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Hyperconjugation to β-Mercury: E.s.r. Studies of $H_2\dot{C}CH_2HgEt$ Radicals formed by radiolysis of Diethyl Mercury [1]

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SUMMARY

Exposure of diethyl mercury or its solutions in tetramethyl silane to ^{60}Co γ-rays at 77 K gave a radical having an isotropic coupling to ^{199}Hg of 750-800 G, which is identified as the radical $H_2\dot{C}CH_2HgEt$. Other radicals detected by e.s.r. spectroscopy included the parent anion, $[Et\dot{H}gEt]^-$ and the ethyl radical.

Low temperature radiolysis coupled with e.s.r. spectroscopy has proven to be an effective alternative to time resolved spectroscopy in the study of unstable or highly reactive molecular species [2]. One of the most interesting recent discoveries using this technique [3], and, for sterically hindered species, using liquid-phase e.s.r. spectroscopy [4,5], is that "heavy atom" groups (X) (such as halogen atoms [6,7] $-PR_2$ and $-PR_3$ groups [3], $-SiR_3$ [4,5], $-SnR_3$ [3] etc.), give rise to extensive delocalisation of the unpaired electron when in the eclipsed configuration, I. It seemed, originally [3], that the eclipsed configuration was preferred because of the hyperconjugation effect, but

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(I)

this concept is open to question [5,8]. One of us has presented arguments which seem to give strong support for the concept of hyperconjugative control of conformation for such radicals [9]. These results for radicals form an interesting link with the theory that such β groups in the eclipsed conformation strongly stabilise carbonium ions [10,11].

There have been very few e.s.r. studies of organo-mercury complexes, and, so far as we are aware, alkyl radicals with β-mercury substituents have never been reported. Fullam and Symons studied the effect of ionizing radiation on dimethyl mercury, ethyl mercury(II) chloride, and methyl mercury(II) bromide and iodide, and detected various α-mercury radicals such as $H_2\dot{C}HgMe$, the radicals EtHg• and ClHg•, and a species thought to be $(MeHgMe)^{\cdot}$ [12]. In all cases, hyperfine coupling to ^{199}Hg and ^{201}Hg was detected. (^{199}Hg, $I = \frac{1}{2}$, $\mu = 0.498$ is 16.86% abundant, and ^{201}Hg, $I = \frac{3}{2}$, $\mu = -0.551$ is 13.24% abundant.) The α-mercury radicals were characterised by a relatively small, almost isotropic, hyperfine coupling of ca. 220 G (^{199}Hg). The EtHg• radical had a very large coupling of ca. 3700 G (^{199}Hg) whilst the molecular anion, $MeHgMe^{-}$ was characterised by an intermediate coupling of ca. 2700 G (^{199}Hg). In the study of EtHgCl a search for the radical $H_2\dot{C}$-CH_2HgCl was unsuccessful. Other mercury radicals studied by e.s.r. spectroscopy include HgH^{2+}, $HgOH^{2+}$, probably $HgOEt^{2+}$ [13-15], and HgH [16].

EXPERIMENTAL

Diethyl mercury (Alfa Products) was irradiated after degassing either as the pure material, or as dilute solutions in tetramethyl silane. The fact that very similar spectra were obtained from both systems suggests that impurities make no significant contribution thereto. Samples were irradiated at 77 K in a Vickrad ^{60}Co γ-ray source and received doses of ca. 1.5 MRad.

E.s.r. spectra were measured on a Varian E.109, calibrated by a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which was standardised with a sample of DPPH.

RESULTS & DISCUSSION

Results for the pure material and for solutions in tetramethyl silane were similar (Table I), except that the central region, showing mainly ethyl radical features for the pure compound, was dominated by features due to $H_2\dot{C}SiMe_3$ radicals for the solutions. Two well defined sets of ^{199}Hg satellite features were obtained (A and B in Fig. 1). In

TABLE I

E.s.r. parameters for radicals A and B formed from diethyl mercury, together with data for some related species

Source	Radical	Isotropic hyperfine coupling/G[a]	g_{av}-value
Et_2Hg in TMS	A($H_2\dot{C}CH_2HgEt$)	(^{199}Hg) 750[b]	1.97
		(^{201}Hg) 276	
	B$(EtHgEt)^{\dot{-}}$	2510	2.025
Me_2Hg[c]	$(MeHgMe)^{\dot{-}}$	2674	ca. 2.0
EtHgCl[c]	EtHg•	3693	ca. 2.0
Me_2Hg[c]	$H_2\dot{C}HgMe$	220	2.0037

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

[b] ca. 800 G in the pure material: from the line shapes we estimate very approximately that $A_{\parallel}(^{199}Hg) \approx 800$ G, $A_{\perp} \approx 720$ G, $g_{\parallel} = 1.99$ and $g_{\perp} = 1.96$.

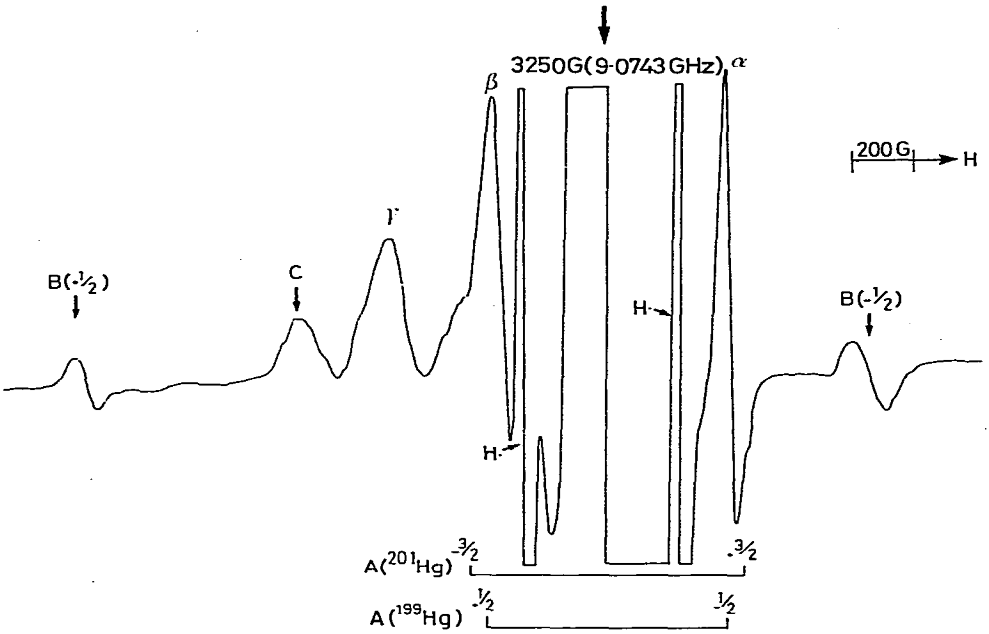


Fig. 1. First derivative X-band e.s.r. spectrum for a solution of diethyl mercury in tetramethyl silane after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to (A) $H_2\dot{C}CH_2HgEt$ and (B) $Hg(Et)_2^-$ radicals.

addition two low-field features were often detected (C in Fig. 1) which do not appear to link with any high-field features. Since it is the high-field features that are normally well defined when hyperfine coupling constants are large, we conclude that these are not due to ^{199}Hg or ^{201}Hg hyperfine coupling.

Centre A. - This centre, with $g_{av} = 1.97$ and $A_{av}(^{199}Hg) = 800$ G (ca. 750 G for the solutions in tetramethyl silane) appears to be almost isotropic, but the high-field ($-\frac{1}{2}$) feature is narrower than the low-field ($+\frac{1}{2}$) feature whose shape suggests an incipient shoulder on the low-field side. This suggests that $g_{\parallel}$ is closer to the free-spin value (2.0023) and that $A_{\parallel} > A_{\perp}$, and an approximate estimate of these differences is indicated in Table I.

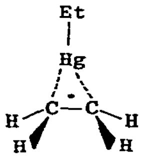
We suggest that this centre is the expected β-mercury radical

$H_2\dot{C}CH_2HgEt$ having the eclipsed structure (I). The ^{199}Hg hyperfine features are too broad to give resolved proton hyperfine coupling, but we estimate that this must be ≤ 20 G. For the radical $H_2\dot{C}CH_2HgEt$, we expect, by analogy with similar species, that the two α-protons will have isotropic hyperfine coupling constants in the 15-20 G range and the β-protons will have constants in the 5-13 G range [3]. We had hoped that in tetramethylsilane some resolution might be achieved on warming above 77 K, but these radicals were lost before any resolution appeared. This suggests a first order mode of decomposition, but we

$$H_2\dot{C}\text{-}CH_2HgEt \rightarrow H_2C{=}CH_2 + \cdot HgEt \qquad (1)$$

have not been able to detect the high-field feature characteristic of •HgEt radicals [12].

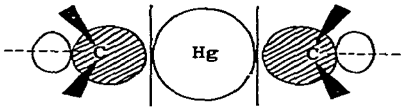
Although we can think of no other radical likely to have the properties of species A, firm identification must rest on the magnitude of the ^{199}Hg hyperfine coupling. For comparison with other radicals in this class we need to estimate an approximate 5s-orbital population from the isotropic coupling. There is no doubt that the wavefunctions of Froese lead to a gross underestimate of A° for heavy atoms, but the experimental value for Hg^+ (ca. 12000 G [14]) is probably high for neutral species because of orbital contraction for the cation. We select a value of 10 000 G to give a very rough value of 8% in the 5s-orbital for this species. The total spin-density on mercury is surely higher than this because of some 5p admixture. By comparison, the well characterised radical $CH_3\dot{C}HCH_2AsO_3H$ had an estimated spin density of ca. 3.7% in the 4s orbital and about 2-3 times this in the 3p(σ) orbital. Similar values were found for the tin derivative $H_2\dot{C}\text{-}CH_2SnR_3$ [3]. Thus there has been a large increase in s-character, but probably little change in total spin-density for the β-mercury radical. Since the s-contribution to the C-Hg σ-bond must be relatively large, this is a reasonable result, which supports our assignment. Before leaving this radical we must stress that, although the results accord with structure (I) for this species, we are not able to rule out the symmetrical cyclic structure II for this species.



(II)

Radical B

The signal-to-noise ratio was such that we were only able to detect ^{199}Hg satellites for this species. The isotropic hyperfine coupling calculated using the Breit-Rabi equation is close to that assigned to the $[\mathrm{Me\text{-}\dot{H}g\text{-}Me}]^-$ radical [12], and we therefore favour such a structure for the diethyl derivative. We were able to detect a septet splitting for the central (^{200}Hg) features of the dimethyl derivative, but in the present case only broad singlets were observed. The *g*- and ^{199}Hg A-tensors are probably slightly anisotropic, but the degree of anisotropy is too small for assessment of the anisotropic parameters. If, in the simplest representation, we consider only two localised *sp*^{3} σ-orbitals on carbon and the 5*s* mercury orbital, there are three σ M.Os for diethyl mercury, and five σ-electrons. The unpaired electron will then be in σ_3, having the form shown in (III):



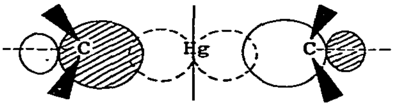
(III)

Our results suggest a spin-density of *ca*. 26% on mercury leaving *ca*. 37% on the two alkyl groups. The fall in spin-density on going from the dimethyl to the diethyl derivative implies a slight increase on the two ethyl groups, as expected for an electron in the σ-framework.

Aspects of Mechanism

The major electron-loss centre seems to be $H_2\dot{C}\text{-}CH_2HgEt$, since there was no clear evidence for $CH_3\dot{C}HHgEt$. We had expected that the cation,

$[EtHgEt]^+$ would be formed. Formation of this centre would be suppressed in tetramethyl silane, but species A and B which could possibly be this ion, were still formed in good yield, so we do not think that either could be the cation. Furthermore, the σ_2 orbital involved has a node at mercury (IV) and hence the isotropic hyperfine coupling to ^{199}Hg and ^{201}Hg is expected to be very small.



(IV)

Possibly ethyl radicals were formed from the parent cation, since there is evidence that such fragmentation of electron-loss species tends to occur [17]:

$$Et_2Hg^+ \rightarrow Et\cdot + EtHg^+ . \qquad (2)$$

Ethyl radicals may also be formed as an alternative to anion formation:

$$Et_2Hg + e^- \rightarrow Et\cdot + EtHg^- . \qquad (3)$$

In tetramethyl silane radical A is probably formed by hydrogen atom attack. It is again surprising that attack on the methyl protons apparently dominates over attack on the methylene protons.

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