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Three-electron σ-Bonded Radicals: An Electron Paramagnetic Resonance Spectroscopic Study of $R_3P\dot{-}Cl$ Radicals in Freon

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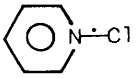
Our main purpose is to draw attention to the relative stability of three-electron σ-bonded radicals (σ_1^2, σ_2^1), the large number of such radicals that have been studied by EPR spectroscopists, and their potential importance as reaction intermediates. The topic is illustrated by experiments which show that when $R_3P^{\bullet+}$ radical cations ($Me_3P^{\bullet+}$ and $Ph_3P^{\bullet+}$) are generated in $CFCl_3$ at 77 K by exposure to ^{60}Co γ-rays, and the system is annealed to *ca.* 155 K, features characteristic of $R_3P\dot{-}Cl$ radicals are detected, with well defined hyperfine coupling to ^{31}P and $^{35/37}$Cl nuclei. It is argued that these must have been formed from chloride ions released from $(CFCl_3)^{\bullet-}$ radical-anions following electron capture.

There has recently been an upsurge of interest in three-electron-bonded systems as possible intermediates in organic reactions.[1–3] Indeed, in a recent review,[1] it is stated that this is a little explored area, and that the three-electron bond 'turned up initially (1987) in studies of chlorine atoms bonded to pyridine nuclei' (see **I**). We have been studying three-electron-bonded systems for many years,[4–7] and wish to stress the major role played by EPR spectroscopy in these studies, which does not seem to have been appreciated in current mechanistic studies.[1–3] Breslow *et al.*[2] adduce convincing kinetic evidence for complex formation between chlorine atoms and various substituted pyridines. However, they stress that these could have a π-structure, as has been proposed for chlorine atom complexes with benzene,[8] or the $(\sigma)^2(\sigma^*)^1$ structure shown in **I**. Marked differences in stability (the pyridine complex is *ca.* 170 times more stable than that of benzene) and in absorption spectra, coupled with the results of their theoretical calculations, all point to structure **I** rather than a π-complex of the benzene type.[2] This conclusion is very strongly supported by all the previous work on three-electron σ-bonded structures, that one of us has suggested should be described simply as σ*-radicals.[9] The EPR and optical[10–12] evidence in favour of the σ* formulation for many intermediates is, in our view, overwhelming.



I

A simple model for three-electron-bonded systems is illustrated in fig. 1. Here we envisage a pure σ^2, σ^{*1} structure, but stress that this is a readily pictured limit for systems of high symmetry, which is likely to be only a first approximation in low-symmetry systems. The EPR technique probes the SOMO *via* hyperfine coupling tensors for the directly bound nuclei, and the proximity of other levels *via* the *g* tensor. The optical technique which usually detects the allowed $\sigma \rightarrow \sigma^*$ transition shown in fig. 1 gives a measure of the bond strength and of the decrease in bond strength on going from the parent σ^2, σ^{*0} structure to the σ^2, σ^{*1} structure.

A range of structures studied with these techniques is given in table 1. Probably the first species to be well characterised were the V_K centres in alkali-metal halide crystals ($F\dot{-}F^-$, $Cl\dot{-}Cl^-$ *etc.*).[13,14] Another well studied class comprises the disulphide radical anions $RS\dot{-}SR^-$,[15,16] which are thought to be important in biological redox reactions. In these the SOMO is found by EPR spectroscopy to be essentially (*np*–*np*) as in **II**. This structure, found for the V_K centres and $RS\dot{-}SR^-$ ions, is also found for $R_2S\dot{-}SR_2^+$ radical-cations.[17,18] However, the analogous diphosphorus radical-cations $R_3P\dot{-}PR_3^+$ use hybrid orbitals with considerable 3s character (as in **III**) which contribute greatly to the form of the EPR spectra.

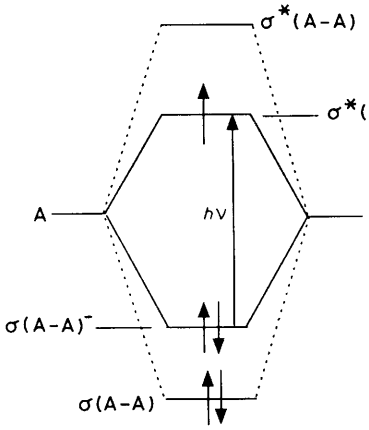
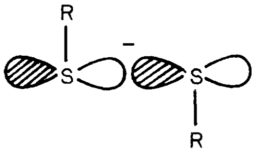


Fig. 1. Qualitative energy-level diagram for a molecule A—A and its radical-anion, $(A—A)^-$, showing how the σ-bond is weakened by the added electron, and the $\sigma \rightarrow \sigma^*$ transition is shifted to low frequencies.



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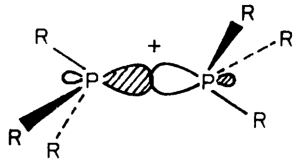


III

Table 1. Examples of $A\dot{-}A$ and $A\dot{-}B$ σ* species (which have been studied in these laboratories)

$\text{hal}\dot{-}\text{hal}^-$	$R_2S\dot{-}SR_2^+$
$\text{hal}\dot{-}OH^-$	$RS\dot{-}SR^-$
$RCONH\dot{-}\text{hal}^-$	$R_2S\dot{-}\text{hal}$
$Br\dot{-}CN^-$	$R_3P\dot{-}\text{hal}$
$HC\equiv C\dot{-}I^-$	$\text{Rhal}\dot{-}\text{halR}^+$
$C_6H_5\dot{-}\text{hal}^-$	imidazole$\dot{-}\text{hal}^-$
$C_6F_5\dot{-}\text{hal}^-$	uracil$\dot{-}\text{hal}^-$
$R_3N\dot{-}\text{hal}$	$H_3N\dot{-}NH_3^+$
$R_3P\dot{-}PR_3^+$	

These centres can be formed by electron capture or by electron loss as in reactions (1) and (2) + (3), respectively.

$$A\dot{-}A + e^- \rightarrow A\dot{-}A^- \qquad (1)$$

$$A^- \rightarrow A^\bullet + e^- \qquad (2)$$

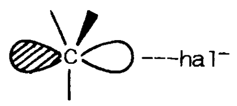
$$A^\bullet + A^- \rightarrow A\dot{-}A^- \qquad (3)$$

Thus, the V_K centres ($hal_2^{\bullet -}$) are formed by electron loss in alkali-metal halide crystals, but the same radical-anions can be formed from halogen molecules by electron capture.

Most three-electron systems that have been studied are 'homonuclear" ($A\dot{-}A^-$), and most of these have been formed from second-row or heavier atoms (table 1). Apart from $F_2^{\bullet -}$, first-row systems are rare, despite the fact that theory suggests that they should be more stable than their analogues. Recently, evidence for $H_3N\dot{-}NH_3^+$ radicals has been presented, but these centres were very unstable, giving $^\bullet NH_3^+$ radicals at *ca.* 140 K, presumably *via* the reaction (4)[19]

$$H_3N\dot{-}NH_3^+ \rightarrow NH_3 + {}^\bullet NH_3^+ \qquad (4)$$

We know of no evidence for $H_2O_2^{\bullet -}$ or $R_2O_2^{\bullet -}$ radical anions. Electron addition to H_2O_2 seems to give $^\bullet OH + OH^-$, implying that the σ^* anion is thermally unstable. However, mixed first–second-row σ^* species appear to be more stable when the orbital energies are reasonably matched. Thus, although $R\dot{-}hal^-$ σ^* radical anions (R = alkyl) do not seem to be stable, adduct radicals, usually written as $R\cdots hal^-$, with very weak interaction have been detected in solid matrices.[20,21] These can be thought of as representing the limit of extremely weak interaction. They are characterised by EPR parameters typical of $R^\bullet$ radicals, but reduced by 5–10%, the radicals remaining planar (**IV**), and small anisotropic couplings to halogen nuclei, the isotropic component being extremely small[22] (table 2). If the electronegativity of the carbon centre in $R^\bullet$ is increased, as in $F_3C^\bullet$,[23] or if relaxation to give a planar 2p-orbital SOMO is impossible (see fig. 2),[24,25] well defined σ^*-electron adducts can often be detected. Examples are given in table 2 for some carbon–halogen anions. The major factors that control the formation of carbon–halogen adducts rather than dissociation products seem to be (i) the electronegativity of groups X in $X_3C\dot{-}hal^-$, and (ii) the extent to which the orbital on carbon can increase its 2p-character. These factors are indicated schematically in fig. 2.



IV

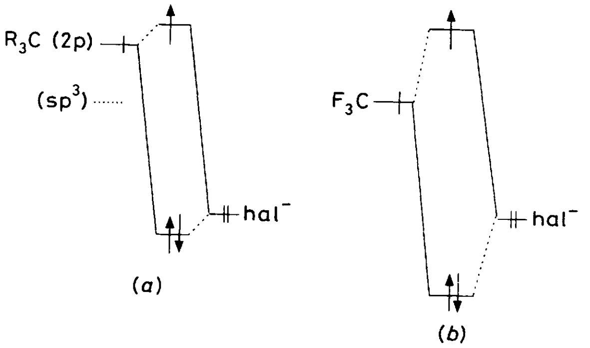


Fig. 2. Qualitative energy-level diagrams for (*a*) an alkyl radical–halide ion adduct, for which little, if any, bonding occurs, and (*b*) for an $F_3C\dot{-}hal^-$ σ^* radical-anion with considerable residual bonding. Note how flattening of the $R_3C^\bullet$ radical contributes to the weakening of the bond.

Also, on going from carbon to nitrogen, there is a great increase in the stability of σ^* radicals.[26–29] This trend nicely illustrates the energy-matching requirement. This is also illustrated by a general increase in spin density on halogen on going from —Cl to —I. Also the increase in relative 2s character on nitrogen on going from $R_3N\dot{-}Cl$ to $R_3N\dot{-}I$ nicely illustrates the concept that, as the bond stretches and weakens, so the R_3N— unit becomes flatter.[30]

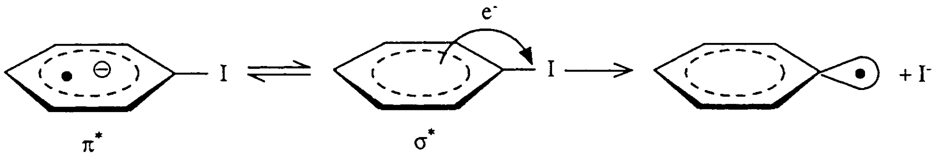
There are two quite separate σ^* systems in which hydrogen is one component. One comprises the $H\dot{-}hal^-$ radical-anions,[31,32] and the other is the $H\dot{-}M(CN)_4^{2-}$ group.[33,34] The former are so simple that there can be no doubt about the σ^* nature of the SOMO. There is the expected fall in $A(^1H)$ and gain in halogen hyperfine coupling on going from $H\dot{-}F^-$, which is close to being an 'adduct' with very low transfer of spin, to $H\dot{-}I^-$ where the ^1H coupling is only 480 G.

The latter are unique in transition-metal chemistry. The ^1H coupling is *ca.* 150 G for the nickel derivative and *ca.* 180 G for the platinum derivative. The form of the *g* tensor components and ^{195}Pt hyperfine coupling suggest that the SOMO largely comprises an antibonding combination of H(1s) and metal (d_{z^2}) atomic orbitals.

Table 2. EPR data for alkyl radical–halide ion adducts

		^1H hyperfine coupling/G[a]			^{81}Br or ^{127}I hyperfine coupling/G		
radical	medium	$A_\parallel$	$A_\perp$	A_{iso}	$A_\parallel$	$A_\perp$	A_{iso}
$Me_3C^\bullet/Br^-$ [b]	adamantane at 209 K	—	—	21.4	—	—	±6.7
$Me_3C^\bullet/Br^-$ [b]	adamantane at 4 K	—	—	*ca.* 21	*ca.* 56	*ca.* (−) 10	*ca.* 12
$Me^\bullet/Br^-$ [c]	CD_3CN	21	21.5	21.5	58.3	(−) 28.3	+0.57
$Me_2CH\dot{C}H_2/Br^-$ [b]	adamantane	—	—	19.0 (αH) 36.2 (βH)	—	—	±4
$Me_2CH\dot{C}H_2/Br^-$ [b]	tetramethylsilane	—	—	20 (α + βH)	75	—	—
$CH_3\dot{C}H_2/Br^-$ [b]	adamantane	—	—	*ca.* 21	—	—	±4
$Me_2\dot{C}H/Br^-$ [b]	adamantane	—	—	20 (αH) 24.3 (βH)	—	—	±4.3
$^\bullet CH_3/I$ [d]	CD_3CN	21	21	21	104	(−) 56.4	−3
$CH_3\dot{C}H_2/I^-$ [b]	adamantane	—	—	*ca.* 21	—	—	±5
$Me_2\dot{C}H/I^-$ [b]	adamantane	—	—	20 (αH) 24.0 (βH)	—	—	±2.8
$Me_3C^\bullet/I^-$ [b]	adamantane	—	—	21	—	—	±2.7

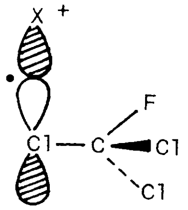
[a] 1 G = 10^{-4} T; [b] M. C. R. Symons and I. G. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1180; [c] C. M. L. Kerr and F. Williams, *J. Am. Chem. Soc.*, 1971, **93**, 2805; [d] S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1973, 391.



(5)

In several cases there is competition between the σ^* orbital and some alternative vacant orbital for the excess electron. Thus for PhI an added electron can be accommodated in the π^* orbital, largely confined to the benzene ring or to the more localised C—I σ^* orbital. These are orthogonal provided the aromatic unit remains planar. Our results show that both radical-anions can be detected, and that the σ^* anion is the natural intermediate in the process of iodide-ion loss.[35] The σ^* orbital is lowered below the π^* level as the C—I bond stretches. Conversion from the π^* to the σ^* structure probably requires a combination of bending and stretching as shown schematically in scheme (5).

An interesting example of σ^*-radical formation seems to occur when certain radical cations (X^+) are generated in freon matrices.[36,37] These are thought to have structures of the type shown in V, involving one unique chlorine atom of the solvent. Cation radicals that form such adducts include $RC \equiv N^{\cdot +}$,[38] $(RO)_3PO^{\cdot +}$,[39,40] and $CH_3(H)C{=}O^{\cdot +}$.[37] We have shown that the chlorine hyperfine coupling is a marked function of the ionization potential of the parent compound, decreasing as expected with decrease in E_i.[41]



V

Molecules with ionization potentials <9–10 eV do not form such solvent adducts (though weak coupling to ^{19}F is sometimes observed[41]). It is important that $R_3P^{\cdot +}$ radical-cations ($E_i \approx 8.5$ eV) do not show any coupling to chlorine in their EPR spectra at 77 K.[42] In the present study we show that on carefully controlled annealing above 77 K features for these cations are reduced, and new features, showing relatively large hyperfine coupling to a single chlorine nucleus as well as to ^{31}P, grow in. These are assigned to $R_3P \doteq Cl$ σ^* radicals. The results are discussed in terms of a current controversy regarding the identity of the electron-capture centres formed in irradiated $CFCl_3$ solutions.[43,44]

Experimental

All the materials used were the highest grades available and were used without further purification. Freon ($CFCl_3$) was purified, if necessary, and solutions were degassed directly prior to freezing as small beads in liquid nitrogen.

Solutions (generally *ca.* 1 : 1000) were exposed to ^{60}Co γ-rays for doses up to *ca.* 1 MRad. EPR spectra were measured using a Varian E109 spectrometer. Samples were annealed above 77 K either using a Varian variable-temperature gas-flow system, or by decanting the liquid nitrogen from the insert Dewar flask and allowing the sample to warm, with continuous EPR monitoring. Samples were recooled to 77 K for study when significant spectral changes were observed.

Results and Discussion

Typical EPR spectra for three types of phosphorus radicals are shown in fig. 3–5. In fig. 3, a spectrum for the parent cations ($R_3P^{\cdot +}$) is shown, together with a simulation based on the data given in table 3. In fig. 4, outer features assigned to dimer cations $(R)_3P \doteq P(R)_3^+$ are shown. These were observed on annealing relatively concentrated solutions. In fig. 5, features assigned to the chlorine adducts are shown. These are maximised, relative to the features for the parent cations and dimer cations, by using high radiation doses, extremely dilute solutions and annealing to near the melting point of the solvent. We identify these species as $R_3P \doteq Cl$ σ^* radicals. Radicals of this general type were previously identified in irradiated methanolic or acidic aqueous glasses containing halide salts together with organic phosphines and sulphides.[45] Data from these species are compared with the present data in table 3. There are small differences which we assign to medium effects, but there can be little doubt that the radicals have the same structure. This comparison helps to confirm our identification.

We suggest that these species are formed from chloride ions:

$$R_3P \xrightarrow{h\nu} R_3P^{\cdot +} + e^- \tag{6}$$

$$e^- + CFCl_3 \rightarrow (^{\cdot}CFCl_3)^- \tag{7}$$

$$^{\cdot}CFCl_3^- \xrightarrow{\text{anneal}} {}^{\cdot}CFCl_2 + Cl^- \tag{8}$$

$$R_3P^{\cdot +} + Cl^- \xrightarrow{\text{anneal}} R_3P \doteq Cl \tag{9}$$

$$R_3P^{\cdot +} + (^{\cdot}CFCl_3)^- \rightarrow R_3P \doteq Cl + {}^{\cdot}CFCl_2 \tag{10}$$

We consider that the alternative route involving reaction (10) can be rejected, since two radicals are involved. Almost certainly the favoured reaction would be (11), in which electron return occurs.

$$R_3P^{\cdot +} + (^{\cdot}CFCl_3)^- \rightarrow R_3P + CFCl_3 \tag{11}$$

These results seem to establish conclusively that reaction (8) occurs on annealing the sample. Distinct EPR features for electron adducts are not detected after exposure at 77 K, only a very broad line being assignable to these centres. Hasegawa and Williams also detected only a broad singlet under conditions favouring the formation of $(^{\cdot}CFCl_3)^-$ anions,[46] and we consider that these are responsible for the freon singlet. However, on annealing the sample to *ca.* 150 K, well defined EPR features clearly due to coupling to ^{19}F and chlorine nuclei appear (fig. 6). These are invariably obtained from these systems. They are less well defined on recooling to 77 K or below, but poorly resolved features are retained, the initial broad line being lost.

The spectrum in fig. 6 was recently assigned to $(^{\cdot}CFCl_3)^-$ radicals by Roncin and co-workers.[43] In order to explain the spectrum a specific rotation about the F—C axis was postulated. In our view, the spectrum is more satisfactorily interpreted in terms of $^{\cdot}CFCl_2$ radicals undergoing a restricted

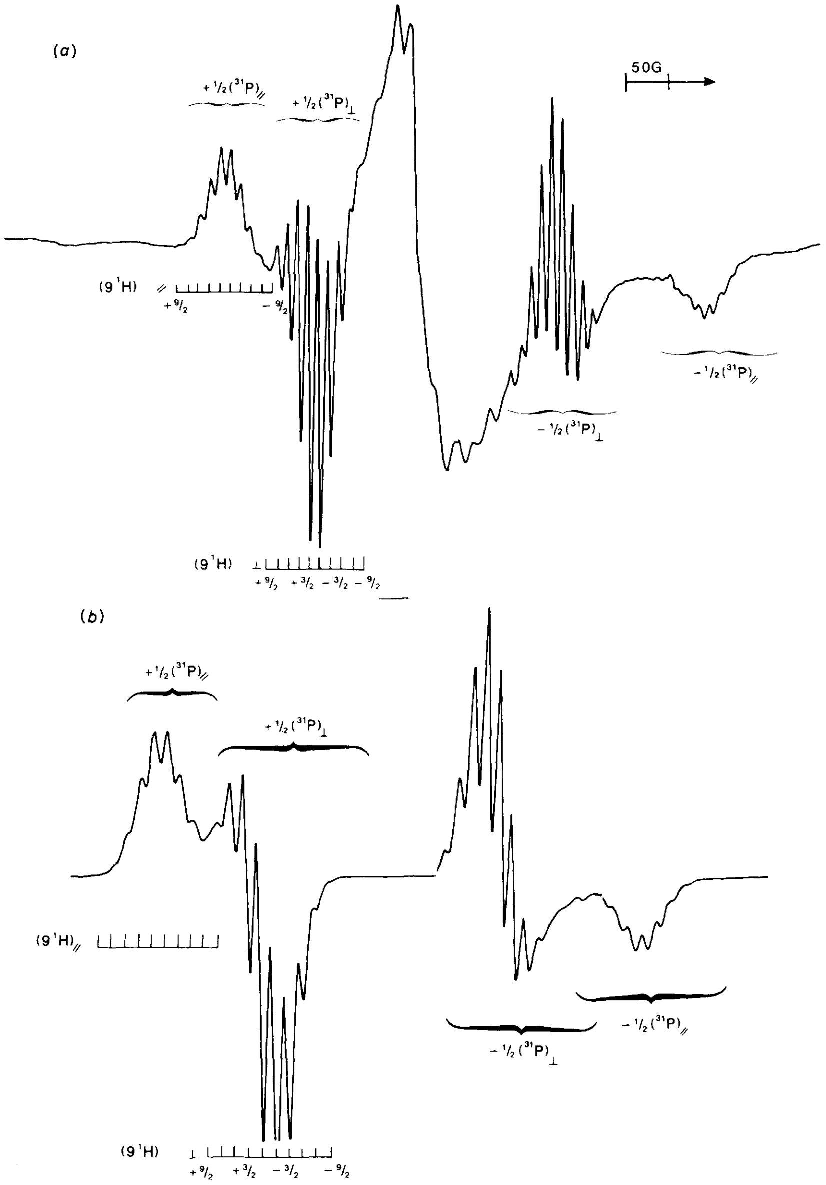


Fig. 3. (*a*) First-derivative Q-band EPR spectrum for a dilute solution (*ca.* 1 : 1000 v/v) of Me_3P in freon after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $Me_3P^{\cdot +}$ cations. (The central features are assumed to be due to impurity species.) (*b*) Simulation using the data for $Me_3P^{\cdot +}$ given in table 3.

rotation which partially averages the anisotropic parameters.[44] Simulations using the parameters reported for $(^{\cdot}CFCl_3)^-$ anions, and those deduced for $^{\cdot}CFCl_2$ radicals are included in fig. 6. The latter were derived with the constraint that the known isotropic fluorine and chlorine coupling constants[47] were used. The fit is quite satisfactory for $^{\cdot}CFCl_2$ radicals and clearly superior to that based on the $(^{\cdot}CFCl_3)^-$ data.[44]

The present results, in our view, demonstrate the formation of chloride ions under these conditions, thus supporting the

Table 3. EPR parameters for some radical cations and $R_3P\dot{-}Cl$ radicals

		^{31}P hyperfine coupling/G[a]			^{1}H hyperfine coupling/G	^{35}Cl hyperfine coupling/G					
substrate	radical	$A_{\parallel}$	$A_{\perp}$	A_{iso}		$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{av}
PMe_3 in $FCCl_3$	PMe_3^+	584	285	385	11.5				2.0019	2.008	2.0059
	$[Me_3P]_2^+$	592	458	503	3.3				—	—	—
PPh_3 in FCCL$_3$	PPh_3^+	455	216	295	—				2.003	2.008	2.006
	$[Ph_3P]_2^+$	—	376	—	—				—	—	—
$PMe_3 + Cl^-$ [b]	$Me_3P\dot{-}Cl$	730	560	617	—	75	40	52	2.00	2.01	2.067
$PMe_3 + FCCl_3$	$Me_3P\dot{-}Cl$	750	580	636	—	—	34	—	—	—	—
$PPh_3 + Cl^-$ [b]	$Ph_3P\dot{-}Cl$	730	550	610	—	78	39	52	2.00	2.01	2.067
$PPh_3 + FCCl_3$	$Ph_3P\dot{-}Cl$	730	555	613	—	79	38	52	2.00	2.01	2.067

[a] 1 G = 10^{-4} T; [b] ref. (45).

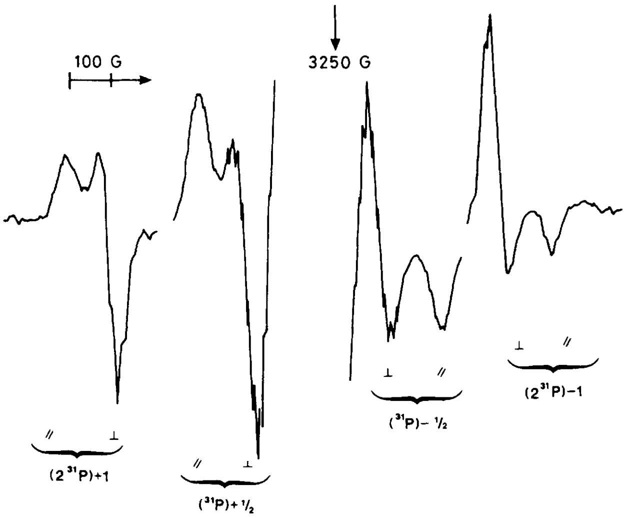


Fig. 4. First-derivative X-band EPR spectrum obtained from a solution (of concentration *ca.* 1 : 200 v/v) of PMe_3 in $FCCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the dimer radical-cation $(Me_3P \dot{-} PMe_3)^+$ and also features assigned to the parent radical-cation $^{\bullet}PMe_3^+$.

$^{\bullet}CFCl_2$ hypothesis. We suggest that the mobile species is the chloride ion, which migrates to the trapped $R_3P^{\bullet +}$ cations as a result of Coulombic attraction. Since the concentration of Cl^- is about equal to that of $R_3P^{\bullet +}$ radicals, reaction (9) would be far less probable than reaction with parent R_3P molecules if $R_3P^{\bullet +}$ cations were the mobile entities. Nevertheless, it may well be that reaction between geminate ions is favoured. They are likely to be much closer to each other than to other reactive centres in these dilute systems.

In order to check this suggestion, low concentrations of $Bu_4N^+Cl^-$ were incorporated. These will be present in the frozen solutions as ion-pairs or clusters, but some Cl^- ions should still be available for reaction with $R_3P^{\bullet +}$ cations. There was no major enhancement in the $R_3P \dot{-} Cl$ signals, nor were these adducts formed at lower temperatures. These results seem to us to favour the concept of geminate ion reaction.

Conclusions

These results illustrate the efficiency of σ^*-adduct formation, and the clear stabilising effect that this has on the radical

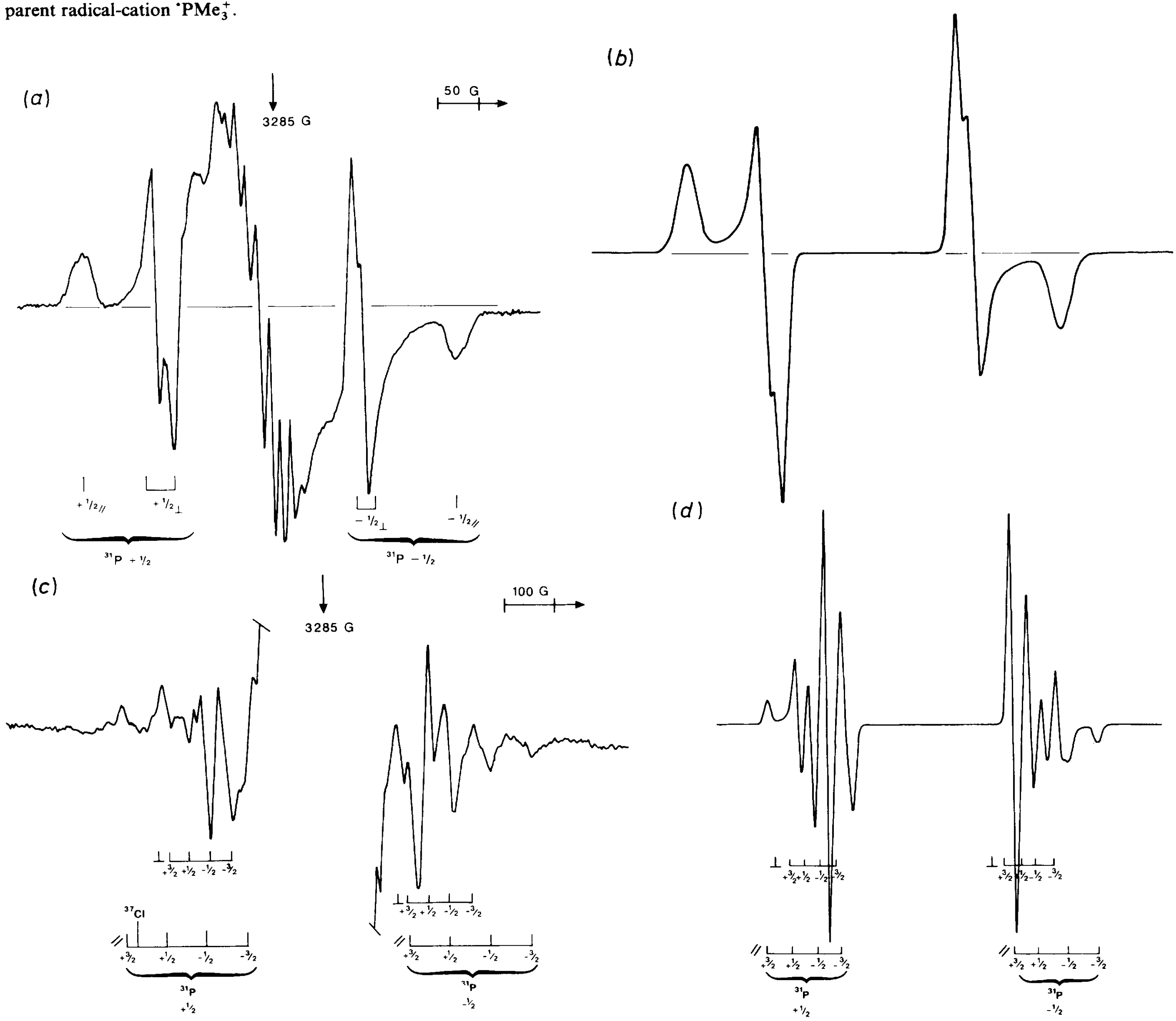


Fig. 5. (*a*) First-derivative EPR spectrum for a dilute solution of PPh_3 in freon after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $^{\bullet}PPh_3^+$. [Central features are assigned to $\dot{P}h^+$—$P(Ph)_2$-type radicals.] (*b*) Simulation using data for $^{\bullet}PPh_3^+$ given in table 3. (*c*) First-derivative EPR spectrum for a dilute solution of PPh_3 in freon after exposure to ^{60}Co γ-rays at 77 K and annealing, showing features assigned to $Ph_3P \dot{-} Cl$ radicals. (*d*) Simulation using data for $Ph_3P \dot{-} Cl$ given in table 3.

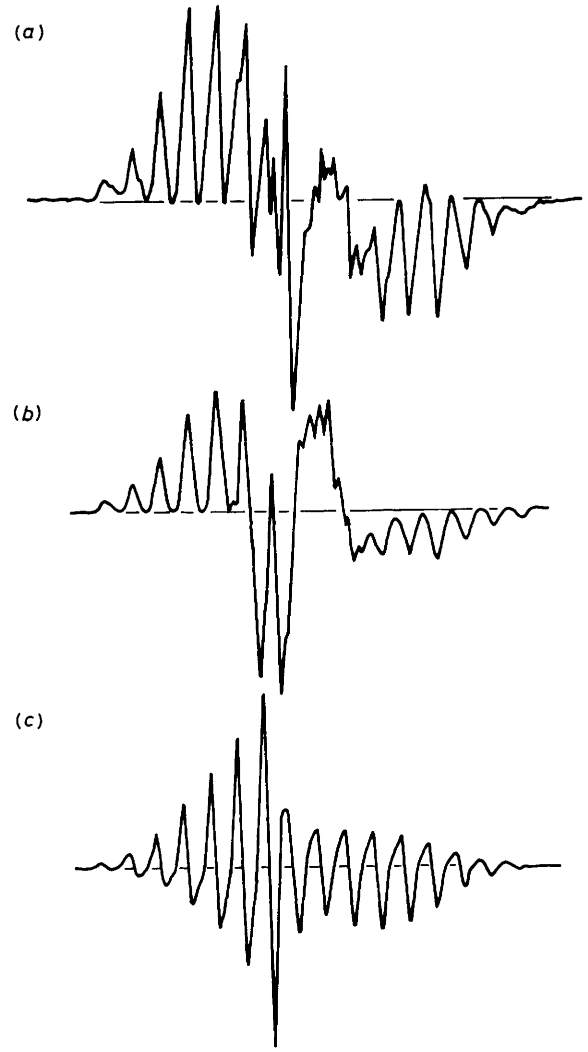


Fig. 6. (*a*) First-derivative X-band EPR spectrum for CFCl$_3$ containing P(OMe)$_3$ (*ca.* 1 : 1000) after exposure to ^{60}Co γ-rays at 77 K, and annealing to *ca.* 155 K. Outer features assigned to $^\bullet$P(OMe)$_3$ cations are not shown. This substrate was selected so that there were no central features for the radical-cations. (*b*) Simulation using the data for $^\bullet$CFCl$_2$ given in ref. (44). (*c*) Simulation using the data for $^\bullet$CFCl$_3^-$ [taken from ref. (43)].

component [A$^\bullet$ in reaction (3)]. There is a curious discrepancy between theory and practice regarding the stability of $A \dot{-} A^-$-type radicals for Group 1, the results strongly suggesting that these are less stable than those from Group 2 and below. There is no doubt that in the reactions of many radicals, σ^* adducts will tend to stabilise the radicals forming intermediates which may enhance rates, selectivity, or even the expected course of the reaction.

Equally important is the process of electron capture to give σ^* radicals. These intermediates are both electron donors and acceptors, and are a source of radicals when they dissociate. There is no doubt that they need to be considered seriously by mechanistic chemists.

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