Unstable Intermediates. Part CXLIV.[1] Organomercury Radicals in Irradiated Alkylmercury(II) Halides and Dimethylmercury

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On exposure to ^{60}Co γ rays at 77 K a range of alkylmercury(II) halides give e.s.r. signals indicative of two types of radical: one, exhibiting only small hyperfine interaction with magnetic mercury isotopes, is identified as $R_2\dot{C}HgX$; and the other, with very large hyperfine coupling to mercury, as $\dot{H}gR$. Dimethylmercury gives the radical $H_2\dot{C}HgMe$ together with a species thought to be $(Me_2Hg)^{\dot{-}}$. Structures of these radicals and mechanisms of the processes are discussed.

PREVIOUS e.s.r. studies of γ-irradiated mercury compounds [2-5] have involved the use of mercury(I) or mercury(II) salts in mainly aqueous acidic media. This approach has produced various radical cations of the type RHg^{n+} (R = H, OH, Cl, or Hg; $n = 1$—3). When acidified ethanol was used as a solvent [5] the

species $HgOR^{2+}$ was produced, this being, to our knowledge, the only mercury radical containing an organic ligand. It was shown in the papers cited above that the presence of very-high-field satellite lines in the e.s.r. spectra (4 000—8 000 G) provides a diagnostic tool for inferring the presence of mercury radicals of this type.

[1] Part CXLI, H. C. Starkie and M. C. R. Symons, J.C.S. Dalton, 1974, 731. (A. R. Lyons and M. C. R. Symons, J. Amer. Chem. Soc., 1973, 95, 3483 and O. P. Anderson and M. C. R. Symons, Inorg. Chem., 1973, 12, 1932 are to be regarded as Parts CXLII and CXLIII respectively.)

[2] R. S. Eachus, M. C. R. Symons, and J. K. Yandell, Chem. Comm., 1969, 979.

[3] R. S. Eachus, I. Marov, and M. C. R. Symons, Chem. Comm., 1970, 633.

[4] M. C. R. Symons and J. K. Yandell, J. Chem. Soc. (A), 1971, 761.

[5] R. J. Booth, H. C. Starkie, and M. C. R. Symons, J. Chem. Soc. (A), 1971, 3198.

This fact has been subsequently supported by matrix-isolation work of Knight and Weltner[6] on Group IIB metal hydrides.

EXPERIMENTAL

Methylmercury(II) bromide and iodide (Alfa Inorganics) were used without further purification. The chloride (K and K Laboratories), when recrystallised from hot ethanol, was found to give the same spectrum as the unpurified material. Dimethylmercury (Pfaltz and Bauer), after thorough degassing by repeated freeze–thaw cycles, was sealed, under vacuum, into silica tubes prior to use. All samples, in suitable containers, were irradiated at 77 K in a Vickrad ^{60}Co source and received doses of *ca.* 4 MCi h^{-1} for up to 6 h. E.s.r. spectra were measured on Varian E3 and V4502/03 X-band spectrometers with 100 KHz field modulation.

RESULTS AND DISCUSSION

Typical e.s.r. spectra of irradiated methylmercury(II) bromide and iodide, dimethylmercury, and ethyl-mercury(II) chloride are given in the Figure for the $g = 2$ region, together with our suggested analyses. Both the bromide and iodide spectra showed evidence of halide coupling though no reliable value for A_X (X = halide) could be derived. The resulting hyperfine splitting constants and g values for the $\dot{C}H_2HgX$ radicals thought to be responsible are given in Table 1.

TABLE 1

Hyperfine coupling constants (G) for a range of mercury and aluminium radicals

| Radical	A_H	$A^{199}Hg$	$A^{201}Hg$	g	Percentage s character on mercury
$\dot{C}H_2HgMe$	21	220	187	2·00	1·75 [a]
$\dot{C}H_2HgI$	21	410		2·0037	3·2 [a]
$\dot{C}H_2HgBr$	23	439	187	2·0036	3·5 [a]
$Me\dot{C}HHgCl$	27 (Me) 21 (H)	450		2·0035	3·7 [a]
$\dot{C}H_2-Al{\Large\langle}^{Me}_{Me}$	19	(^{27}Al) 18·9		(Al) 1·93 [b]	
$Me\dot{C}H-Al{\Large\langle}^{Me}_{Cl}$	21·2	(^{27}Al) 21·2		(Al) 2·16 [b]	
$Me\dot{C}HAlCl_3$	25·9	(^{27}Al) 25·9		(Al) 2·64 [b]	

[a] This work. [b] Ref. 13.

Both ethylmercury(II) chloride and dimethylmercury had weak lines in their spectra in the 4 000—6 000 G region which, as stated above, indicates the presence of radicals in which the unpaired electron is strongly localised on the mercury atom.[5] Table 2 gives actual and predicted field values for these species. The expected line positions were calculated using the full Breit–Rabi equation;[5,7,8] the assumption that $g = 2$ was used throughout the calculations and was justified by the close agreement achieved.

[6] L. B. Knight, jun., and W. Weltner, jun., *J. Chem. Phys.*, 1971, **55** (5), 2061.
[7] G. Breit and I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.
[8] J. E. Nafe and E. B. Nelson, *Phys. Rev.*, 1948, **73**, 718.

$R_2\dot{C}HgR$ *Radicals.*—The form of the proton coupling constants, together with the presence of weak satellite
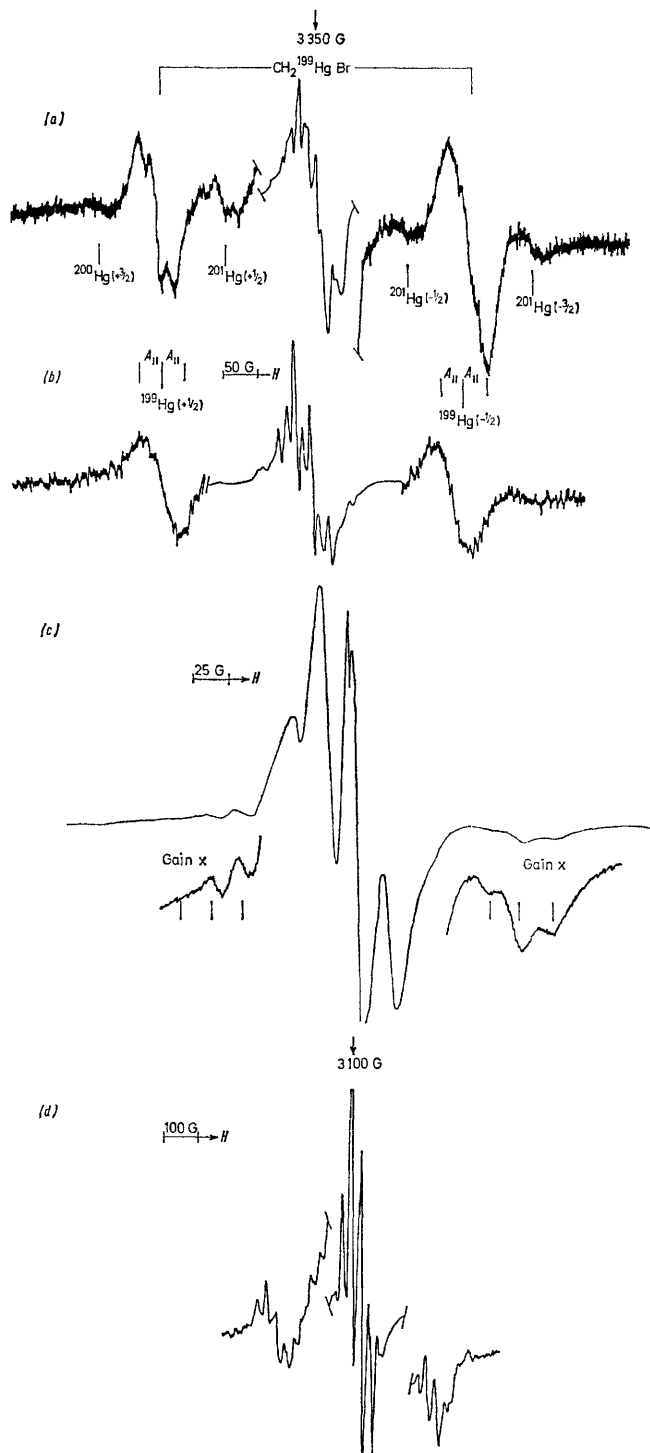
Spectra of the $R_2\dot{C}HgX$ radicals together with our suggested assignments: (*a*) $\dot{C}H_2HgBr$; (*b*) $\dot{C}H_2HgI$; (*c*) $\dot{C}H_2HgMe$; and (*d*) $Me\dot{C}HHgCl$

lines from the ^{199}Hg–^{201}Hg isotopes, strongly supports identification of the major central features in terms of

$R_2\dot{C}HgR$ radicals. Comparison of the proton hyperfine splittings with those reported for structurally similar radicals [9,10] shows that there is little or no delocalisation of the unpaired electron. The normal value of ca. 21 G for α-proton hyperfine coupling is maintained. The isotropic coupling to ¹⁹⁹Hg can be used in a rough estimate of the percentage s character of the unpaired electron on the mercury atom. There is uncertainty relating to the best value to use, and we have used the 'experimental' result for Hg⁺ ions as a rough guide. The results show that the percentage s character is larger than that normally found for $R_2\dot{C}AB_3$ radicals,[9] and they reveal a clear increase in spin density on the mercury atom as the electronegativity of the ligand increases (Table 2).

TABLE 2

Hyperfine data and orbital populations for the radicals Et$\dot{H}$g, $\dot{H}$gCl, and Me₂Hg⁻

Radical		Field position (G) Experimental	Predicted	A_{Hg} [a]	Percentage s character on mercury
Et$\dot{H}$g	¹⁹⁹Hg	4 392	4 392	3 693	29·5
	²⁰¹Hg	b	630		
		2 740	2 714	1 363	
		4 860	4 911		
		6 150	6 305		
$\dot{H}$gCl	¹⁹⁹Hg	5 200	5 200	10 595	
(MeHgMe)⁻	¹⁹⁹Hg	4 155	4 155	2 674	21·7
		b	920		
	¹H			20	
	²⁰¹Hg		1 462	987	
		2 800	2 798		
		4 375	4 378		
		4 500	4 494		

[a] Isotropic hyperfine coupling (A/G) to ¹⁹⁹Hg–²⁰¹Hg calculated using the Breit–Rabi equation and assuming $g = 2·00$. [b] The expected low-field line could not be detected because of poor instrument performance in this region.

Although, in principle, $R_2\dot{C}HgX$ radicals, which are expected to be linear with respect to the co-ordination to the mercury atom and locally planar at the radical centre, could exhibit p_π–p_π bonding and p_π–d_π between carbon and mercury, the high value of the α-proton coupling constants seem to rule this out as a major effect. Also, the near-isotropic mercury coupling is not in accord with this. We therefore suggest that coupling to ¹⁹⁹Hg–²⁰¹Hg arises primarily from spin polarisation of the carbon–mercury σ electrons. We have previously stressed that for such polarisation the isotropic coupling must reflect the s–p-orbital hybridisation on the substituent,[11] and the high value for mercury suggests a large s-orbital contribution to the σ-bond, as expected. Indeed, if the rough correlation given in the figure of ref. 10 is used, we deduce a 50% s contribution from the mercury atom in the C–Hg

bond for $H_2\dot{C}HgMe$ radicals, corresponding to sp hybridisation. This contribution rises to ca. 75% for the radical Me$\dot{C}$HHgCl.

This increase on replacing a methyl group by halide follows, on the present argument, the tendency for more electronegative substituents to favour the use of p orbitals for σ-bonding. Thus our results, in so far as they can be generalised, favour a description of the bonding to the mercury atom in RHgX (X = halide) molecules in which the localised σ-bond involving the R group utilises mainly the 6s orbital, whilst that involving halide utilises mainly the $6p_z$ orbital on the mercury atom. This argument was used previously [12] to explain changes in phosphorus coupling constants for the series PO_4^{2-} (20—30 G), O_3PF^- (39·1 G), and O_2PF_2 (43·8 G), all of which have the unpaired electron largely confined to the oxygen atoms. A similar trend has been noted for a range of radicals containing aluminium $(R_2\dot{C}AlX_3)$ [13] and the results are included in Table 1 for comparison.

Mercury-centred Radicals.—Identification of the species which give rise to the high-field lines with irradiated dimethylmercury and ethylmercury(II) chloride is somewhat tentative because of the lack of any proton-hyperfine splitting. Two likely candidates for the latter compound are $\dot{H}$gEt and $\dot{H}$gCl, and since two species are involved we suggest that the species with the lower mercury coupling is $\dot{H}$gEt [A(¹⁹⁹Hg) ca. 3 693 G] and that with the higher coupling is $\dot{H}$gCl [A(¹⁹⁹Hg) ca. 10 000 G]. This assignment is based on the expectation that $\dot{H}$gCl will have considerable ionic character (Hg⁺Cl⁻) and would, therefore, be expected to exhibit hyperfine coupling close to that for the ion Hg⁺ (ca. 10 000—12 000 G). (Clear features from ²⁰¹Hg were only obtained for the $\dot{H}$gEt species in these studies.) This result accords nicely with the conclusion drawn above, that Cl⁻ will utilise the $6p$ rather than the 6s orbital for σ-bonding. Similarly, the lower value for A_{iso} assigned to $\dot{H}$gEt reflects, in part, the presence of greater use of the 6s orbital for σ-bonding. This forces the unpaired electron partially into a σ*-orbital which will have both $6p_z$ character on the mercury atom and considerable ligand character. Both effects will serve to reduce A_{iso} ($\dot{H}$g): both should introduce some anisotropy, which was certainly present, but was too ill defined to utilise.

We had expected to obtain the radical $\dot{H}$gMe from the dimethyl derivative, but the lower coupling constant of ca. 2 674 G (¹⁹⁹Hg) suggests that the species is structurally different from $\dot{H}$gEt. When the sample was annealed such that the features for the radical $H_2\dot{C}HgMe$ were lost, a central seven-line spectrum was revealed

[9] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 807.
[10] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[11] T. F. Hunt and M. C. R. Symons, *J. Chem. Soc.* (A), 1967, 1770.
[12] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (A), 1970, 1323.
[13] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (A), 1971, 2388.

which we tentatively assign to $(Me_2Hg)^{\bar{\cdot}}$. The high-field features were still present and their widths were such that the seven components could well be concealed therein. We therefore tentatively assign these features to the radical anion $(Me_2Hg)^{\bar{\cdot}}$. Since radicals of this class are unknown, we cannot make an identification by analogy. However, the lower value for the isotropic coupling to mercury relative to $\dot{H}gEt$ is in good accord with simple bonding theory.