

Nuclear magnetic resonance and mass spectra of organomercury hydrides and deuterides, Part II

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Abstract

Further mass spectroscopic and NMR evidence is given for the existence of several organomercury hydrides and deuterides.

Key words: Mass spectrometry; Nuclear magnetic resonance; Mercury; Hydride; Deuteride

1. Introduction

We recently prepared the compound CH_3HgH , and characterized it by mass spectrometry and NMR spectroscopy [1,2]. At the same time this compound was also reported by Filipelli *et al.* [3]. We identified the composition of the compound primarily by MS studies involving the $\text{CH}_3^{204}\text{HgH}$, $\text{CH}_3^{204}\text{HgD}$, ^{204}HgH and ^{204}HgD MS peaks at 220, 221, 205 and 206 respectively. These identifications made use of the heaviest naturally occurring mercury isotope (^{204}Hg) and its bond with H or D. We also confirmed the presence of CH_3 and H attached to mercury by ^1H NMR spectroscopy by noting that the same coupling constant was observed for the CH_3 resonance (d, $J = 4.2$ Hz) and the H resonance (q, $J = 4.4$ Hz). Spin decoupling was used to confirm the assignments [2]. A characteristic of the ^1H NMR spectrum of CH_3HgH was the unusually high δ value for the hydride resonance (17.2 ppm). In view of this, and of the unusual nature of the CH_3HgH complex, we have studied further examples of complexes of this type.

2. Results and discussion

2.1. NMR spectroscopy

NMR details are presented in Table 1. It can be seen that all the hydrides show resonances assigned to the Hg–H moiety, at 11 ppm or higher, confirming that the appearance of the CH_3HgH resonance in this region is not unique. None of the deuterium compounds has a peak in this region, again supporting the Hg–H assignment. Aliphatic and aromatic protons are found in the expected regions, with appropriate coupling constants. The coupling constants $J(^{199}\text{Hg}-\text{CH}_2-)$ and $J(^{199}\text{Hg}-\text{CH}_3)$ were in the region *ca.* 80–100 Hz in the alkyl compounds, such values being typical for this coupling. For the ethylmercury compounds $J(^{199}\text{Hg}-\text{CH}_2\text{CH}_3)$ was in the region 120–130 Hz, again typical for ethylmercury compounds, and confirming the bonding of the alkyl group to mercury. The ^{199}Hg alkyl proton coupling constant in $\text{C}_2\text{H}_5\text{HgCl}$ is about 200–300 Hz, and so it seems that no halogen is bound to mercury in the present case [4].

The fine structures of the RHgH resonances are complex. Only CH_3HgH , where a single carbon is present in the alkyl group, shows the expected coupling to H (*viz.* quartet). For all the other alkyl mercury hydrides the coupling is complex, implying interaction with protons or fluorine nuclei on carbon atoms β or further from the HgH moiety. The observed HgH peaks are therefore attributable to overlap of H/FC α

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TABLE 1(a). NMR spectra data for of organomercury hydrides and deuterides ^a

	δRCH_2Hg	δCH_3CH_2Hg	δC_6H_5Hg	δHgH
CH ₃ HgH	0.10 (d, $J(^{199}Hg-CH_3) = 103$) $J(HgH-CH_3) = 4.19$	NA	NA	17.2 q $J = 4.43$ (CH ₃ coupling to Hg proton)
C ₂ H ₅ HgH	0.85 (q, $J = 8.3$) $J(^{199}Hg$ coupling shows as 2 satellite quartets (internal $J = 8.1$) $J(^{199}Hg-CH_2) = 95$ $J = 8.3$ is CH ₃ CH ₂ coupling	1.26 (t, $J = 8.0$) $J(^{199}Hg$ shows as 2 satellite triplets (internal $J = 8.1$) $J(^{199}Hg-H) = 122.5$ $J = 8.0$ is CH ₃ CH ₂ coupling	NA	17.14 (sextet, $J = 4.9$ apparent)
C ₆ H ₅ HgH	NA	NA	7.18 (m)	14.1 (sextet, $J = 1.1$ apparent). Peak vanished after 36 h
C ₆ F ₅ HgH	NA	NA	NA	11.94 (pentet, $J = 6.5$)
CH ₃ HgD	0.09 (t, $J(^{199}Hg-CH_3) = 103$) $J(HgD)$ vs. CH ₃ = 6.7	NA	NA	No peak observed
C ₂ H ₅ HgD	0.86 (q, $J = 8.0$) $J(^{199}Hg$ coupling shows as 2 satellite quartets (internal $J = 8.0$) $J(^{199}Hg-CH_2) = 100$ $J = 8.0$ is CH ₃ CH ₂ coupling.	1.26 (t, $J = 8.0$) $J(^{199}Hg$ shows as 2 satellite triplets (internal $J = 8$) $J(^{199}Hg-H) = 130$ $J = 8$ is CH ₃ CH ₂ coupling	NA	No peak observed
C ₆ H ₅ HgD	NA	NA	7.20 (multiplet)	No peak observed
C ₆ F ₅ HgD	NA	NA	NA	No peak observed

and H/F-C β couplings to the proton bound to mercury. The HgH resonance for PhHgH vanished after 36 h. Further study is being undertaken on the fine structures of the signals from protons bound to mercury.

The relative positions of the methyl and methylene protons in the ethylmercury species are informative. Where the ethyl group is close to electron withdrawing species the methylene group is downfield of the methyl (e.g. in CH₃Si(OC₂H₅)₃ or C₂H₅HgCl). Where the ethyl group is in the vicinity of electron donor or neutral ligands, the positions of methylene and methyl are reversed (e.g. in Si(C₂H₅)₄ or Hg(C₂H₅)₂ for

example, the methyl peak is downfield of the methylene) [5,6]. In the case of C₂H₅HgH and C₂H₅HgD this latter is observed to be the case, in accordance with the relative electronegativities of H or D compared with e.g. Cl (2.1 vs. 3.0). These observations argue in favour of the assignment of the complexes as C₂H₅HgH and C₂H₅HgD respectively.

2.2. Mass spectrometry

Isotopic abundance and mass spectrometric details are given in Tables 2 and 3. For definitive identification of the presence of the HgH and HgD moieties we mainly make use of the highest naturally occurring mercury isotope (²⁰⁴Hg, Table 2). For each proposed

TABLE 1(b) ^a

	δRCH_2Hg	δCH_3CH_2Hg	δC_6H_5Hg
CH ₃ HgCl ^b	0.425 $J(^{199}Hg-CH_3) = 215.2$	NA	NA
C ₂ H ₅ HgCl	0.76 (q, $J = 8.0$) $J(^{199}Hg$ coupling shows as 2 satellite quartets (internal $J = 8.0$) $J(^{199}Hg-H) = 187.5$	0.54 (t, $J = 7.8$)	NA

^a Coupling constants are in Hz. ^b From ref. 4. d = doublet; t = triplet, q = quartet.

TABLE 2. Mercury isotopes

Mass	Abundance (%)
196	0.15
198	10.10
199	17.00
200	23.10
201	13.20
202	29.65
204	6.80

TABLE 3. Mass spectra of organomercury hydrides and deuterides

CH ₃ HgH: expected RMM range 212–220		
CH ₃ HgH ⁺ /CH ₃ Hg ⁺	HgH ⁺ /Hg ⁺	Assignments/comments
210	196	197 is ¹⁹⁶ HgH ⁺
211	197	205 is ²⁰⁴ HgH ⁺
212	198	203 is ²⁰² HgH ⁺
213	199	220 is CH ₃ ²⁰⁴ HgH ⁺
214	200	218 is CH ₃ ²⁰² HgH ⁺
215	201	212 is CH ₃ ¹⁹⁶ HgH ⁺
216	202	
217	203	No gap between 196 and 198,
218	204	202 and 204, 211 and 213,
219 (small)	205	217 and 219 showing HgH ⁺
220		units present at 197, 203,
		212 and 218.
CH ₃ HgD: expected RMM range 213–221		
CH ₃ HgD/CH ₃ Hg ⁺	HgD ⁺ /Hg ⁺	Assignments/comments
212	198	206 is ²⁰⁴ HgD ⁺
213	199	221 is CH ₃ ²⁰⁴ HgD ⁺
214	200	
215	201	
216	202	
217	203	
218	204	
219	206	
221		
C ₂ H ₅ HgH: expected RMM range 226–234		
RHgH ⁺ /RHg ⁺	HgH ⁺ /Hg ⁺	Assignments/comments
226	198	226 is C ₂ H ₅ ¹⁹⁶ HgH ⁺
227	199	203 is ²⁰² HgH ⁺
228	200	205 is ²⁰⁴ HgH ⁺
229	201	232 is C ₂ H ₅ ²⁰² HgH ⁺
230	202	234 is C ₂ H ₅ ²⁰⁴ HgH ⁺
231	203	
232	204	No gaps between 202 and 204,
233	205	226 and 228, 231 and
234		233 shows HgH ⁺ units present
		at 203, 227, 232
C ₂ H ₅ HgD: expected RMM range 227–235		
RHgD ⁺ /RHg ⁺	HgD ⁺ /Hg ⁺	Assignments/comments
227	198	227 is C ₂ H ₅ ¹⁹⁶ HgD ⁺
228	199	233 is C ₂ H ₅ ¹⁹⁶ HgD ⁺
229	200	235 is C ₂ H ₅ ²⁰⁴ HgD ⁺
230	201	198 is ¹⁹⁶ HgD ⁺
231	202	204 is ²⁰² HgD ⁺
232	203	206 is ²⁰⁴ HgD ⁺
233	204	205 peak is v. small
234	205	
235	206	
C ₆ H ₅ HgH: expected RMM range 274–282		
RHgH ⁺ /RHg ⁺	HgH ⁺ /Hg ⁺	Assignments/comments
275	196	282 is C ₆ H ₅ ²⁰⁴ HgH ⁺
276	198	205 is ²⁰⁴ HgH ⁺
277	199	280 is C ₆ H ₅ ²⁰² HgH ⁺
278	200	
279	201	
280	202	No gaps between 202 and 204,
281	203	279 and 281 shows HgH ⁺ units
282	204	present.
	205	

TABLE 3 (continued)

C ₆ H ₅ HgD: expected RMM range 275–283		
RHgD ⁺ /RHg ⁺	HgD ⁺ /Hg ⁺	Assignments/comments
275	197	283 is C ₆ H ₅ ²⁰⁴ HgD ⁺
276	198	281 is C ₆ H ₅ ²⁰² HgD ⁺
277	199	No ¹⁹⁶ Hg ⁺ is detected
278	200	206 is ²⁰⁴ HgD ⁺
279	201	
280	202	
281	203	
282	204	
283	206	
C ₆ F ₅ HgH: expected RMM range 364–372		
RHgH ⁺ /RHg ⁺	HgH ⁺ /Hg ⁺	Assignments/comments
366	196	370 is C ₆ F ₅ ²⁰² HgH ⁺
367	199	372 is C ₆ F ₅ ²⁰⁴ HgH ⁺
368	202	203 is ²⁰² HgH ⁺
369	203	No ²⁰⁴ HgH ⁺ is detected
370	204	
371	207	
372	208	
C ₆ F ₅ HgD: expected RMM range 365–373		
RHgD ⁺ /RHg ⁺	HgD ⁺ /Hg ⁺	Assignments/comments
367	196	371 is C ₆ F ₅ ²⁰² HgD ⁺
368	198	373 is C ₆ F ₅ ²⁰⁴ HgD ⁺
369	199	No ²⁰⁴ HgD ⁺ is detected
370	200	
371	201	
373	202	
	203	
	204	
	208	

compound it can be seen from Table 3 that the expected m/e peak for RHgH⁺, RHgD⁺, HgH⁺ and HgD⁺ is observed as R²⁰⁴Hg⁺ + 1 (or 2 respectively). Compounds of similar structure, but without the presence of H or D ligands (*e.g.* C₂H₅HgCl) do not show MS peaks at these m/e values. It should be noted that a given MS peaks can come from an ion containing more than one mercury isotope; this can be exemplified by considering the phenyl compound. The group of MS peaks containing C₆H₅HgH⁺ also contains C₆H₅Hg⁺ fragments. The existence of these mixed isotope species, incrementally heavier by one or two mass units, demonstrates that RHg⁺ and RHgH⁺ (or RHgD⁺) are present (illustrated in Fig. 1) *i.e.* the existence of these mixed species demonstrates that mercury hydrogen or deuterium linkages are present. Proof for the presence of HgH⁺ moieties is also alluded to in Table 3, *viz.* the absence of gaps in the MS peaks attributable to the intervals that would occur if the peaks were caused only by RHg⁺ or Hg⁺; *e.g.* for CH₃HgH⁺ and C₂H₅HgH⁺ we see MS peaks at 197 and 203, demonstrating the presence of HgH⁺ (since ¹⁹⁷Hg⁺ and ²⁰³Hg⁺ do not exist).

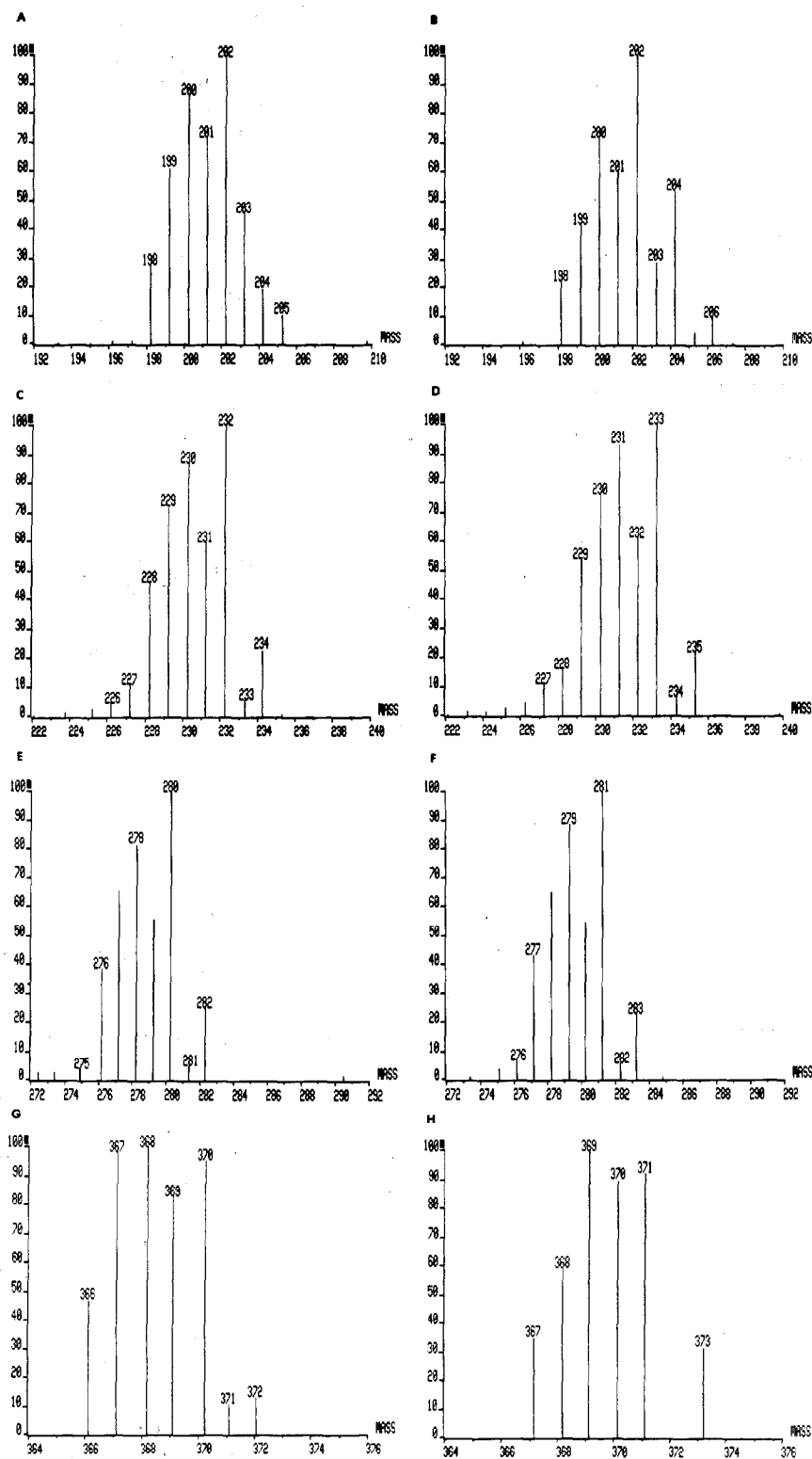


Fig. 1. Mass spectra of selected organomercury hydrides and deuterides. A = C_2H_5HgH (HgH^+ region); B = C_2H_5HgD (HgD^+ region); C = C_2H_5HgH ($RHgH^+$ region); D = C_2H_5HgD ($RHgD^+$ region); E = C_6H_5HgH ($RHgH^+$ region); F = C_6H_5HgD ($RHgD^+$ region); G = C_6F_5HgH ($RHgH^+$ region); H = C_6F_5HgD ($RHgD^+$ region).

3. Experimental details

The preparation and sampling of CH_3HgH and CH_3HgD has been described previously [2]. $\text{C}_2\text{H}_5\text{HgH}$, $\text{C}_2\text{H}_5\text{HgD}$, $\text{C}_6\text{H}_5\text{HgH}$, $\text{C}_6\text{H}_5\text{HgD}$, $\text{C}_6\text{F}_5\text{HgH}$ and $\text{C}_6\text{F}_5\text{HgD}$ were prepared from aqueous solutions of the appropriate organomercury chloride at pH4 (citrate buffer) by use of NaBH_4 or NaBD_4 . The amounts of the precursor organomercury chlorides depended on their solubility (*viz.* 100 cm^3 of 200 ppm $\text{C}_2\text{H}_5\text{HgCl}$; 200 cm^3 of 100 ppm $\text{C}_6\text{H}_5\text{HgCl}$; 20 cm^3 of 1000 ppm $\text{C}_6\text{F}_5\text{HgCl}$). The solutions were placed in a volumetric flask of such a size that the solution extended into the neck of the flask. To the solutions in each case were added 2 cm^3 of 4% NaBH_4 or NaBD_4 . On top of the aqueous solution was added 5 cm^3 of benzene- d_6 (for NMR work) or hexane (analytical grade, for GC MS work). After treatment with NaBH_4 or NaBD_4 the vessel was stoppered and the solution left for 15 min without agitation. A Pasteur pipette was used to withdraw *ca.* 3.5 cm^3 of the organic layer, and this was dried over anhydrous MgSO_4 prior to analysis. The dried solutions were used for the GC-MS and NMR experiments.

NMR studies were carried out on the solution using a Bruker 250Hz instrument. GC-MS investigations were carried out with a VG Mass Lab Trio triple quadrupole instrument with a 30 M SE54 capillary column and a HP5890 GC. GC-MS analysis of the solution or of the vapour in the headspace above the solution (contained after drying in a sealed crimp top vial) showed the presence of $\text{C}_2\text{H}_5\text{HgH}$ or $\text{C}_2\text{H}_5\text{HgD}$. The gas chro-

matograph was fitted with a 12 m SE54 capillary column (Altech) interfaced to the VG Mass Lab Trio 3 mass spectrometer. In the case of aromatic species, the analysis was carried out on the solution, not the vapour in the headspace.

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