select a correct value, nor has there yet been any explanation for the

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[48] S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1492.

[49] H. Kubodera, T. Shida, and K. Shimokoshi, *J. Phys. Chem.*, 1981, **85**, 2583.

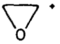
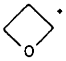
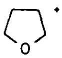
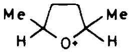
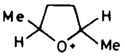
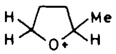
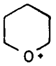
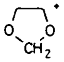
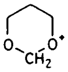
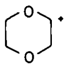
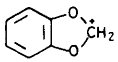
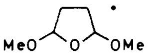
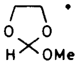
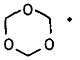
[50] J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1981, **103**, 6994; L. D. Snow, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 2602.

[51] M. C. R. Symons and B. W. Wren, *J. Chem. Soc., Chem. Commun.*, 1982, 817.

[52] M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, 1978, **100**, 1964.

[53] H. E. Radford and D. K. Russell, *J. Chem. Phys.*, 1977, **66**, 2222; 1980, **72**, 2750.

Table 3 *E.s.r. parameters for ether radical cations*

Cation	*Proton hyperfine coupling* (G)[a]	
(CFCl$_3$ *solvent*)	β-H	γ-H
$Me_2O^{\cdot+}$	43 (6 H), 43[b] 43.6, 42.8, 42.5[c]	
$Et_2O^{\cdot+}$	68.7 (4 H)	
$(Me_2CH)_2O^{\cdot+}$	45[d]	
	16 (4 H)	
	64 (4 H)	11 (2 H)
	89 (2 H), 40 (2 H) 89 (2 H), 40 (2 H)[b] 59 (2 H), 22 (2 H)[c]	
	97 (2 H)[b]	
	95 (1 H), 35 (1 H)[b]	
	83 (1 H), 42 (2 H) 78 (1 H), 49 (2 H) (146 K)[b]	
	34.5 (2 H), 14 (2 H)	11 (2 H), 3 (2 H)
	–OCH$_2$O– β-protons	Other β-protons
$MeOCH_2OMe^{\cdot+}$	136.1 (2 H)	31.3 (2 H), 6.0 (4 H)
$MeOCH_2CH_2OMe^{\cdot+}$	*ca.* 10 (10 H)	
	153 (2 H) 153 (2 H)	11 (4 H) 11.2 (4 H)
	140 (2 H$_{av}$) 140.6 (2 H)	26 (2 H), 12.5 (2 H) 26.3 (2 H), 12.4 (2 H)[f]
	11 (4 H), 8 (4 H)	
	22.4 (2 H)	5.0 (2 H, aromatic)
	135 (2 H)	32 (2 H)
	*ca.* 150 (1 H)	
	162 (2 H$_{av}$) 160.2 (2 H)	23 (1 H), 11 (1 H)

[a] G = 10^{-4} T. [b] *Ref.* 49. [c] *Ref.* 50. [d] Tentative. [e] D$_2$SO$_4$ solvent. [f] *Ref.* 56.

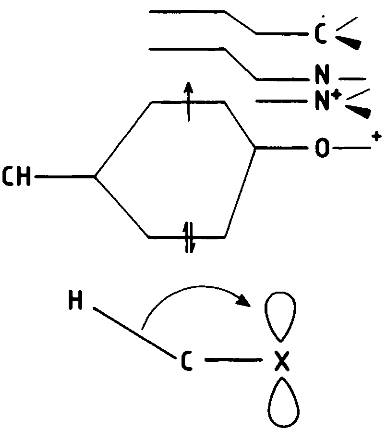
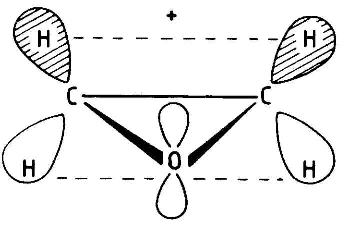


Figure 5 *Qualitative scheme showing why electron donation from a* C–H *σ-orbital in the optimum orientation increases on going from* C *to* O

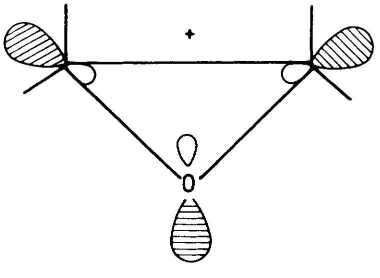
difference. From a qualitative viewpoint, I wonder if the difference lies in the fact that orbital motion is quenched for the radical in methanol, but not in the gas-phase. Does this orbital motion inhibit hyperconjugative interaction?

Some interesting facets of the results for ethers include the change from axial (2H, 89G) and equatorial (2H, 40G) coupling of the four β protons in the THF cation to an average value (4H, 64.5G) on annealing, giving an activation energy of *ca.* 1.65 kcal mol ^{1}.[49] Both axial and equatorial protons are strongly coupled. However, for the tetrahydropyran (oxacyclohexane) cation, the couplings are greatly reduced (34.5G and 15G). We suggest that, in this case, the conformation has changed so that the total overlap has been reduced.[54,55]

Results for the four-membered ring (oxetane) cation were normal, with four equivalent β-protons having A = 64G. However, the three-membered ring (oxirane) cations had four equivalent protons with greatly reduced coupling (16G).[54,55] This result eliminates the normal π-structure (12) (b_1). We originally



(12)



(13)

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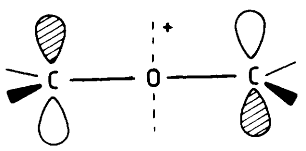
[54] M. C. R. Symons and B. W. Wren, *Tetrahedron Lett.*, 1983, **24**, 2315.

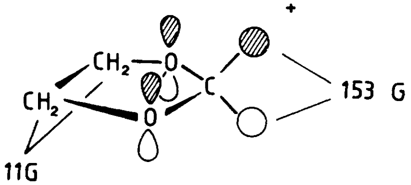
[55] M. C. R. Symons and B. W. Wren, *J. Chem. Soc., Perkin Trans. 2*, 1984, 511.

suggested the alternative σ-structure, (13) (a_1), with a stretched C–C bond, since this should exhibit greatly reduced proton coupling constants.[54] However, it seems that ring opening to form the allyl-type radical (14) is more probable.[56,57] This certainly fits the spectrum satisfactorily, and accords well with current theory,[37] but, at present, no clear distinction can be made.

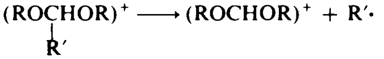
All three groups discovered independently that the $-O-CH_2-O-$ protons of acetal cations such as (15) exhibit unusually large splittings (*ca.* 140G). These results show the importance of delocalization within the $-OCH_2O-$ π system, indicated in (15). Indeed, the spin-density is quite evenly distributed within this unit, and delocalization onto the other two CH_2 groups is small. However, if one of the CH_2 protons is replaced by an alkyl group, the cation readily loses an alkyl radical (14).[58] Evidently, the incentive for this reaction is the stability of the $(RO)_2CH^+$ carbocation.



(14)



(15)



$$(RO\underset{\displaystyle R'}{C}HOR)^+ \longrightarrow (ROCHOR)^+ + R'\cdot \qquad (14)$$

The cation of 1,4-dioxane is of interest since the proton hyperfine coupling was far less than those for any other ether cations. This led us to consider the possibility of weak σ* bonding between the two oxygen *p*-orbitals for the boat form of the cation of the type observed for the sulphur analogue (see below). If such bonding does occur, then the small proton coupling is a natural consequence of such bonding.[55]

7 Carbonyl Cations

In this section I discuss results for aldehyde, ketone, and ester cations, despite the fact that the ester structures (SOMOs) turn out to be quite different from those for aldehyde and ketone cations.

Aldehyde Cations.—Prior to the introduction of freon and related solvents, the only cation in this class was that of formaldehyde, which we prepared in a sulphuric acid matrix.[59] For reasons that we do not understand, no clear features for $H_2CO\cdot^+$

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[56] L. D. Snow, J. T. Wang, and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 193.

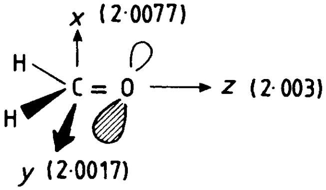
[57] T. Clark, *J. Chem. Soc., Chem. Commun.*, 1984, in press.

[58] K. Ushida and T. Shida, *J. Am. Chem. Soc.*, 1982, **104**, 7332.

[59] S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1975, 909.

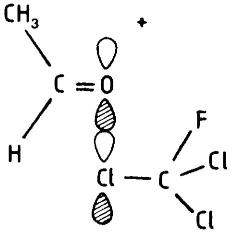
cations have been obtained from solutions of formaldehyde in freon solvents, but the complementary technique of photoionization using a rare-gas matrix gave very good e.s.r. features for this cation.[60]

These cations, which are isoelectronic with the well-known H_2CN radicals, exhibit the expected large coupling to the two protons (Table 4). A careful analysis of this coupling have led Knight and his co-workers to suggest the interactions and axes indicated in insert (16). A surprising but compelling conclusion is that $g_{\text{max.}}$ does not lie along the C–O axis as has generally been supposed because of the expected facile coupling between the π^* and n orbitals. In fact, this direction is associated with a free-spin g-value, the suggestion being that coupling between the SOMO and the filled and unfilled π and π^* orbitals effectively cancel.



(16)

Although we were unable to obtain clear evidence for H_2CO^+ cations, other aldehyde and ketone cations were readily prepared in $CFCl_3$.[61] The aldehyde spectra are characterized by a doublet splitting of *ca.* 135G. We now realise[62,63] that an extra anisotropic quartet splitting which appeared on the acetaldehyde cation features was due to a weak hyperfine interaction with chlorine which is lost reversibly on annealing. The structure (17) is thought to be similar to that discussed above for the alkyl halide cations. The chlorine interaction was lost reversibly on annealing.



(17)

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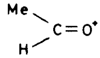
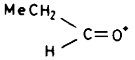
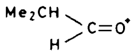
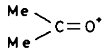
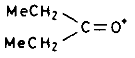
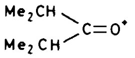
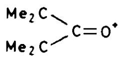
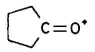
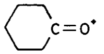
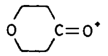
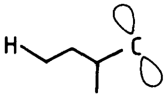
[60] L. B. Knight and G. Steadman, *J. Chem. Phys.*, 1984, in press.
[61] P. J. Boon and M. C. R. Symons, *Chem. Phys. Lett.*, 1982, **89**, 516.
[62] A. Hasegawa, J. Rideout, G. W. Eastland, and M. C. R. Symons, *J. Chem. Res.* (*S*), 1983, 258.
[63] L. D. Snow and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 198.

Table 4 *Observed and calculated e.s.r. parameters for various aldehyde and ketone radical cations*

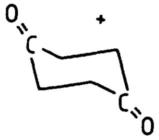
			Hyperfine coupling constants (G)[a,b]		
No.	*Radical*	*T*/K	β-*Protons*	γ-*Protons*	δ-*Protons*
1	 [c]	77	136(63.7)[d]	(−3.9, −3.9, −0.4)	
2		120	135(61.9)	(−4.0, −4.0)	12.5 (1 H)[e] (4.9, 0.4, 0.4)
3		77	138(68.2)	(1.3)	20 (2 H) (3.1, 1.4, 0.9) × 2
4		77		(−2.3, −2.3, −1.6) × 2	
5		77		(−2.6) × 4	11 (2 H)[f] (5.8, 1.1, 1.1) × 2
6		77		(−0.6) × 2	15 (4 H) (3.0, 1.6, 0.9) × 4
7		77			15 (4 H) (5.7, 1.0, 1.0) × 4 (2.9, 1.5, 0.9) × 2
8		77		(−1.6, −1.5) × 2	13 (2 H) (2.2, 0.0) × 2
9		77		(−1.9, −1.4) × 2	27.5 (2 H) (5.5, 0.4) × 2
10		77		(−1.8, −1.7) × 2	19.5 (2 H) (4.1, 0.3) × 2

[a] G = 10^{-4} T. [b] Average *g*-values *ca.* 2.0035 ± 0.001. $A_{\parallel}(^{35}Cl)$ 19.0 G; $A_{\perp}(^{35}Cl)$ *ca.* 6 G(CH_3CHO^+); *ca.* 4 G(CO_3CHO^+). [d] The numbers in parentheses are the results of INDO calculations. [e] Lost reversibly on annealing. [f] Changes to 3 (4 H) reversibly on annealing.

One particularly interesting aspect of the spectra for these cations is that the γ-proton coupling [for example, the methyl group in $(MeCHO)^+$] is very small. Our ENDOR results for the acetone cation gave splittings of 1.5 G and 0.3 G for two different types of protons suggesting preferred orientations for both methyl groups. In contrast, δ-protons can exhibit couplings as great as *ca.* 30 G.[64,65] These large couplings are only found for specific protons having conformations close to the ideal W plan, as in (18). For example, two of the four δ-protons of cyclohexanone have near optimum locations, and exhibit *ca.* 29 G splitting.



(18)

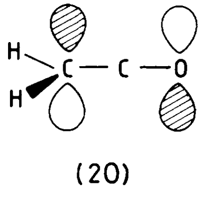


(19)

Our result for the 1,4-diketone cation (19) is particularly interesting, since the e.s.r. spectrum comprises a well-resolved quintet (A = 12.5 G) from four equivalent protons.[66] If we rule out rapid interconversion at 77 K, this can only mean that there is delocalization across the two carbonyl groups so that all four equatorial protons are involved. This surprising result contrasts markedly with our result for the benzoquinone cation, which has hyperfine coupling to only two protons, thereby establishing that the SOMO is strongly localized.[67]

In a preliminary study of the acetone cation, in addition to our ENDOR results mentioned above, we have studied the spectra for $(^{13}CH_3)_2CO^+$ cations in $CFCl_3$ and CCl_3.[68] The results suggest that the spin-density on each methyl group is *ca.* 22%. If this is correct, then hyperconjugative delocalization must be large, though probably less than that for C–H bonds (*ca.* 26%) as seems to be required by our results for $(Ph–Et)^+$ cations discussed below.

Ketene Cations.—E.s.r. results[69] show that these have the expected π-SOMO shown approximately in (20). Indeed, the α-proton coupling of *ca.* 20.5 G suggests that the spin-density on the (CH_2) group is close to unity, as required by the limiting structure, $R_2\dot{C}–C{=}O^+$.



(20)

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[64] L. D. Snow and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 1090.

[65] P. J. Boon, M. C. R. Symons, K. Ushida, and T. Shida, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1213.

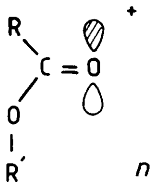
[66] Unpublished result.

[67] H. Chandra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1983, 29.

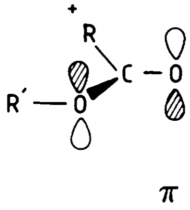
[68] P. J. Boon, L. Harris, M. Olm, J. L. Wyatt, and M. C. R. Symons, *Chem. Phys. Lett.*, 1984, **106**, 408.

[69] D. Becker, K. Plante, and M. D. Sevilla, *J. Phys. Chem.*, 1983, **87**, 1648.

Ester Cations.—These are of special interest since the carbonyl *n*(O) orbital (21) is similar in energy to the π orbital (22). The *n* orbital is comparable with the SOMO for aldehydes and ketones, whilst the π orbital is strongly delocalized, but has its major spin-density on the 'ether' oxygen. Various theoretical calculations have been presented in favour of either of these orbitals as the SOMO for the cation.

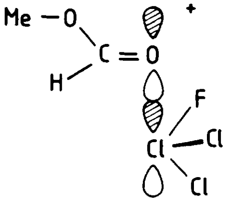


(21)



(22)

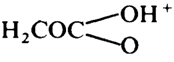
The first ester cation prepared in freon, that of methyl formate, proved to be exceptional since a species exhibiting strong coupling to a single chlorine nucleus was obtained at 77 K.[62,69] This is expected to be derived from the *n*-cation, as in (23).



(23)

There is a single proton coupling of *ca.* 17 G which can be assigned to the formyl proton. This coupling is much smaller than expected for the free *n*-cation but, as stressed above, the formation of a σ bond tends to localise the SOMO, so the results are in reasonable accord for this structure (see Section 11).

On annealing there is an irreversible change to a new species which we think is the π-cation.[62,69] This exhibits strong coupling to two of the three methyl protons, the splitting (*ca.* 23 G) [the average coupling being significantly less than that for the methyl protons of $(\mathrm{Me\dot{O}Me})^+$ cations (43 G)] showing that delocalization is indeed extensive. (We originally thought that this radical might be


$\mathrm{H_2COC}\genfrac{}{}{0pt}{}{\diagup \mathrm{OH}^+}{\diagdown \mathrm{O}}$

, but work on other ether cations does not support such a rearrangement.[62])

These results suggest that the first-formed cation is the *n*-cation, but this may be only because of stabilization of the system *via* the σ/σ* interaction. Clearly, the thermodynamically stable structure is the π-cation.

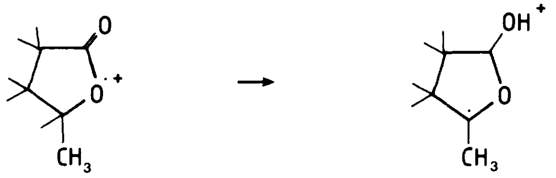
Other esters seem to favour the π-SOMO directly. Some of our results are shown in Table 5, together with those of Sevilla and his co-workers. The most noteworthy result is the relatively large hyperfine coupling often obtained for γ-hydrogen atoms. Again, a preferred conformation is required.

Table 5 *Experimental e.s.r. parameters for π-cations of esters*

	Hyperfine coupling/G^{a,b}		
Esters	A^{H}_{acyl}	A^{H}_{β}	A^{H}_{γ}
HCO_2CH_3	5.5	23 (2H), 4 (1H)	
$CH_3CO_2CH_3$	5 (3H)	22 (2H)	
$CH_3CO_2CD_3$	5	3.5 (2^2H)	
$CH_3CH_2CO_2CH_3$	7 (1H)	25 (2H)	
$HCO_2CH_2CH_3$	2.5	22 (2H)	10 (2H), (160 K) 16 (1H), (77 K)
$CH_3CO_2CH_2CH_3$		22 (1H), 31 (1H)	8 (1H), 17 (1H)

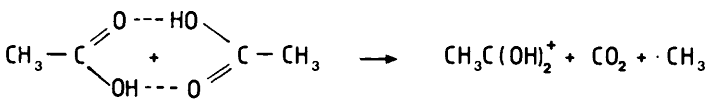
^{a}G = 10^{-4} T. $^b g_{av} \sim 2.0026$.

We have also made a combined study with Sevilla's group of electron-loss from lactones.[70] In general, the results are compatible with the results for esters, and in several cases there is evidence for intramolecular proton transfer to give alkyl-type radicals as indicated, for example, in reaction (15). (See note added in proof, p. 439.)



(15)

Carboxylic Acids.—As with the alcohols, it is impossible to isolate carboxylic acid monomers by freezing dilute solutions in freon solvents. However, in contrast with the alcohols, well-defined cyclic dimers can be isolated and these might yield specific cations on irradiation. However, for acetic acid dimers, high yields of methyl radicals were obtained, even after irradiation at *ca.* 4 K (16).[71]



$$(CH_3COOH)_2^{+} \longrightarrow CH_3C(OH)_2^{+} + CO_2 + \cdot CH_3 \quad (16)$$

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[70] M. D. Sevilla *et al.*, unpublished results.

[71] J. Rideout and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, in press.

8 Sulphur Cations

Several of the important classes of sulphur cations had already been studied by e.s.r. spectroscopy before the advent of freon solvents. Because of the lower ionization potentials of the precursors and especially because of their lower reactivity, they are often stabilized in the pure compounds at low temperatures, in contrast with their oxygen analogues. However, in early studies it was not realised that dimerization is a major reaction and dimer-cations were frequently misidentified as monomer cations (see *ref.* 72 for detailed arguments and references to these early studies).

Using freon solvents, the dimerization step (17) can be avoided or followed on annealing.[72] It is probably diffusion controlled and seems to be irreversible in the solid state. This process has been extensively studied by Asmus and co-workers in the liquid-phase, using the intense $\sigma \rightarrow \sigma^*$ transition in the visible region which characterizes these species.

$$\mathrm{R_2S}\cdot^{+} + \mathrm{R_2S} \longrightarrow \mathrm{R_2S}\dot{-}\mathrm{SR_2}^{+} \qquad (17)$$

E.s.r. results for the monomer cations, $\mathrm{R_2S}\cdot^{+}$ follow closely those of the isostructural ether cations, $\mathrm{R_2O}\cdot^{+}$, except that the proton hyperfine coupling constants are reduced by about a factor of two.[73,74] [Compare $\mathrm{Me_2O}\cdot^{+}$ (43 G) and $\mathrm{Me_2S}\cdot^{+}$ (21 G).] This reduction is expected because of the lower electron affinity of sulphur and the poorer overlap with the more diffuse sulphur orbitals.

When dimer cations form, the proton coupling falls to *ca.* 6.8 G.[75] This reflects the extra confinement of the unpaired electron discussed above for the alkyl halide cation dimers.

An important generalization can be drawn from these and other results, namely, that whilst radicals centred on second and subsequent row elements (*e.g.* $\mathrm{R_3P}\cdot^{+}$, $\mathrm{R_2S}\cdot^{+}$, and $\mathrm{RCl}\cdot^{+}$) normally react to form dimer radical cations with σ^* SOMOs, the corresponding first row radical cations (*e.g.* $\mathrm{R_3N}\cdot^{+}$, $\mathrm{R_2O}\cdot^{+}$) react in other ways. This may occur because first row dimer cations are innately less stable, as suggested by Glidewell[76] and steric factors may play a significant rôle. However, our inability to detect these dimers may occur because hydrogen atom abstraction processes are more favoured for the first row cations. Our results with cyclic ether cations[55] suggest that if intra- and inter-molecular hydrogen atom transfers are prevented, intramolecular formation of σ^* SOMOs may indeed occur (see Section 6 above).

Cyclic monosulphide cations again closely resemble the corresponding ether reactions except for the three-membered ring cation which, with hyperfine coupling of 31 G to four equivalent protons, appears to have the normal π-structure. It is especially noteworthy that there seems to be no tendency in the temperature range 77—160 K to form the ring-opened cation $(\mathrm{H_2}\overline{\mathrm{C{-}S{-}C}}\mathrm{H_2})^{+}$.

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[72] R. L. Petersen, D. J. Nelson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2005.

[73] D. N. R. Rao, M. C. R. Symons, and B. W. Wren, *J. Chem. Soc., Perkin Trans. 2*, 1681.

[74] J. T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 1184.

[75] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748.

[76] C. Glidewell, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1285.

Cyclic disulphides tend to form intramolecular S–S bonds, giving σ^* SOMOs.[72,77] This aspect of sulphur chemistry has been most effectively studied by Asmus and co-workers, since the energy of the $\sigma \rightarrow \sigma^*$ or related transitions are markedly dependent upon the strength of the bond, whereas e.s.r. parameters are relatively insensitive to such changes. It is noteworthy that even disulphides of type $(RS\text{–}CH_2SR)^+$ seem to form weak S–S bonds at 77 K despite steric difficulties, rather than adopting the π-delocalized structure favoured by acetal cations.

$(RS\text{–}SR)^+$ Cations.—Persulphides form π^* cations on irradiation. These have also been studied by e.s.r. spectroscopists prior to the introduction of freon-type solvents.[78,79] We have shown that the same species are readily formed in $CFCl_3$ thereby confirming the previous identifications.

9 Selenium-centred Cations

These have not been extensively studied, but the available results show the expected trends. The 'parent' cation, $Me_2Se\cdot^+$ was briefly reported by Wang and Williams,[74] but they only reported the methyl proton coupling (*ca.* 15 G). Our own results show that the *g*-values have diverged markedly relative to those for $Me_2S\cdot^+$ and there is an extra doublet splitting of *ca.* 8 G for solutions in $CFCl_3$ which is absent for solutions in CCl_4.[80] It might be thought that these radicals are good candidates for forming weak σ-bonds to chlorine but, instead, they clearly select fluorine.

The enhanced *g*-shifts are in accord with the greater spin-orbit coupling for selenium. They facilitate spectral interpretation relative to the sulphur cations since all three components are well separated instead of overlapping.

10 Nitrogen-centred Cations

Although the $\cdot NH_3{}^+$ and $\cdot NMe_3{}^+$ cations have been extensively studied by e.s.r. spectroscopists both in liquid and solid systems,[81–83] there had been no systematic studies of $R_3N\cdot^+$ cations prior to the introduction of freon-type solvents. We have recently studied a range of such ions in $CFCl_3$ and can draw some conclusions about their properties.[84]

The most significant result stemming from e.s.r. studies has been that these cations are planar, as judged by the ^{14}N hyperfine tensor components. This is the same criterion that has been used to argue that most alkyl radicals are planar but, in contrast with the situation for alkyl radicals, the concept of preferred planarity of $R_3N\cdot^+$ radicals has not been questioned.

Our results for $Et_3N\cdot^+$ are of interest in that strong coupling (38 G) to only three protons is observed at 77 K. This changes reversibly to coupling to all six protons

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[77] D. N. R. Rao, M. C. R. Symons, and B. W. Wren, *Tetrahedron Lett.*, 1982, **23**, 4739.

[78] H. C. Box and H. G. Freund, *J. Chem. Phys.*, 1964, **41**, 2571.

[79] F. K. Truby, *J. Chem. Phys.*, 1964, **40**, 2768.

[80] A. Hasegawa and M. C. R. Symons, unpublished results.

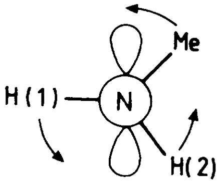
[81] T. Cole, *J. Chem. Phys.*, 1961, **35**, 1169.

[82] A. J. Tench, *J. Chem. Phys.*, 1963, **38**, 593.

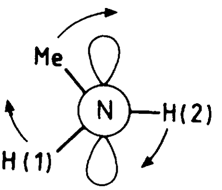
[83] J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc. (A)*, 1969, 1942.

[84] G. W. Eastland, D. N. R. Rao, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1551.

on annealing, the coupling changing to 19 G. This value is well below the expected average coupling (28 G) so that rotation must remain restricted, as in (24) and (25). Thus, in this case, steric control dominates. Results for other amine cations are in good accord with expectation.[84] Results for 1,1-diamine cations, $(R_2NCH_2NR_2)^+$, show that the SOMO is confined to one nitrogen atom. This makes an interesting contrast with our results for acetal cations and 1,1-disulphide cations discussed above. There are two alternative structures, one with the SOMO equally distributed on the two nitrogen atoms, with equal flattening, the other with the SOMO confined to one, planar, nitrogen atom, the other retaining the normal amine pyramidality. Clearly, the latter asymmetric structure is favoured. This is a more extreme and perhaps more obvious example of the asymmetric structure that I propose for the pyrimidine cation (see Section 15 below).

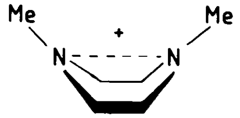


(24)



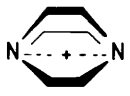
(25)

As with the ethers, and in contrast with phosphine cations (see Section 11 below), there is no tendency to form amine dimer cations, $(R_3N\overset{\cdot}{-}NR_3)^+$, the preferred reaction being hydrogen atom transfer. However, possible evidence for very weak intramolecular σ^* bonding was adduced for the cation of *N,N'*-dimethylpiperazine (26), on the basis of greatly reduced proton hyperfine coupling constants.[84] However, there can be no doubt that the cation of triethylenediamine (TED) (27) is truly delocalized, and this is surely aided by the fact that it is now impossible to form a cation planar at one nitrogen only.



(26)

TED $^+$



(27)

Before leaving the topic of amine cations, I consider another aspect of σ^* bonding which is certainly exhibited very well by $R_3N\cdot^+$ cations. Some time ago, in a paper ignored by e.s.r. chemists,[85] Patten established that $H_3N\cdot^+$ radicals form

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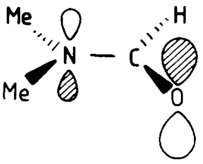
[85] F. W. Patten, *Phys. Rev.*, 1968, **175**, 1216.

weak o* bonds to Cl^- and Br^-. I have shown how significant this result is relative to the far weaker interactions found for alkyl radicals and halide ions which are, at best, only weak charge-transfer interactions.[86]

This work has been extended to a range of alkylamine cations, all of which form σ^* bonds to Cl^-, Br^-, and I^- ions.[87] In all cases, the R_3N– moiety is clearly pyramidal and there is extensive transfer of spin-density onto halogen. These $R_3\overset{\delta+}{N}\overset{\delta-}{\dot{-}}X$ complexes are structurally similar to the $R_3\overset{\delta+}{P}\overset{\delta-}{\dot{-}}X$ halide complexes studied by Symons and Petersen.[88]

Amide Cations.—Apart from a brief study of the cations of dimethylformamide and dimethylacetamide,[89] no attention has been paid to these species. Our results show that, in accord with theoretical predictions and photoelectron spectroscopic results, the SOMO for these cations is the π orbital shown in (28). The spin is quite strongly confined to nitrogen, the spin-density calculated from the hyperfine components being *ca.* 78% in both cases. The *N*-methyl groups are 'freely' rotating and exhibit large splittings (32 G) whereas the C–H and C–Me protons couple very weakly.



(28)

It is interesting to compare trends for the amides and esters, *i.e.* for $HC(\overset{+}{O})NMe_2$ and $HC(\overset{+}{O})OMe$, since both have similar π SOMOs. The most noteworthy difference is that the apparently *less* restricted methyl group for the ester is firmly fixed, giving coupling to only two protons. This coupling is less than the *average* value for the amide, the estimated spin-densities on nitrogen and ester oxygen being *ca.* 78% and *ca.* 50% respectively. In both, the spin-density on the C–H moiety is low, so that on the carbonyl oxygen must be considerably greater for the ester. Is this possibly a reason for the restricted rotation of the methyl group? (However, see footnote p.439.)

Nitroalkane Cations.—Perhaps there should have been classified under oxygen-centred radicals since the parent cations are expected to have a SOMO which is non-bonding (π or σ) on oxygen. However, these cations are evidently very unstable, and rearrange even at 77 K to give species having spectra very similar to that of $\cdot NO_2$ radicals. It was originally argued that these must be the rearranged

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[86] M. C. R. Symons, *J. Chem. Research (S)*, 1981, 161.

[87] I. Rowland, J. B. Raynor, and M. C. R. Symons, unpublished results.

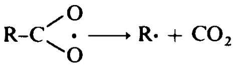
[88] M. C. R. Symons and R. L. Petersen, *J. Chem. Soc., Faraday Trans. I*, 1979, 210.

[89] D. N. R. Rao and M. C. R. Symons, *Chem. Phys. Lett.*, 1982, **93**, 495.

nitrite cations $ONOR^+$ which are expected to have SOMOs closely resembling that for $\cdot NO_2$.[90] This postulate has now been modified by the observation of a large ^{13}C splitting in the spectrum for the cation of $^{13}CH_3NO_2$.[91] The results suggest that the carbon and nitrogen hyperfine tensor components are co-linear, the estimated spin-density on carbon being *ca.* 46% with a $p{:}s$ ratio of *ca.* 4.7. Delocalization onto carbon for $ONOR^+$ cations is not expected to be large, so we now propose the σ-structure $H_3C{\cdot}NO_2{}^+$ for the first formed cations, with a stretched C–N bond. [This resembles one of the structures for $N_2O_4{}^+$ cations discussed below in Section 17.] On annealing, however, the ^{13}C splitting was lost irreversibly but the ^{14}N splitting was retained. We suggest that this represents the formation of the nitrite structure. Thus we propose the sequence shown in equation (18) for the overall process:

$$R\text{–}N\dot{O}_2{}^+ \longrightarrow R{\cdot}NO_2{}^+ \longrightarrow O\dot{N}OR^+ \tag{18}$$

It is interesting to consider this rearrangement in the light of reaction (18) for the isoelectronic $RCO_2\cdot$ radicals. These do have the expected SOMO confined to oxygen but reaction (19) is generally fast at 77 K. It is, in fact, nicely illustrated by the work on carboxylic acids in freon discussed above, and by the recent study of irradiated lithium acetate,[92,93] There seems to be no evidence for the formation of $O\dot{C}OR$ radicals in these reactions, even though they have been prepared by other routes. Also, we have not detected any R· radicals which might have been formed together with $NO_2{}^+$ by a reaction analogous to (19). Probably a major factor is the low reactivity of CO_2 relative to $NO_2{}^+$.



$$R\text{–}C\overset{O}{\underset{O}{\cdot}} \longrightarrow R\cdot + CO_2 \tag{19}$$

11 Phosphorus-centred Radicals

Phosphine Radical Cations.—Some time ago, we reported the formation of various $R_3P\cdot^+$ radical cations when dilute solutions in sulphuric acid glasses were irradiated.[94,95] Although the results looked reasonable, identification was based solely on the large hyperfine coupling to ^{31}P, the lines being so broad that proton hyperfine coupling was not resolved. We therefore thought it wise to study these radicals again using $CFCl_3$ solvent so that electron-loss could be guaranteed.[96,97] Fortunately, the results strongly supported our original assignments.

The most important result is that these radicals are pyramidal, the estimated p/s ratio being in the region of 10, with the electron strongly confined to phosphorus.

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[90] D. N. R. Rao and M. C. R. Symons, *Tetrahedron Lett.*, 1983, **24**, 1293.

[91] D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc.. Faraday Trans. 1*, in press.

[92] D. P. Lin and L. Kevan, *Radiat. Phys. Chem.*, 1981, **17**, 71.

[93] M. C. R. Symons, *J. Phys. Chem.*, 1983, **87**, 1833.

[94] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 2290.

[95] G. W. Eastland and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1977, 833.

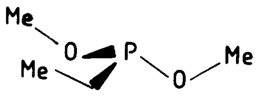
[96] M. C. R. Symons and G. D. G. McConnachie, *J. Chem. Soc.. Chem. Commun.*, 1982, 851.

[97] A. Hasegawa, G. D. G. McConnachie, and M. C. R. Symons, *J. Chem. Soc.. Faraday Trans. 1*, 1984, **80**, 1005.

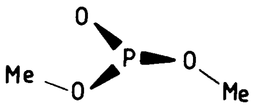
This makes an interesting contrast with planar $R_3N\cdot^+$ radicals. There are various explanations for this contrast, but it is not unexpected in view of the large decrease in bond angle on going, for example, from NH_3 ($\theta \approx 107°$) to PH_3 ($\theta \approx 91°$).

Various trends are of interest. Thus, on going from $\cdot AlH_3^-$ to $\cdot SiH_3$ and $\cdot PH_3^+$, there is very little change in bond angle despite the marked change in electronegativity of the central atom. Nevertheless, on going from PO_3^{2} to $MeO\dot{P}O_3^{2}$, $(MeO)_2\dot{P}O$ and $(MeO)_3P\cdot^+$, there is a large increase in A_{iso} (^{31}P) (*ca.* 300G) implying a marked fall in bond angle. Also, on going from $\cdot PMe_3^+$ to $\cdot P(OMe)_3^+$ there is a large increase in A_{iso} and fall in the p:s ratio, and hence, presumably, in bond angle.

The methyl proton coupling for $\cdot PMe_3^+$ radicals is *ca.* 11.5 G but $\cdot P(OMe)_3^+$ gave very narrow lines with no sign of proton splitting. However, the latter gave different species in CCl_4 and $CFCl_3$ solvents. In CCl_4 a single species was obtained with hyperfine coupling constants considerably greater than the major species found in $CFCl_3$. We attempted to explain this contrast in terms of two major conformations (29) and (30), both species being detached in mixed solvents. The triethyl derivative gave only the species with smaller coupling constants in both solvents. We tentatively suggested that the sterically unfavoured but more spherically compact conformation (29) is responsible for the large splitting, because the extent of pseudo π-delocalization is expected to be reduced.



(29)



(30)

A minor species formed in $CFCl_3$ from $P(OMe)_3$ probably has a small ^{19}F doublet splitting and such a splitting was also found for the $\cdot P(OPh)_3^+$ cations.[97]

Phosphine Dimer Cations.—Dimers $(R_3P\dot{-}PR_3)^+$, were detected on annealing systems containing $\cdot PR_3^+$ cations, or directly for more concentrated solutions.[97] The ^{31}P hyperfine parameters show that the spin is less delocalized onto the ligands and that the p:s ratio has greatly decreased (*ca.* 4) relative to that for the monomer cations. Also, for $(Me_3P\dot{-}PMe_3)^+$, the proton hyperfine coupling is drastically reduced. This extra confinement has been interpreted in terms of the anti-bonding nature of the σ^* orbital.[97] The relative increase in 3s-character is a natural consequence of the need to equalise the bond angles for the $\cdot PR_3^+$ and PR_3 moieties. These dimers have been studied in the liquid phase by Gara and Roberts.[98]

Some Group IV heteroatom radical-cations are now discussed.

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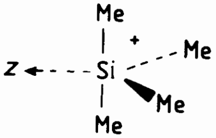
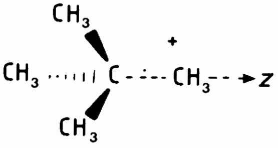
[98] W. B. Gara and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 150.

12 Silicon- and Germanium-centred Radical Cations

These have been studied mainly by Williams and his co-workers.[99,100] Results for the cation of tetramethylsilane show two sets of six equivalent protons suggesting a distortion of the type shown in (31). This makes an interesting contrast with that found for the CMe_4^+ cation (32). Unfortunately, ^{29}Si satellite features have not yet been detected, so nothing definitive can be said about the precise nature of the SOMO for this radical. The reasonable postulate is that it is largely $3p_z$ on silicon, where z bisects the small MeSiMe angle.[100] The selection of a non-hybridized *p*-orbital accords with our conclusions for $(SnMe_4)^+$ cations discussed below.



(31)



(32)

Results for the di-silicon derivative, $(Me_3Si)_2^+$, on the other hand, suggest that the SOMO comprises mainly the Si–Si σ-bond.[99] This structure is then similar to that originally proposed for the $(Me_3C)_2^+$ cation,[24] although again there are no detectable ^{29}Si satellites so details of the SOMO cannot be derived directly. In contrast with the situation for the hydrocarbon analogue, however, all the protons were equivalent on the e.s.r. time-scale for this cation.

Results for the corresponding germanium cations were very similar and these are clearly isostructural with their silicon counterparts.[99,100] This is in marked contrast with our results for $SnMe_4^+$ cations, as outlined in the following Section. These are somewhat more informative because satellite features from magnetic tin isotopes were detected.

13 Tin- and Lead-centred Cations

Although tentative evidence for radical cations and anions was adduced in e.s.r. studies of the effects of ionizing radiation on a range of tin and lead alkyls,[101,102] the first definitive results were obtained using $CFCl_3$ solutions.[103] In collaboration with Hasegawa and his colleagues, we have now studied the series of cations $\cdot SnH_4^+$, $Me\dot{S}nH_3^+$, $Me_2\dot{S}nH_2^+$, $Me_3\dot{S}nH^+$, and $Me_4Sn\cdot^+$.[104,105] The

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[99] J. T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 176.

[100] B. W. Walther and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 270.

[101] S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1974, 1966.

[102] R. J. Booth, S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 1506.

[103] M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1982, 869.

[104] A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1983, 1199.

[105] A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M. C. R. Symons, and J. Rideout, *J. Chem. Soc., Dalton Trans.*, 1984, 1667.

results reveal some remarkable trends. Although $\cdot SnH_4{}^+$ is one of the few purely inorganic radical-cations studied in this way, I include it here rather than in Section 17 in order to illustrate the trends observed through this sequence of radicals.

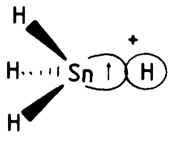
The dominating result for $\cdot SnH_4{}^+$ cations is the large coupling to ^{117}Sn and ^{119}Sn nuclei, together with the large proton coupling (Figure 6). Two cations were formed in almost equal concentrations at 77 K, one, with C_{3v} symmetry, has a single strongly coupled proton and the other, with C_{2v} symmetry, exhibits coupling to two equivalent strongly coupled protons. The C_{2v} cations converted slowly to the C_{3v} form on standing at 77 K.

The major cationic species formed at 77 K from $MeSnH_3$, Me_2SnH_2, and Me_3SnH had apparent 'C_{2v}' symmetry and all exhibited large tin hyperfine coupling constants indicating large *s–p* admixture in the SOMO. In marked contrast, the $^{117}Sn/^{119}Sn$ coupling for Me_4Sn^+ cations is relatively small, indicating effectively pure *p*-character. Studies using $^{13}CH_3$ indicated that this cation has extensive $Me_3Sn^+ - - - \cdot CH_3$ character and this conclusion was supported by annealing studies (see below).

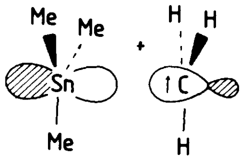
The results nicely illustrate that the choice for all the cations between C_{2v} and C_{3v} distortion is a subtle one which may well be influenced by medium effects. Also, there seems to be no clear choice as to which of the two ligands, H or CH_3, participates strongly in the SOMO. Thus the major species for $MeSnH_3{}^+$ and $Me_2SnH_2{}^+$ cations had two strongly coupled protons, whereas that for Me_3SnH^+ had no resolved proton splittings. We assume that this cation (Me_3SnH^+) must have pseudo C_{2v} symmetry since the results are so different from those for Me_4Sn^+ cations.

Electron loss from the T_d molecules SnH_4 and $SnMe_4$ is expected to occur from the triply degenerate t_2 orbitals and should be followed by a Jahn–Teller distortion. This theorem predicts D_{2d} or C_{3v} distortions, whereas we observe C_{2v} and C_{3v} distortions, with no clear evidence for D_{2d} species.

It is interesting to compare the C_{3v} versions of $SnH_4{}^+$ and $SnMe_4{}^+$ The former has structure (33) according to the e.s.r. results, with *ca.* 70% spin-density on tin which retains a strongly pyramidal H_3Sn^- unit, as evidenced by the *ca.* sp^3 hybridization. In marked contrast, the structure for $SnMe_4{}^+$ seems to be that shown in (34) with a nearly planar Me_3Sn– moiety and probably a nearly planar CH_3 unit, the major spin-density having shifted away from tin onto carbon. These results nicely illustrate the relaxations involved as the tin-ligand bond stretches. The extra driving force for the latter is presumably the extent to which hyperconjugative overlap stabilizes the Me_3Sn^+ cation.



(33)



(34)

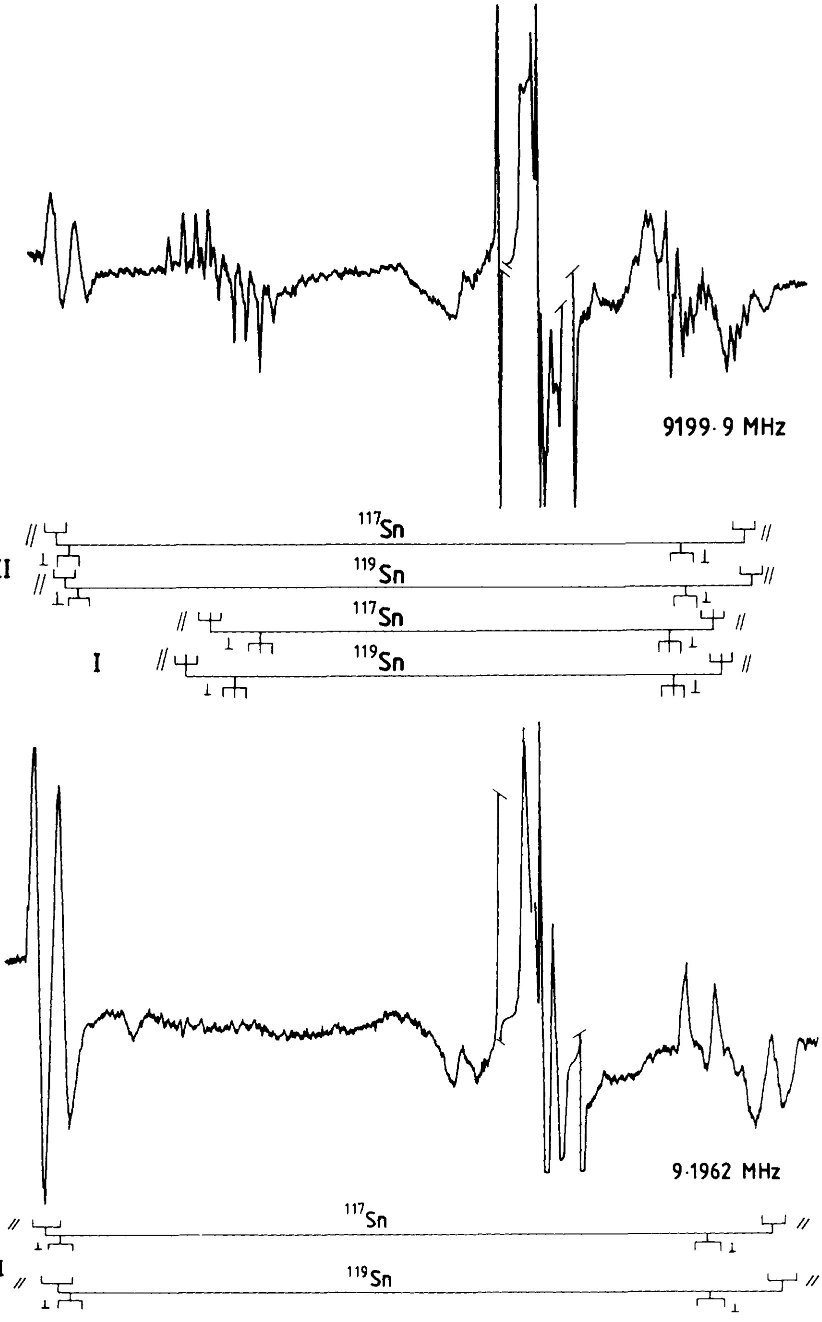
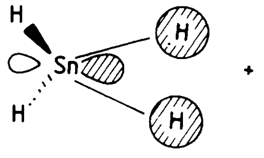


Figure 6 *First derivative X-band e.s.r. spectrum for a solid solution of* 4 mol % SnH_4 *in* $CFCl_3$ *recorded* (*a*) *immediately after exposure to* ^{60}Co γ*-rays at* 77 K, *showing features assigned to* C_{2v} *and* C_{3v} *structures of* $SnH_4{}^+$ *radical cations, and* (*b*) *after storage of the irradiated sample for one week at* 77 K

The extra stability of the ethyl radical causes Me_3SnEt^+ cations to give Me_3Sn^+ and $\cdot CH_2CH_3$ radicals even at 77K.[104,105] However, only the parent cations, $Me_3SnCMe_3{}^+$, were detected for the t-butyl derivative, although $\cdot CMe_3$ radicals are even more stabilized. We have discussed this result in terms of equilibrium [20] and have presented evidence for the reversible generation of $\cdot CMe_3$ radicals on annealing. [These are unable to migrate away from the Me_3Sn^+ cations so the original fragments reunite on cooling.] We suggest that, curiously, it is the effect of methyl group repulsions that helps to stabilize the weak Sn–C bond relative to that for the ethyl derivative. Thus, as the system moves towards dissociation, the methyl group cannot swing inwards to give the planar radical and hence the activation energy cannot be lowered as much as for less restricted systems. However, the difference may be more apparent than real because of the reversible nature of the reaction for the $-CMe_3$ derivative and the irreversible break-down of the ethyl derivative.

(20)

It is of interest to compare our results for $SnH_4{}^+$ cations with those for the $CH_4{}^+$ and BH_4 cations discussed above. The key difference is that tin uses its *s*-orbital extensively for both forms of $SnH_4{}^+$, whilst only $2p$ orbitals are involved for BH_4.[27a] We suggest that this is because tin selects the $2a_1$ SOMO (35) for which *s–p* mixing is expected, whereas $\cdot BH_4$ selects the ${}^2b_1$ SOMO which cannot mix with *s*. Alternatively, the differences may be connected to the comparable differences observed for $\cdot AR_3$ radicals. Thus, for example, $\cdot BH_3{}^-$ radicals are planar,[107] with a pure $2p$ SOMO, whilst $\cdot AlH_3{}^-$ radicals are pyramidal with considerable *s–p* hybridization.[108,109]



(35)

The Hexamethyldistannane Radical Cation.—Our results for this cation suggest strongly that the SOMO is confined to a ($5p + 5p'$) combination, the two Me_3Sn units being effectively planar with a stretched Sn–Sn bond.[103] This is the structure

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[106] B. W. Walther, F. Williams, W. Lau, and J. K. Kochi, *Organometallics*, 1983, **2**, 688.

[107] R. C. Catton and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2001.

[108] J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 1167.

[109] M. C. R. Symons and L. Harris, *J. Chem. Soc., Faraday Trans. I*, 1982, **78**, 3109.

that I originally proposed for the $Me_3C{-}CMe_3{}^+$ cation, although it now seems that the two Me_3C units are unable to attain complete planarity. Walther *et al.*[106] have shown that the tin coupling is small for the $(Me_3Sn{\cdot}GeMe_3)^+$ cation, so the Me_3Sn unit, and probably the $GeMe_3$ unit, are also planar for this cation.

Lead-centred Radical Cations.—These have so far been less extensively studied. Walther *et al.* reported the spectrum for $\cdot PbMe_4{}^+$ cations which shows that the structure must be very similar to that for $\cdot SnMe_4{}^+$ cations, with the expected larger shift in g because of the larger spin-orbit coupling constant.[106]

Several common elements emerge from these studies of organic radical cations having their SOMOs formally localized on one hetero-atom.

(*i*) If that atom is from the second or subsequent rows of the Periodic Table and forms one, two, or three σ-bonds only, the cation shows a marked tendency to 'dimerize' to give σ^* dimer cations. This tends to localize the unpaired electron to the σ^* bond.

(*ii*) Nitrogen- and oxygen-centred radicals do not normally react in this way. This is, in part, because of their far greater tendency to extract hydrogen.

(*iii*) Delocalization onto neighbouring alkyl groups can be extensive, especially for first-row cations. This is particularly marked for acetal cations.

(*iv*) Localized σ-radicals having the SOMO confined largely to the X–X σ-bond are formed when Group IV dimeric molecules, $R_3X{-}XR_3$, lose an electron.

(*v*) Electron-loss for aldehydes and ketones is from the non-bonding, in-plane $2p$ orbital on oxygen, and hyperconjugative delocalization is extensive. However, for the esters there seems to be a fine balance between this orbital and the π-orbital centred largely on the two oxygen atoms. Also, the internal transfer of hydrogen from the ester alkyl group to the carbonyl oxygen seems to be remarkably facile.

Aromatic Cations

The pioneer studies of aromatic cations were carried out many years ago, the first being on anthracene cations,[4,110,111] which are remarkably stable. The first indication of an important positive-charge effect on methyl-group hyperconjugation came from a study of the 9,10-dimethylanthracene cation,[112] and the first study of alkyl-substituted benzene cations was our work on hexamethylbenzene cations in sulphuric acid.[113] A recent study of methyl-substituted benzene cations extends these studies,[114] but in pride of place must go the most interesting study of Iwasaki *et al.* on the benzene cation.[115]

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[110] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **40**, 3307.

[111] A. Carrington, F. Dravnicks, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 947.

[112] J. A. Brivati, R. Hume, and M. C. R. Symons, *Proc. Chem. Soc.*, 1961, 384.

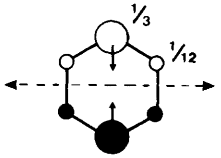
[113] R. Hume and M. C. R. Symons, *Proc. Chem. Soc.*, 1963, 241; *J. Chem. Soc.*, 1965, 1220.

[114] M. C. R. Symons and L. Harris, *J. Chem. Res.* (*S*), 1982, 268; (M) 1982, 2746.

[115] M. Iwasaki, K. Toriyama, and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 1983, 320.

The Benzene Cation.—This, like the anion, is an orbitally degenerate system so distortion must occur on electron loss. Many people have studied the dynamic Jahn–Teller distortion for $C_6H_6^-$ anions but liquid-phase studies are complicated by the fact that exchange is extremely fast and perturbing effects from the cations may seriously interfere with the true behaviour. However, even when $C_6H_6^-$ ions are generated in solids by electron addition and cooled to very low temperatures, any inequivalence of the proton coupling constants is lost within the linewidths.

In marked contrast, the distortion experienced by the cations is very large, as has been recently established by Iwasaki and his co-workers.[115] At 4.2 K in freon, the e.s.r spectrum comprises a major triplet from two equivalent, strongly coupled protons (A = 8.2 G) and four weakly coupled protons (A = 2.4 G). On annealing, the distortion becomes dynamic and the six couplings are averaged. Clearly, the symmetric orbital (36) has been selected. This suggests that there has been a distortion which shortens the C(2)–C(3) and C(5)–C(6) bonds and stretches the remainder, as indicated in (36), since this stabilizes ψ_A and destabilizes ψ_S. The interesting question as to why this turns out to be the preferred mode of distortion is not yet answered.



(36)

Alkyl Substituted Cations.—The results obtained with freon solutions[114,117] confirm, in general, those previously obtained. They show that the orbital selected for the SOMO is that for which electron-release from the C–H σ orbitals is maximized (b_1, ψ_S). Furthermore, proton splitting from methyl groups is very large, showing that such electron-donation really is important. There seems to be no need to postulate admixture of ψ_A and ψ_S of the type invoked to explain the e.s.r. spectra of the corresponding anions.

An unexpected result was obtained for ethyl benzene cations,[116] in that a major triplet splitting of *ca.* 29 G was observed. This surely means that the preferred conformation is close to that in (37) which is expected to be the least favourable conformation on steric arguments. Having argued that this nicely illustrates the concept that C–H hyperconjugative electron-release is more important than that for C–C bonds, we then found that for the *para*-diethyl derivative, the major species had four protons with coupling constants of only *ca.* 11 G, suggesting the reverse as in (38) for both ethyl groups.[117] We do not understand why this switch occurs but it certainly establishes that the choice is a subtle one.

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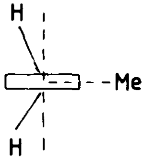
[116] D. N. R. Rao, H. Chandra, and M. C. R. Symons, *J. Chem. Soc., Perkin 2*, 1984, 1201.

[117] D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, in press.



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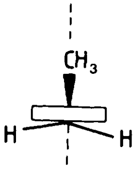


(38)

Cations with –C(O)R Substituents.—In general, results were unexceptional, the –C(O)R groups being found at sites of high electron density, although delocalization thereon was relatively small. However, the spectrum for benzaldehyde cations was unexpected in indicating an extra splitting of *ca.* 12 G in addition to that assigned to the *para*-proton. This is tentatively assigned to coupling to a ^{19}F nucleus of a solvent molecule but why this particular aromatic cation should uniquely opt for such an interaction is quite unclear to us.

What is certain is that the n(O) orbital is not selected as the SOMO, since a search for species exhibiting a doublet splitting in the 100—150 G region was unsuccessful. This is interesting since calculations suggest that the π and n.b. orbitals should be very close together and at least one group predict the SOMO to be the n.b. orbital on oxygen.

For the ester cations, $[ArC(O)OR]^+$, we detected small splittings from certain protons in groups R which, by comparison with our results for saturated ester cations gave spin-densities on the –OR groups of *ca.* 24%.

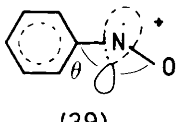
Results for various cyano-derivatives were similar and require no further comment. Coupling to ^{14}N nuclei was not resolved and it seems that delocalization is small.

Styrene and Related Cations.—The e.s.r. results show that the SOMO for cations of styrene, methyl styrene, and ethyl cinnamate are very similar. There is an estimated spin-density on the outer (CH_2) carbon of *ca.* 35—40%.

Nitrobenzene and Related Cations.—Our results for $PhNO_2{}^+$ cations (4 H, $A \approx 6$ G) are in good accord with expectation for the b_1 (ψ_A) orbital with a node through nitrogen. However, the directing power of the $-NO_2$ group is less than that of a $-CH_3$ group since, for *p*-nitrotoluene cations, the SOMO has switched from the ψ_A orbital to the ψ_S (a_2) orbital. Nevertheless, there was no detectable delocalization onto ^{14}N, in marked contrast with the SOMO for the corresponding radical-anions which has a high spin-density on the NO_2 group.

An unexpected result was the detection of a spectrum similar to that for $\cdot NO_2$ radicals from aromatic nitro-cations on annealing. These spectra were very similar to those obtained from $(RNO_2)^+$ cations (R = alkyl) and, presumably, have the same structure (see Section 10). This rearrangement requires a more drastic electronic change than that for the alkyl derivatives which accords with the higher temperatures required for the reaction.

Aryl Nitroso-cations.—Our results for $PhNO^+$ cations $[A_{\parallel}(^{14}N) = 50G, A_{\perp} = 30$ G][118] give an isotropic coupling constant (36, 7G) close to that assigned to this cation in the liquid-phase.[119] This result nicely confirms the previous assignment and supports the in-plane, non-bonding structure for this species (39). These results give a *p*:*s* ratio of *ca.* 6 and an estimated spin-density on nitrogen of *ca.* 47%.



(39)

Halogenobenzene Cations.—As expected, the SOMO selected for the mono-substituted cations is the 'a_2' orbital, placing high spin-density on the halogen.[120] Thus, the ability of the halogen atoms to act as π-electron donors is more significant than their high electronegativities. Nevertheless, this property controls the extent of delocalization, as can be seen in the plot shown in Figure 7. Delocalization onto fluorine (*ca.* 8%) is a little less than that onto oxygen for $PhOMe^+$ cations, the estimated order being F > OR > Cl > Br > I ≈ NR_2.

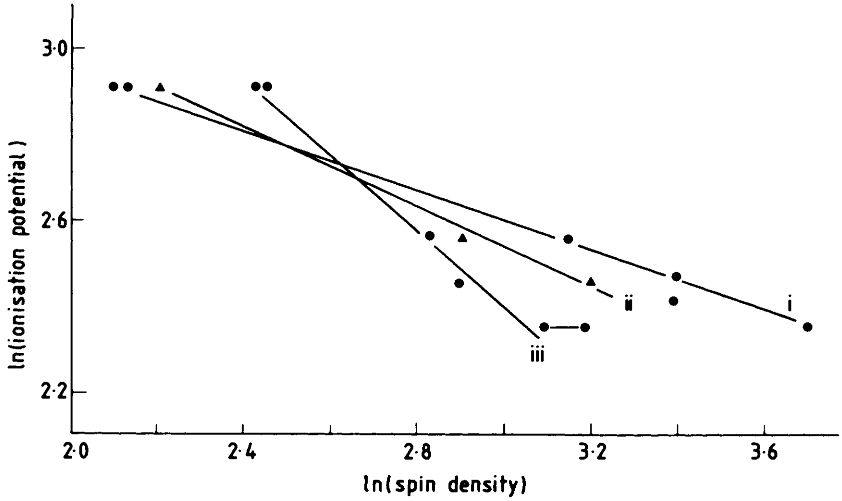


Figure 7 *Correlations between the ionization potentials of* F, Cl, Br *and* I *and the estimated spin-densities on halogen for* (*i*) $C_6H_5X^+$ *cations* (ii), *halogenouracil cations. and* (*iii*) $R_2\dot{C}$–X *radicals*

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[118] H. Chandra and M. C. R. Symons, unpublished results.

[119] G. Cauguis, M. Genies, H. Lemaire, A. Rassat, and J. P. Ravel, *J. Chem. Phys.*, 1967, **47**, 4642.

[120] M. C. R. Symons, A. Hasegawa, and S. P. Maj, *Chem. Phys. Lett.*, 1982, **89**, 254; *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1931.

The extent of delocalization varies with the nature of the *para*-substituents (X) for $XC_6H_4hal^+$ cations. For example, *p*-Me groups cause a small reduction in spin-density on halogen (*ca.* 2%). This is more than outweighed by the large delocalization (*ca.* 8%) onto the methyl group so the effect of methyl is largely to remove spin-density from the ring. It is noteworthy that *para*-OR substituents greatly reduce the spin-density on bromine, the reduction being larger than that caused by a second bromine substituent. This result is in contrast with the delocalizing order given above.

Most interesting is the large increase in spin-density on bromine induced by a *para*-nitro-group (*ca.* 5%). The nitro-group is a strong electron-acceptor and since the bromine atom directs the SOMO so as to place the nitro-group at a position of high positive-charge, the bromine feeds π-electrons into the ring to reduce this enforced constraint as far as possible.[117]

Benzyl Derivatives.—These are of interest because of the range of conformations available to the $-CH_2X$ group, which may be largely electronically or largely sterically controlled. Generally the SOMO is the 'a_2' orbital placing high spin and charge density on the $>C-(CH_2X)$ ring carbon atom. Hence it is of interest to compare the e.s.r results with those for the neutral radicals $R_2C\dot{C}H_2X$. It has not, in general, been possible to make this comparison with the corresponding radical anions since the SOMO is then $\psi_A(b_1)$, with a node passing through the $-CH_2X$ group.

As with the neutral radicals,[121,122] we had expected to find that 'heavy atom' groups such as Cl, Br and I would favour the extreme out-of-plane site, with $\theta \rightarrow 0$.[117,123] This was fulfilled for X = Br but not for $(PhCH_2Cl)^+$. The former give two species, both having large hyperfine coupling to bromine. However, the latter gave no detectable coupling to chlorine but large coupling to the methylene protons, suggesting $\theta \rightarrow 90°$. Before drawing any firm conclusions from this, however, we note that the *para*-methyl derivative $Me\overset{+}{C}_6H_4CH_2Cl$ gave the expected large chlorine coupling, suggesting that, as expected, $\theta \rightarrow 0$.[117] Thus, as with the ethyl derivative discussed above, there is a subtle balance of electronic and steric factors controlling the value(s) of θ adopted by a particular cation. What is clear is that hyperconjugative delocalization onto halogen, when it occurs, is large when θ is small.

15 Five-membered Hetero-aromatic Cations

Both Shiotani and co-workers and my own group have shown that radical-cations of pyrrole, furan, and thiophene derivatives are readily formed in freon solvents and are well characterized by their e.s.r. spectra.[124,125] In all cases, the SOMO is unambiguously the $1a_2$ π orbital having a node through the hetero-atom, as can be

[121] M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, 1897.

[122] A. R. Lyons, G. W. Neilson, S. P. Mishra, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1975, 363.

[123] S. P. Maj, D. N. R. Rao, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, in press.

[124] M. Shiotani, Y. Nagata, M. Tasaki, and J. Sohma, *J. Phys. Chem.*, 1983, **87**, 1170.

[125] D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1983, 135.

judged from the selected data in Table 6. We have pointed out that the ring-proton hyperfine coupling constants are similar to those the radical cation of cyclopentadiene for which a similar SOMO is selected. Also, the large proton hyperfine splittings observed for the 2,5-dimethyl derivatives are significantly larger than those for 1,3-dimethyl cyclopentadienyl radicals (*ca.* 18 G *versus ca.* 13.5 G). This increase for the cations is probably largely due to the positive charge effect. The value quoted for the dimethyl cyclopentadienyl radical is a limiting value for the pure $1a_2$ orbital, so that partial population of the alternative π-orbital, thought to be important for substituted cyclopentadienyl radicals,[126] is not responsible for this difference.

Table 6 *Hyperfine coupling constants of radical cations derived from pyrrole, furan, and thiophene derivatives and of related radicals*

Radical		*Hyperfine Coupling Constants*/G[a]			
X	R	$H_{2.5}$	$H_{3.4}$	$H(CH_3)$	*Other nuclei*
S	H	13	2.5		
S	CH_3		3.5	18.1	
O	H	14	3.5		
NH	H	16	3.0		*ca.* 3(^{14}N)
NH	CH_3		3.5	17.5	*ca.* 3(^{14}N)
NCH_3	H	15.5	3.6		*ca.* 3.5(^{14}N)
CH_2	H[b]	11.6	3.5		< 2(CH_2)
CH	H[c]	13	3.45		1.0(CH)
CH	CH_3[c,d]		3.7	13.5	1.1(CH)

[a] G = 10^{4} T. [b] T. Shida, Y. Egawa, H. Kato, and H. Kubodera, *J. Chem. Phys.*, 1980, **73**, 5963. [c] A. G. Davies, E. Lusztyk, and J. Lusztyk, *J. Chem. Soc., Perkin Trans. 2*, 1982, 729. [d] These are limiting values.

Our hope that, for thiophene, there might be some cations having their unpaired electrons on sulphur in the *n*(σ)-orbital was not fulfilled. It seems that it is not possible for this five-membered ring to undergo sufficient angle distortion to lower this orbital below the π-level.

Pyridine and Related Cations.—*The Pyridine Cation.* In one of the earliest reports of e.s.r. studies of radical-cations formed by radiolysis. Shida and his co-workers[127,128] established that the ground-state SOMO for the pyridine cation is the $n(a_1)$ orbital on nitrogen (40) rather than one of the aromatic π-orbitals. This was not an obvious result since the π orbitals are close in energy to the $n(a_1)$ orbital and theoreticians had not reached agreement as to the best choice. The e.s.r. results are definitive but I stress that they relate to the relaxed cation rather than to that formed on vertical ionization. As I show below, I think that bond-angle relaxation is extensive for these ions.

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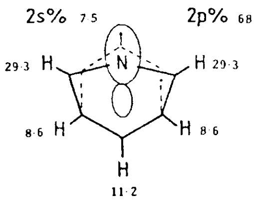
[126] P. J. Barker, A. G. Davies, and M.-W. Tse, *J. Chem. Soc., Perkin Trans. 2*, 1980, 941.

[127] T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869.

[128] T. Shida and T. Kato, *Chem. Phys. Lett.*, 1979, **68**, 106.



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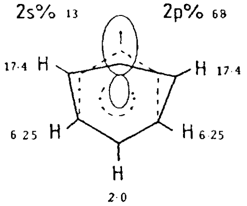
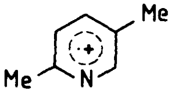


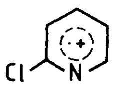
(41)

E.s.r. results shown in structure (40) make an interesting comparison with those for the isoelectronic phenyl radical (41).[129] The approximate p:s ratio, deduced in the usual way from the ^{14}N and ^{13}C hyperfine tensor components, is *ca.* 9 for $(py)^+$ but *ca.* 5 for phenyl, the total spin-density on N and C being *ca.* 75%. This suggests that the desire for more linear co-ordination for nitrogen is greater than that for carbon. This accords with the greater delocalization onto the *ortho* C–H groups for py^+.

Substituted Pyridine Cations. Our aim in studying these cations was to try to modify the energy of the SOMO resulting from π-electron loss so that this was favoured over loss from the n-orbital.[130] We succeeded with the cations shown in (42), (43), and (44), which gave only π-cations. For the 3-chloro-derivative both π- and n-cations were detected. This is a particularly interesting result, since it is very rare that species which can be interchanged by simple electron-transfer are found to co-exist. We think that they are probably formed together initially and that the major ring distortion of the n-cation then provides a large barrier to interconversion.



(42)



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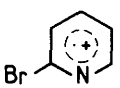

(44)

Diaza-derivatives. The definitive work is again that of Shida and Kato.[127] Results for the 1,2- and 1,4-derivatives are clear-cut but I am uncertain about the 1,3-derivative. The natural assumption is that the SOMO is distributed between the two in-plane n-orbitals on nitrogen and this is clearly established for the 1,2-and 1,4-derivatives by the e.s.r. spectra. However, we find that the spectrum for the 1,3-derivative is very similar to that of the pyridine cation with one strongly coupled nitrogen and is not well accommodated by the concept of two equivalent nitrogen nuclei.[131]

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[129] P. K. Kasai, E. Hedeya, and E. B. Whipple, *J. Am. Chem. Soc.*, 1969, **91**, 4364.

[130] D. N. R. Rao, G. W. Eastland, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, in press.

[131] D. N. R. Rao, G. W. Eastland, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, in press.

A possible explanation lies in the preferred method of distortion. For the 1,2-derivative delocalization is unavoidable and for the 1,4-derivative a tendency to flatten can occur at both nitrogen atoms. However, we suggest that for the 1,3-derivative a distortion in which one CNC angle increases whilst the other decreases may be preferred, thereby localizing the SOMO. Given that interaction between the two nitrogen *n*-orbitals is small, this could well occur. The situation is somewhat reminiscent of the very ready distortion of *m*-dinitrobenzene anions from the symmetrical structure by solvent perturbations[132] and of that for $(R_2\dot{N}CH_2NR_2)^+$ cations discussed in Section 10 above.

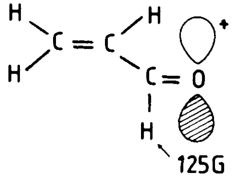
16 Vinyl Cations

This section links closely with Section 4 on alkene cations and the same problems connected with the degree of twist in the cations persists. Most work has been on $(H_2C{=}CHX)^+$ cations but there has been some work on di- and poly-substituted derivatives also. In some cases, the e.s.r. results are ambiguous and, certainly, more work is needed.

Thus, for methyl acrylate and, especially, methyl methacrylate, the spectra are difficult to interpret. Tabata and Lund obtained a 25G triplet for the former cation[133] but we have obtained a 12G triplet in addition at very low concentrations.[134] Whichever is correct, such a simple spectrum is surprising since it implies very little delocalization, whereas significant spin-density on the CH_2 unit and on the ester moiety might be expected since the ionization potentials of the separate units are comparable.

However, for the methacrylate cation both groups have established that replacing the $-OCH_3$ group by $-OCD_3$ has no effect on the e.s.r. spectrum. Thus, unless some rearrangement has occurred (which remains obscure), it seems that there is again little delocalization into the ester group. Unfortunately, the task of unravelling the very complicated spectrum has not yet been accomplished. The results may mean that the degree of twist is large for these cations.[134]

The cation of acrolein (45) makes an interesting contrast[133] since, in this case, electron loss is from the in-plane oxygen orbital, as evidenced unambiguously by the large (125G) ^1H hyperfine coupling.



(45)

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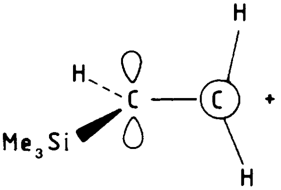
[132] D. Jones and M. C. R. Symons, *Trans. Faraday Soc.*, 1971, **67**, 961.
[133] M. Tabata and A. Lund, *Chem. Phys.*, 1983, **75**, 379.
[134] G. W. Eastland, Y. Kurita, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, in press.

The spectrum for acrylonitrile cations suggests coupling of 24 G to two protons, *ca.* 12 G to a third and parallel coupling to nitrogen of *ca.* 20 G.[134] Thus, in this case, the expected π-delocalization seems to be occurring although the large methylene proton coupling may imply a considerable degree of twist.

For vinyl bromide cations we obtained a well-defined bromine splitting characteristic of an α-bromine structure. Also, there was a poorly resolved 15 G triplet tentatively assigned to the CH_2 protons. The estimated spin-density on bromine was *ca.* 39% which is remarkably large [*cf. ca.* 18% for R_2C–Br radicals and 30% for $(PhBr)^+$ cations]. If the radical is planar, the estimated spin-density on the CH_2 unit is *ca.* 65% but if it is twisted these numbers have no significance.

We have suggested that the 19—20 G triplet observed for the cations $(H_2\dot{C}–C{=}OR)^+$ and also $(H_2\dot{C}–CH{=}OCOMe)^+$ have structures close to the limiting valence-bond structures indicated. This must be true if the (^1H) coupling is negative but if, by any chance, the cations are strongly twisted it might be positive, in which case this argument is again meaningless.

Results for various $-SiMe_3$ derivatives are of particular interest since they require that the cations be twisted.[134,135] For the vinyl derivative we found two protons with $A = 40$ G and one with $A = 18$ G. The former must be positive but this is not certain for the latter. These results imply considerable twisting with a tendency to favour the limiting structure (46). This is expected to be favoured since β-Me_3Si groups can thereby stabilize the cationic H_2C^+ unit by σ–π overlap to a maximum extent. One interesting aspect of our results is the ready breakdown of these ions to give methyl radicals.[134] This implies that the cation $H_2C{=}CH–SiMe_2{}^+$ or some rearranged or cyclized version must have a relatively high stability.



(46)

Results for the cations of allyl chloride and bromide are of interest since they clearly establish that the halogen adopts the out-of-plane site favoured both for steric and electronic reasons. The chlorine and bromine splittings were large, indicating extensive delocalization (*ca.* 23% on chlorine and 29% on bromine). Triplet splittings of *ca.* 16 G indicate a spin-density of *ca.* 70% on the CH_2 moiety – again if we assume no twisting for the cations.

The styrene cation [$a(CH_2) = 10$ G] has been discussed above. Results for 2-vinyl pyridine cations show that these are structurally similar but weak outer

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[135] M. Kira, H. Nakazawa, and H. Sakurai, *J. Am. Chem. Soc.*, 1983, **105**, 6983.

features suggested the presence of a second species. Similar outer lines were favoured for 4-vinyl pyridine cations, the spectrum being very similar to that for unsubstituted pyridine cations, having the SOMO strongly confined to the $n(\sigma)$ N orbital (see Section 15 above).[134] The former results represent another example in which two alternative structures, not involving major rearrangements, have been stabilized in a single matrix. Clearly interchange between them must be very slow.

18 Inorganic Cations

This is, perforce, a surprisingly short section. Apart from various small cations formed in inert-gas matrices by Knight and his co-workers and the SnH_4^+ prepared in $CFCl_3$, discussed above (Section 13), there has been little progress. We have prepared $N_2O_4^+$ cations in $CFCl_3$ but several other attempts to obtain good e.s.r. spectra for various inorganic cations have failed. For example, we have been unable to detect any resonance features for Br_2^+ or I_2^+ despite the fact that their formation is indicated by optical spectroscopy. Also, attempts to prepare cations of various neutral transition-metal complexes have largely failed, although some evidence for the formation of $Fe(CO)_5^+$ from $Fe(CO)_5$ in $CFCl_3$ was forthcoming.[136]

The Cations CO^+ and N_2^+.—These have been isolated in inert-gas matrices at *ca.* 4 K after formation by photoionization just prior to, or during, deposition.[10,11] This work is an extension of techniques developed especially by Lester Andrews[137] for the preparation of cations for spectroscopic studies.

For $^{13}CO^+$ a very clean spectrum was obtained using a neon matrix at 4K (Figure 8).[11] Thus the e.s.r. parameters given in Table 7 are very precise. Also given are the gas-phase results of Pilch *et al.*[138] Agreement is good, so one can reasonably deduce that there is very little perturbation from the matrix in this case. The

Table 7 *E.s.r. parameters for some inorganic radical cations in rare-gas matrices* (*refs.* 10, 11, 139)

		g-Values			*Hyperfine coupling constants*/MHz				
Cation	*Medium/T*	g_x	g_y	g_z	A_x	A_y	A_z	A_{iso}	2B
$^{13}CO^{+a}$	Ne/4	2.004,	1.9996,	1.9996	1 665,	1 527,	1 527,	1 573,	92
$^{13}CO^{+b}$	gas	—	—	—	—	—	—	1 506,	96.4
$^{14}N_2^+$	Ne/4	2.0004 (av)			—	—	—	104.1,	
H_2O^+		2.0093 (av)			—	—	—	73.7 (^1H),	
					—	—	—	83.5 (^{17}O),	

[a] Ref. 11. [b] Ref. 139.

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[136] B. M. Peake, M. C. R. Symons, and J. L. Wyatt, *J. Chem. Soc., Dalton Trans.*, 1983, 1171.

[137] L. Andrews, *Ann. Rev. Phys. Chem.*, 1979, **30**, 79.

[138] N. D. Pilch, P. G. Szanto, T. G. Anderson, C. S. Gudeman, T. A. Dixon, and R. C. Woods, *J. Chem. Phys.*, 1982, **76**, 3385.

Figure 8 *Low- and high-field e.s.r. powder pattern spectrum of* $^{13}CO^+$ *in neon matrix at* 4K. (*Taken from ref.* 10)

parameters give calculated 2*s* and $2p_z$ populations of 43% and 42% respectively. Thus the simple representation of the SOMO as a non-bonding sp_z hybrid orbital on carbon is nicely supported.

In marked contrast, the $N_2{}^+$ cation was found to be rotating even at 4K in neon.[10] It is not clear why this should be when ^+CO is so firmly fixed that libration is apparently unimportant. Furthermore, the ^{14}N isotropic coupling corresponds to only *ca.* 6% 2*s* character on each nitrogen. Hence the 2*p* character must be *ca.* 44% suggesting that, in this case, the SOMO is primarily 2*p* in character. Such a drastic switch seems very surprising to me but the results are convincing.

H_2O^+ and $NH_3{}^+$.—Knight and Steadman have reported a very thorough study of the water cation in many of its isotopic forms (H_2O^+, HDO^+, D_2O^+, and $H_2{}^{17}O^+$).[139] The results present no surprises but it is good to have a firm identification of this important cation and to have some precise data. The results for both this cation and $\cdot NH_3{}^+$ cations in neon at 4K[11] show that they are apparently freely rotating. The only previous reports of e.s.r. studies of the H_2O^+ cation for which reasonable parameters were forthcoming was our own for H_2O^+ in aqueous acid media[140] and one of a species thought to be H_2O^+ formed in γ-

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[139] L. B. Knight and J. Steadman, *J. Chem. Phys.*, 1983, **78**, 5940.

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irradiated beryl.[141] It is interesting to note that, in our case, the relatively large *g*-shift (2.0093) for H_2O^+ in neon was not observed. This probably reflects the effect of strong hydrogen bonding in the aqueous matrix. Results for $\cdot NH_3{}^+$ agree very well with the many previous reports for this species which is nice confirmation that these results are indeed reliable. It is often implied in the literature that large environmental interactions render results for radicals in matrices other than the inert gases unreliable but, in general, my experience is that this is not usually the case.

The $N_2O_4{}^+$ Cation.—We have recently reported our results for this cation in a freon matrix.[142] We had previously suggested that cationic species were formed in an irradiated single crystal of $N_2O_4{}^+$,[142] and Morton *et al.* tentatively identified a species formed from N_2O_4 in SF_6 as a nitrosyl nitrate ion, $ONONO_2{}^{\pm}$.[143]

The results using $CFCl_3$ are clear-cut – the species detected is not the σ-radical $(O_2N{\cdot}NO_2)^-$ tentatively identified in N_2O_4 crystals but the rearranged cation $O_2N^+ - - - O\dot{N}O$, which can be viewed as an $\cdot NO_2$ molecule relatively weakly bound to a linear $NO_2{}^+$ cation. The e.s.r. results are quite unambiguous; not only are the features for the 'NO_2' unit similar to, but quite distinct from, those for genuine $\cdot NO_2$, but also weak interaction with ^{14}N of the $NO_2{}^+$ unit was resolved.[142] I think that the driving force for this change lies in the high stabilities of both $NO_2{}^+$ and NO_2. It is important that the theoretical calculations of Yoshioka and Jordan actually predicted that this should be the most stable form of the cation.[144] Clearly the species reported by Morton *et al.* was the same species.[143]

19 Conclusion

I conclude that in a remarkably short period a new Chapter in e.s.r. spectroscopy has largely unfolded. I hope that the techniques involved will now be treated as standard and that anyone interested in the structure and reactivity of radical-cations will consider using this approach.

Finally, I wish to thank my students (Dr. D. N. R. Rao, B. W. Wren, P. J. Boon, G. D. G. McConnachie, and Dr. H. Chandra) for all their help, Professor T. Shida and Dr. M. Iwasaki for many helpful discussions and, especially, Professors Akinori Hasegawa and George Eastland for extensive and continuing collaboration. I would also like to thank Miss V. Orson-Wright and Mrs. C. A. Crane for their valuable help in preparing the typescript.

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[*] Note added in proof. It now seems probable that all the ester cations studied at 77 K (p. 417) are not the π cations, but are rearranged cations of this type. (M. Iwasaki, H. Muto, K. Toriyama, and K. Numone, Chem. Phys. Lett., 1984, **105**, 586.)

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