Radical Cations of Dialkylmercury Derivatives, Radiation Synthesis and Electron Spin Resonance Detection†

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Exposure of very dilute solutions of $Hg(CD_3)_2$ in tetrachloromethane to ^{60}Co γ-rays at 77 K gave a species whose e.s.r. spectrum is characteristic of the parent cation. Interpretation of the g-values and ^{199}Hg tensor component B derived from a computer synthesis of the spectrum suggests that the unpaired electron is strongly confined to the linear σ orbital having a node through the mercury atom. This has a large 6p(Hg) character. No extra features were obtained using $Hg(^{13}CH_3)(CH_3)$, confirming that the spin density on the CH_3 groups is small (<20%). When $CFCl_3$ was the solvent extra poorly defined splittings were observed which are assigned to weak, but specific interaction with one solvent molecule (^{19}F). The spectra for $Hg(CH_3)_2$ in this solvent were analysed in terms of the same solvent features together with coupling to at least five and probably seven protons. The small ^1H coupling was almost isotropic at ± 4.5 G. In contrast, $Hg(C_2H_5)_2$ gave no resolved coupling to ^{19}F, but there was a large, well defined, triplet splitting (42 G) assigned to two specific CH_3 protons. This suggests that rotation about the C–C bonds is restricted. We were unable to detect free rotation on annealing, although the lines broadened considerably, prior to radical loss. Attempts to detect $^{\bullet}CH_3$ or $^{\bullet}CH_2CH_3$ radicals in these systems were unsuccessful, but clear evidence for $^{\bullet}CD_3$ radicals was obtained for $Hg(CD_3)_2$ in $CFCl_3$ on annealing.

Heavy-metal compounds have major biological significance, mainly because of their often high toxicity. Organometallic derivatives are especially important because they may be formed biochemically from less toxic ionic derivatives. Such compounds include mono- and di-alkyl mercurials. For example, formation of diethylmercury is considered to be environmentally important in soils.[1] Such compounds may, of course, be taken up by food sources such as fish and vegetables.

A wide range of organic radical cations have been matrix isolated and studied by e.s.r. spectroscopy over the past few years.[2] The methods developed by Knight and his co-workers are most satisfactory for small cations.[3–5] Using rare-gas matrices, the cations are generated by various methods just prior to, or during, deposition. Generally well defined e.s.r. spectra result, and for unknown reasons electron-capture centres do not contribute to the spectra. This method works well for small cations such as $H_2O^{\bullet +}$, $CH_4^{\bullet +}$, $H_2CO^{\bullet +}$, *etc.* but seems to be less useful for larger cations. The alternative technique involves the use of very dilute solutions of substrates (< 1:1 000) in solvents such as $CFCl_3$, CCl_4, SF_6, *etc.* which are exposed to ionizing radiation at low temperatures. In these solvents electron capture is highly efficient and the resulting solvent radicals either give well defined spectra that can be readily subtracted (*e.g.* SF_6) or give such broad spectra that no subtraction is required (*e.g.* $CFCl_3$).

In certain cases the primary cations are not detected because of some facile unimolecular breakdown or rearrangement, and in others solvent 'adducts' are detected with resolved hyperfine coupling either to one fluorine or one chlorine nucleus of the solvent.[6,7] The former interaction is small, non-specific, and is only found for compounds with relatively low ionization potentials. The latter can be very large,[8] the interaction increasing with ionization potential. It probably involves specific σ bonding between solvent chlorine and the cation.

There has been relatively little work on inorganic cations or organometallic cations. Some time ago we reported attempts to prepare $Fe(CO)_5^+$ unambiguously,[9] but the data, though reasonable for this species, do not agree well with results assigned to $Fe(CO)_5^+$ in sulphuric acid.[10] Results for the series of cations of $SnH_4^{\bullet +}$ to $SnMe_4^{\bullet +}$ are, we think, unambiguous,[11] and for the $SnMe_4^{\bullet +}$ cations there was clear evidence for reaction (1) on annealing above 77 K.

$$Sn(CH_3)_4^{\bullet +} \longrightarrow Sn(CH_3)_3^+ + {}^{\bullet}CH_3 \qquad (1)$$

A study of radiolysis products in various crystalline HgL_2 compounds (L = methyl or chloride) failed to give any definitive evidence for the trapping of primary radical cations, the major species identified by e.s.r. spectroscopy being $HgR^{\bullet}$ radicals, $RHg\dot{-}Cl^-$ anions, $H_2\dot{C}HgL$ species, and probably $HgR_2^{\bullet -}$ anions.[12] In the light of our present results we have re-examined our original spectra, and confirmed that primary $HgR_2^{\bullet +}$ cations were apparently not stabilized in the pure compounds. We suggest that reactions such as (2) are facile in these compounds.

$$Hg(CH_3)_2^{\bullet +} + Hg(CH_3)_2 \longrightarrow Hg(CH_3)^+ + H_2\dot{C}HgCH_3 + CH_4 \qquad (2)$$

In a study of $Hg(C_2H_5)_2$[13] the novel radical $H_2\dot{C}CH_2Hg(C_2H_5)$ was detected, which, judging from the magnitudes of the small β-proton coupling and the large ^{199}Hg coupling, has a preferred conformation with maximum σ–π overlap between the semioccupied $2p_z$(C) orbital and the C–Hg σ orbital.

Dialkylmercury derivatives have been studied by photoelectron spectroscopy.[14,15] These studies give ionization potentials of *ca.* 9.0 eV. Hence their cations should be formed readily in $CFCl_3$ or CCl_4 matrices, and any solvent interaction should be *via* ^{19}F rather than ^{35}Cl or ^{37}Cl.[7]

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† *Non-S.I. units employed:* G = 10^{-4} T, eV ≈ 1.60×10^{-19} J, rad = 0.01 Gy.

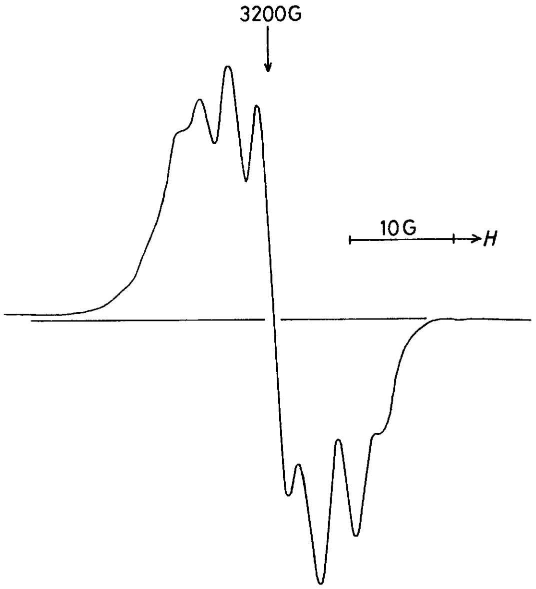


Figure 1. First-derivative X-band e.s.r. spectrum, assigned to $^{\bullet}CD_3$ radicals, obtained by exposure of $Hg(CD_3)_2$ in $CFCl_3$ to ^{60}Co γ-rays at 77 K, and annealing to *ca.* 135 K

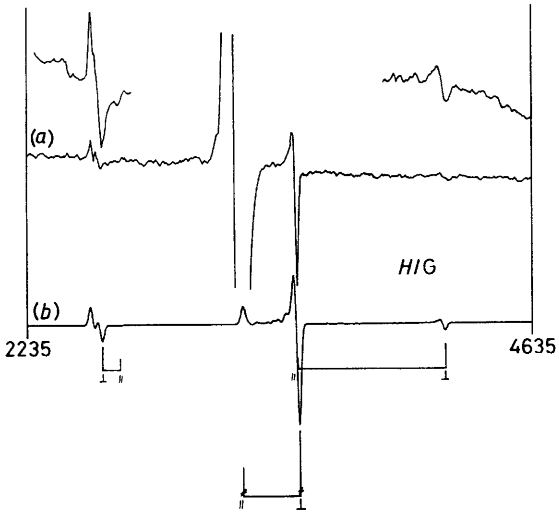


Figure 2. (*a*) First-derivative X-band e.s.r. spectrum for a dilute solution of $Hg(CD_3)_2$ in CCl_4 after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $Hg(CD_3)_2{}^{\bullet +}$ radical cations, including outer features for $^{199}Hg(CD_3)_2{}^{\bullet +}$ cations. [The central line is due to impurity radicals, and there are some features expected for $^{201}Hg(CD_3)_2{}^{\bullet +}$, which have intensities slightly higher than the noise level.] (*b*) Simulated spectrum using the e.s.r. parameters listed in the Table, assuming linewidths of 20 G and neglecting the lines for $^{201}Hg(CD_3)_2{}^{\bullet +}$

Table. E.s.r. parameters for $Hg(CD_3)_2{}^{\bullet +}$ radicals in CCl_4

		Hyperfine tensors for ^{199}Hg	
$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$	$A_{\parallel}$
1.850	1.995	(−)1 568 G (−)4 060 MHz	(−)807 G (−)2 253 MHz

Experimental

Dimethyl- and diethyl-mercury were prepared from CH_3I or C_2H_5I and $HgCl_2$ using standard procedures. Their purities were checked using proton n.m.r. spectroscopy. The compound $Hg(^{13}CH_3)(CH_3)$ were prepared from $^{13}CH_3I$ and $Hg(CH_3)Cl$, and $Hg(CD_3)_2$ from CD_3I and $HgCl_2$. Solutions (*ca.* 0.1% mole fraction) were prepared by weight in $CFCl_3$ or CCl_4 which were of the best grades available and were degassed prior to use. The former was further purified using an alumina column.

Samples were frozen to 77 K as small beads and exposed at this temperature to ^{60}Co γ-rays in a Vickrad source. Doses up to *ca.* 1 Mrad were sufficient to give good e.s.r. signals.

E.s.r. spectra were mainly recorded on a Varian E-109 X-band spectrometer, calibrated with a Hewlett-Packard 5246L frequency counter and a Brucker B-H12E field probe. Diphenylpicrylhydrazyl samples were used as standards for g-value measurements. Samples were annealed above 77 K either using a Varian variable temperature Dewar, or by decanting the liquid nitrogen from the insert Dewar and continuously monitoring the e.s.r. spectra as the sample warmed. When significant changes were observed the samples were recooled to 77 K for measurement.

Results and Discussion

E.S.R. Spectra.—In all cases poorly defined features in the free-spin region were detected. However, the only well defined central features were recorded for $Hg(CD_3)_2$ in $CFCl_3$ which we assign primarily to $^{\bullet}CD_3$ radicals (Figure 1). These were only trapped under carefully controlled conditions, and we were not able to prove conclusively the formation of $^{\bullet}CH_3$ from $Hg(CH_3)_2$, nor of $CH_3\dot{C}H_2$ from $Hg(CH_2CH_3)_2{}^{\bullet}$. Nevertheless, the positive result for $^{\bullet}CD_3$ suggests that the cations do dissociate unimolecularly, equation (3).

$$HgR_2{}^{\bullet +} \longrightarrow {}^{\bullet}R + HgR^{+} \qquad (3)$$

Spectra for the novel mercury cations were best defined using $Hg(CD_3)_2$ in tetrachloromethane solvent. We have found on other occasions that better defined features were obtained with CCl_4 rather than with $CFCl_3$.[16] The spectrum [Figure 2(*a*)] comprises a major feature for non-magnetic Hg nuclei, and satellites at either side assigned to ^{199}Hg and ^{201}Hg species.[17]

Since the satellites have very large separation it is necessary to use a strict matrix-diagonalization method for their analysis. Also, analyses by computer simulation are important to get a reasonable assignment for the spectrum and to obtain accurate e.s.r. parameters. A computer program for simulation was written, containing a strict matrix diagonalization for axially symmetric hyperfine interactions. In the program, the relative intensity of the satellites for $^{199}Hg(I = \frac{1}{2})$ with reference to the major signals due to $Hg(I = 0)$ was assumed to be 0.12 because the natural abundance for ^{199}Hg is 16.86% and that for $Hg(I = 0)$ is 69.90%. Equal linewidths were assumed. Using the e.s.r. parameters listed in the Table, a good fit was obtained between the observed and the simulated spectra, as shown in Figure 2. In the simulation, the lowest-field feature is an abnormal divergence peak appearing at a turning point. Such anomalous peaks in powder e.s.r. spectra were first discovered by Neiman and Kivelson[18] for some copper complexes, and detailed investigations have been published.[19–21] Recently, we have also reported an abnormal peak in the e.s.r. spectrum for $[HPt(CN)_4]^{2-}$ formed by irradiation of $K_2[Pt(CN)_4]$ in CH_3OH.[22] In the present case, the abnormal peak appears because of the large anisotropies in both g and hyperfine tensors. Numerical analysis using a computer revealed that the extra turning point appears at $\theta = 47°$, where θ is the angle between the magnetic symmetry axis (the parallel axis) of the complex and the direction of the applied magnetic field. Some features for radicals containing ^{201}Hg were also obtained in the expected regions, but we have not attempted a full analysis.

Among the e.s.r. parameters listed in the Table, the values of

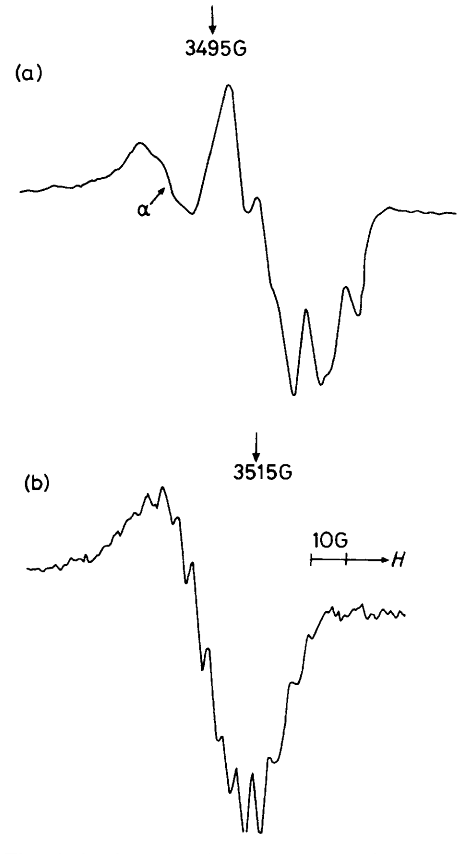


Figure 3. First derivative *X*-band e.s.r. spectra (*a*) of $Hg(CD_3)_2$ in $CFCl_3$ showing extra unassigned splitting, and (*b*) of $Hg(CH_3)_2$ in $CFCl_3$ showing further multiplet splitting of 4.5 G assigned to coupling to the six methyl protons. [Feature α in (*a*) is not part of the main spectrum]

Figure 4. First-derivative *X*-band e.s.r. spectrum for a dilute solution of $Hg(C_2H_5)_2$ in $CFCl_3$, showing the perpendicular feature assigned to $Hg(C_2H_5)_2^{\cdot +}$ cations, with a triplet splitting of 42 G assigned to hyperfine coupling to two equivalent protons. The extra central line is due to organic radicals

$g_{\parallel}$ and $A_{\parallel}$ for the ^{199}Hg nucleus are less precise than the remainder, because peaks corresponding to the parallel features for the major signal and the high-field component of the satellites were hidden by more intense features in the spectra. However, since the hyperfine coupling constants for the satellites are very large, the value selected for $A_{\parallel}$ significantly affects the separations between the three perpendicular peaks. Thus, the values for $g_{\parallel}$ and $A_{\parallel}$ in the Table must be good approximations. The large negative shift for $g_{\perp}$ is in accord with expectation for the $6p^1$ configuration of mercury having axial bonding.[14]

The e.s.r. spectra for $Hg(CD_3)_2$ in $CFCl_3$ were less well defined, having considerable structure [Figure 3(*a*)]. This was further increased using $Hg(CH_3)_2$ [Figure 3(*b*)], suggesting the presence of some ^1H hyperfine coupling [$Hg(CH_3)_2$ in CCl_4 gave broad, unresolved features]. The fact that this fine structure was lost for $Hg(CD_3)_2$ in CCl_4 suggests that solvent nuclei are responsible. However, neither a doublet for ^{19}F nor a quartet for $^{35}Cl + {}^{37}Cl$ was well enough defined for us to be sure of the analysis. It is clear, however, that extra features (five or seven lines) with a splitting of 4.5 G result when $Hg(CH_3)_2$ was used, which were most reasonably assigned to the six methyl protons. In order to estimate the spin density on the carbon atom in the cations, e.s.r. measurements were carried out with $Hg(^{13}CH_3)(CH_3)$. However, no extra features were obtained in the spectra, confirming that the spin density on the CH_3 groups is small (< 20%).

For the diethyl derivative, coupling to the α-protons was not resolved, but a large, well defined triplet splitting (42 G) was observed (Figure 4), which we assign to one of the CH_3 protons for each ethyl group. Attempts were made to obtain spectra at higher temperatures in which the six CH_3 protons become equivalent on the e.s.r. time scale, but only pronounced line broadening was observed prior to radical loss.

Hyperfine Couplings to ^{199}Hg.—Mercury has two magnetic isotopes, ^{199}Hg with $I = \frac{1}{2}$ in 16.86% abundance, and ^{201}Hg with $I = \frac{3}{2}$ in 13.24% abundance. The present results (see Table) are unusual in that $|A_{\parallel}| < |A_{\perp}|$, which is the reverse of expectation for electrons primarily in a *p*-orbital on a central atom. The only combination of signs which results in reasonable values for the anisotropic coupling is that where both $A_{\parallel}$ and $A_{\perp}$ are negative. This is discussed further below.

The ^{199}Hg features for $Hg(C_2H_5)_2^{\cdot +}$ cations appear in similar places to those for $Hg(CD_3)_2^{\cdot +}$, although the splittings are slightly reduced, indicating a small reduction in spin density on mercury. However, there was no difference in the data for $Hg(CD_3)_2$ or $Hg(CH_3)_2$ in CCl_4 and $CFCl_3$ within experimental error.

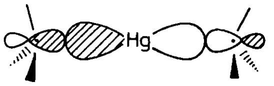
Structure of $HgR_2^{\cdot +}$ *Radical Cations.*—The parent molecules are strictly linear, the highest occupied molecular orbital (h.o.m.o.) being σ_2 comprising of *sp* hybrid orbitals on the α-carbon atoms and the $6p_{\sigma}$ orbital on mercury. Electron loss is therefore expected to occur from this m.o. and our results agree well with this model [structure (**I**) for $Hg(CH_3)_2^{\cdot +}$]. In order to obtain approximate orbital populations from the experimental data, we used equations (4) and (5), which are suitable for an

$$A_{\parallel} = A_{iso} + 2B \qquad (4)$$

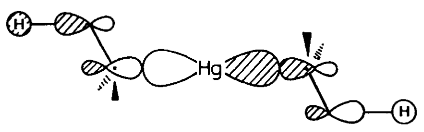
$$A_{\perp} = A_{iso} - B(1 + \Delta g_{\perp}) \qquad (5)$$

electron in a *p* orbital where $\Delta g_{\perp} = g_{\perp} - 2.0023$. These give $A_{iso} = -3\,633$ MHz and $2B = 1\,380$ MHz. The large negative isotropic coupling establishes that the 6*s* orbital makes no significant direct contribution. It is well established that for metal atoms or ions in ionic crystals having an np^1 configuration ($n > 4$), large negative isotropic couplings are obtained,[23] so this result supports our assignment. The coupling arises from spin polarization of electrons in *s*-orbitals, and has no significance in the calculation of orbital populations.

Unfortunately, reliable data are not yet available for us to obtain an estimate of the $6p_{\sigma}$ orbital population from the ^{199}Hg anisotropic coupling. The value obtained is remarkably large, seeming to indicate a very large population on Hg. However, large values are expected for heavy atoms because of a major



(I)



(II)

relativistic contribution.[24] The large coupling to two β-protons in the diethyl derivative shows that there must be some delocalization onto the alkyl groups.

We know that for Hg$\dot{-}$H^{+} radicals the spin is fairly evenly distributed between the mercury (6*s*) and hydrogen orbitals.[25] This can be compared with the σ_1 orbital for $\mathrm{HgR_2}$ molecules and $\mathrm{HgR_2}^{\cdot+}$ radicals. The higher σ_2 orbital is expected to be more concentrated on the metal, but unfortunately we are unable to estimate the extent of delocalization with any confidence.

An alternative description needs to be considered in these solid-state results, namely that there is a specific distortion in which only one Hg–C bond is stretched, giving a structure $[\mathrm{R{-}Hg}-\dot{-}-\mathrm{R}]^{+}$. Just such a single-bond distortion was postulated for the $\mathrm{Sn(CH_3)_4}^{\cdot+}$ cation $[(\mathrm{CH_3})_3\mathrm{Sn}-\dot{-}-\mathrm{CH_3}]^{+}$.[11] However, in this case some distortion is required by the Jahn–Teller theorem, which is not the case for the mercury compounds. Against such a distortion are the absence of a large quartet splitting from a unique $\mathrm{CH_3}$ group, and the detection of a relatively small multiplet splitting. Also, the absence of any contribution from the 6*s* orbital on mercury, and the detection of two very strongly coupled protons for the diethyl derivative, give cogent reasons for rejecting such an asymmetric structure.

It is interesting to speculate on the origin and significance of the two relatively strongly coupled protons in the $\mathrm{Hg(CH_2CH_3)_2}^{\cdot+}$ cation. We suggest that structure (**II**) offers a qualitative explanation provided relative rotation is restricted. We recall that for the ethane cation there are also only two strongly coupled protons, with a hyperfine coupling of 152 G each.[26] This delocalization arises from a structure in which nearly 100% of the semi-occupied molecular orbital is confined to the two C–H bonds. Comparing this ^{1}H coupling with the value for $\mathrm{Hg(CH_2CH_3)_2}^{\cdot+}$ of 42 G, we find that the spin density in the combined C–H orbitals is *ca.* 28%. This seems to be a very reasonable result, confirming the concept that most of the spin density is located in the p_z orbital on mercury.

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