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Electron Addition to Triphenylmethyl Arsonium Iodide

An Electron Spin Resonance Study

By Martyn C. R. Symons* and Glen D. G. McConnachie

Department of Chemistry, The University, Leicester LE1 7RH

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Exposure of crystalline $Ph_3AsMe^+I^-$ crystals to ^{60}Co γ-rays at 77 K yields an electron-adduct having e.s.r. parameters characteristic of methyl radicals weakly interacting with a Ph_3As molecule. We now find that, on annealing, this species dissociates to give normal methyl radicals, whilst solutions in methanol (CD_3OD) give, on electron addition at 77 K, the normal arsoranyl radical $[Ph_3\dot{A}sMe]$ together with methyl radicals, there being no trace of the adduct formed in the crystalline material. Reasons for these differences are discussed and it is suggested that the arsoranyl radical rearranges to a σ^* species as a necessary step in the dissociation process.

Geoffroy and Llinares[1] have recently established that electron addition to Ph_3AsMe^+ ions in triphenylmethyl arsonium iodide crystals at 77 K yields a species having e.s.r. parameters (^1H, ^{13}C and g) characteristic of methyl radicals, except that there was also a well defined splitting from a single ^{75}As nucleus. They estimated a spin density of *ca.* 0.75 on carbon for this adduct. No further species were detected on annealing. They drew attention to the surprising difference between this species and the phosphoranyl radicals $^{\cdot}PL_4$ normally formed by electron addition to similar phosphorus compounds.

Our interest in these results stemmed from a recent controversy regarding possible structures for the radical anions of alkyl halides and fluorinated alkyl halides.[2-14] Discussion centred around the fact that $(F_3C^{\cdot}—hal)^-$ anions have a well defined σ^* structure, but similar alkyl halide anions, $(R^{\cdot}—hal)^-$, have never been prepared. We argued that a major contributory factor must be the tendency for alkyl radicals to prefer a planar structure, whereas $^{\cdot}CF_3$ radicals are pyramidal. Clearly another factor is the electron-withdrawing power of the fluorine atoms, which lowers the energy of the carbon σ level thus increasing the covalency of the anion. These factors are illustrated in fig. 1. The force of these arguments is nicely illustrated by results for the isostructural ammonia derivatives, $[H_3N^{\cdot}—hal]$.[12] These species are σ^* anions, with considerable spin density on the halogen and with significant 2*s* contribution from nitrogen indicating pyramidality for the H_3N group. Delocalisation onto halogen and 2*s* character on nitrogen increase on going from Cl to I, thus establishing the expected trend in orbital hybridisation.

The aim of the present study was to discover conditions under which the As—Me bond does not break on electron addition and to learn more about the structure of the adduct. This work links with our recent study of the $(Br—CN)^-$ radical anion which was shown to exist in a linear, σ^* structure on initial electron addition, but rather than undergoing dissociation this rearranged to a bent, σ_{nb} structure[14] on annealing above 77 K.[15]

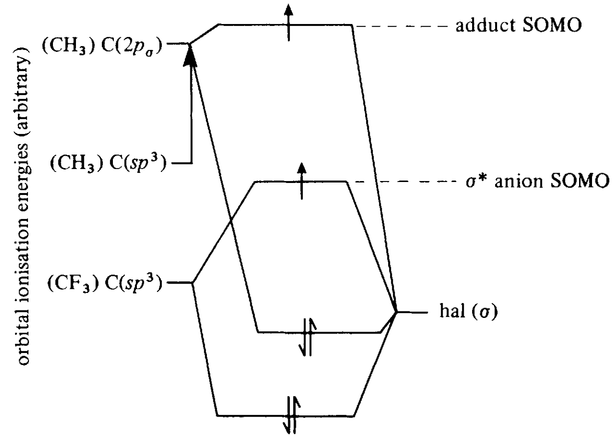


Fig. 1. Bonding scheme for $H_3C^{\cdot}$----hal^- 'adduct' and for $(F_3C^{\cdot}$—$hal)^-$ σ^* radical anion. The vertical arrow shows how the rehybridisation that occurs as the CH_3 unit flattens aids in weakening the C—hal bond.

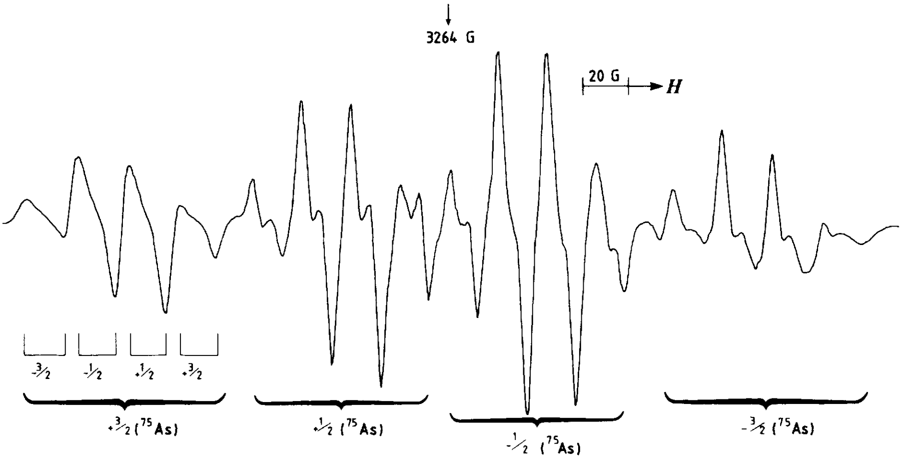


Fig. 2. First-derivative X-band e.s.r. spectrum for $Ph_3AsMe^+I^-$ after exposure to ^{60}CO γ-rays at 77 K showing features assigned to Ph_3As----$^{\cdot}CH_3$ adducts.

EXPERIMENTAL

Triphenylmethylarsonium iodide was obtained from Lancaster Synthesis. The pure compound and its solutions in CD_3OD were exposed to ^{60}Co γ-rays at 77 K in a Vickrad γ-cell with doses up to 1 Mrad.

E.s.r. spectra were measured at 77 K with a Varian E109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe. Samples were annealed by decanting the liquid nitrogen from the insert Dewar and recooling whenever significant spectral changes were observed.

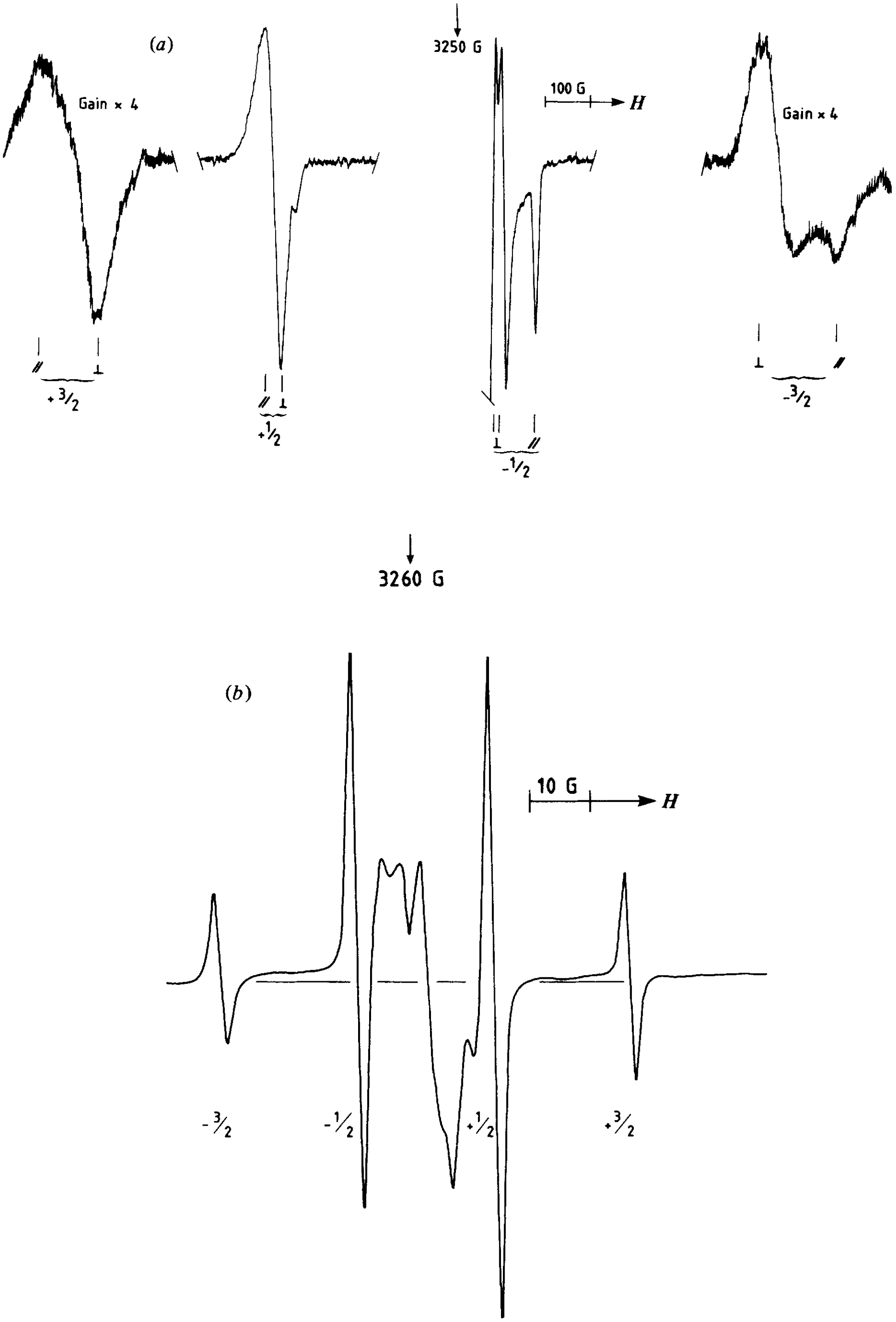


Fig. 3. First-derivative X-band e.s.r. spectra for a dilute solution of $Ph_3AsMe^+I^-$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, (*a*) showing features assigned to $[Ph_3\dot{A}sMe]$ arsoranyl radicals and (*b*) showing features assigned to methyl radicals. The centre features are largely due to solvent radicals.

RESULTS AND DISCUSSION

The e.s.r. spectrum obtained from the pure compound is shown in fig. 2. The data derived therefrom are very close to those obtained by Geoffroy and Llinares from their single-crystal experiments. In marked contrast, solutions in CD_3OD gave the spectrum shown in fig. 3. The central region of this spectrum is shown in fig. 3(*b*). The four features shown in fig. 3(*a*) are assigned to the arsoranyl radical $Ph_3\dot{A}sMe$. ^{75}As has $I = \frac{3}{2}$, but because of the large magnitude of the hyperfine coupling the four features corresponding to $M_I = \pm\frac{3}{2}, \pm\frac{1}{2}$ are unequally spaced. The features exhibit parallel and perpendicular components with a small x, y splitting for the $M_I = -\frac{1}{2}$ line. The $M_I = +\frac{1}{2}$ line is fortuitously almost isotropic. The results have been analysed using the axially symmetric spin Hamiltonian

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y). \quad (1)$$

Table 1. E.s.r. hyperfine parameters

radical	hyperfine coupling to ^{75}As, Br or $^{127}I/G^a$ $A_{\parallel}$	$A_{\perp}$	A_{iso}	g-tensor components^a $g_{\parallel}$	$g_{\perp}$	^1H hyperfine coupling constant/G	ref.
$Ph_3\dot{A}sMe$	592	505 525	541	1.97	2.014 2.027	—	this work
$Ph_4\dot{A}s$	592.6	505 524.8	541	1.97	2.014 2.027	—	16
$Ph_3As^{\cdot}$—Me	102±2	98±2	99±4	2.0028	2.0017 2.0010	(∥)22.7 (⊥)22.0	this work
$Ph_3As^{\cdot}$—Me	97	88 86	90	2.0021	2.0014 2.0009	—	1
CH_3Br^-	58	−28	0.7	—	—	20.6	22
CH_3I^-	108	−60	−4	—	—	20.6	22

^{a} Calculated using the Breit–Rabi equation.

The resulting tensor components are given in table 1, together with those for the $Ph_4As^{\cdot}$ radical[16] for comparison.

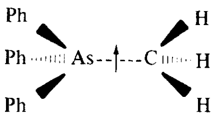
The four narrow features shown in fig. 3(*b*) are characteristic of 'free' methyl radicals, with no trace of any residual interaction with the Ph_3As molecule. In their single-crystal study Geoffroy and Llinares were unable to detect any break-down products from the [Ph_3As-----$Me^{\cdot}$] adduct. However, using our technique of rapid quenching outlined above we have been able to obtain well defined features for normal methyl radicals on annealing, together with features assigned to $H_2\dot{C}AsPh_3$ radicals, presumably formed by

$$Ph_3AsCH_3 + {}^{\cdot}CH_3 \rightarrow Ph_3As\dot{C}H_2 + CH_4. \quad (2)$$

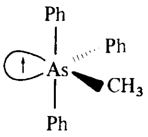
ASPECTS OF MECHANISM

Irradiation of the pure salt, $Ph_3AsMe^+I^-$, is expected to give electron-gain and electron-loss centres. The former is clearly the methyl radical addult, there being no trace of either the arsoranyl radical or of the substituted benzene anion derivatives such as are usually formed from the phosphorus analogues.[17] The electron-loss centre is almost certainly I_2^-, with very broad, ill defined features such as are often found in 'loose' matrices in which extensive libration can occur.

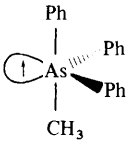
In marked contrast, electron addition to Ph_3AsMe^+ ions in a CD_3OD matrix gave no sign of the methyl radical adduct, but low yields of methyl radicals together with relatively high yields of arsoranyl radicals.



(I)



(II)



(III)

When the electron comes into the sphere of attraction of the 'tetrahedral' cation it can be stabilised either by bond stretching to give a σ^* radical, structure (I),[18, 19] or by bond-bending to give an arsoranyl radical, structure (II) or (III). We suggest that structure (I) is a necessary precursor to the formation of methyl radicals, whilst structure (II) or (III) must convert to structure (I) before giving methyl radicals. This suggestion is similar to our postulate for the formation of phenyl radicals and halide ions from halogenobenzenes.[14] Initial electron addition is partitioned between the π^* aromatic orbital and the C—hal σ^* orbital. The latter anion can move smoothly to give products, but the former cannot so a $\pi^* \rightarrow \sigma^*$ excitation is required. For the arsine, a similar excitation is required for structure (II), which is probably the favoured structure. However, for structure (III) there is already extensive delocalisation onto the two axial groups so direct loss of methyl could occur without any electronic excitation. Hence the rate-determining step could well be thermal conversion of structure (II) to structure (III).

ASPECTS OF STRUCTURE

THE ARSORANYL RADICAL

We cannot readily distinguish between structures (I)–(III) from the e.s.r. parameters alone. However, note that the parameters are identical, within experimental error, to those for the $Ph_4As^\cdot$ radical.[16] Since the parameters are known to depend primarily on the nature of the axial ligands in such structures, this suggests that structure (III) should be favoured. This is also expected in terms of the observation that the more electronegative substituents favour the axial sites. The σ^* structure (I) is unlikely because it is not expected to resemble closely the $Ph_4As^\cdot$ radical. This is unlikely to have a σ^* structure, and even if it had it would not be identical with structure (I). However, the most important argument against the σ^* structure (I) is the one we have used to explain the absence of σ^* alkyl halide anions.[10, 13, 14, 20] If this structure represents a minimum along the reaction coordinate leading to $Ph_3As: + {}^\cdot CH_3$, then given that these units are in close contact in the methyl radical adduct, we would expect 'recombination' to give the σ^* structure. In other words, we think it is unacceptable to have such a high barrier between the σ^* state and the methyl radical adduct state that the two species can be quite stable at 77 K with no tendency to interconvert.

We therefore conclude that the arsoranyl radical centre detected in CD_3OD has structure (III).

THE METHYL RADICAL ADDUCT

It was previously concluded that this centre has *ca.* 75% spin density on $^\cdot CH_3$ and, presumably, 25% on the Ph_3As group. In our view, however, the species is essentially a pure methyl radical undergoing a very weak charge-transfer interaction with the Ph_3As molecule. Data for this adduct and for a range of other adducts are given in table 1. The ^1H hyperfine coupling is seen to be a sensitive probe for delocalisation, in which case there is almost zero loss of spin density for the Ph_3As adduct. Certainly the anisotropic ^{13}C coupling is less than that expected for stationary $^\cdot CH_3$ radicals, but that can be understood in terms of libratory motions of these small radicals rather than delocalisation. Indeed, this is normal for $^\cdot CH_3$ radicals at 77 K. If the isotropic coupling is used to estimate the spin density on carbon it must again be close to unity. Had there been some 25% delocalisation, indicative of considerable σ-bonding, the CH_3 unit should have become pyramidal, as for the NH_3 group in the hal$^\cdot$—NH_3 centres.[12] This would lead to a reduction in $|A(^1H)|$ and a major increase in $A(^{13}C)$, neither being observed. We conclude that the centre is essentially a methyl radical. In that case the small coupling to ^{75}As represents a slight electron transfer. If the isotropic and anisotropic coupling constants are analysed in the usual way[21] we find *ca.* 0.018 4*s* character and *ca.* 0.033 4*p* character, in reasonable agreement with the model. Similar values were actually estimated by Geoffroy and Llinares, but they apparently favoured the ^{13}C results. Since even this degree of delocalisation is not evidenced by the isotropic ^1H and ^{13}C coupling constants, it is possible that the ^{75}As results are due to a spin-polarisation mechanism rather than representing real delocalisation.

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