JOM 23152

Mass spectroscopic and nuclear magnetic resonance evidence confirming the existence of methyl mercury hydride

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(Received June 29, 1992)

Abstract

Mass spectroscopic and NMR evidence involving deuterium labelling is presented for the existence of CH_3HgH.

1. Introduction

A recent literature search for CH_3HgH [1] produced only a single reference [2]. In a communication [2], Devaud presented evidence for the existence of RHgH species in methanol solution based on their polarographic oxidation waves. She derived rate constants for the decomposition of the RHgH species and stated that 'la stabilité de cet hydrure est beaucoup plus grande que celle qui avait été généralement admise'. We have investigated these species as part of our work on the volatilization and derivatization of organometallic compounds for analysis. We have recently demonstrated the use of $NaB(C_2H_5)_4$ for the generation of volatile $CH_3HgC_2H_5$ from CH_3Hg^+ in fish or sediments, etc. for subsequent analysis [3–5]. $NaBH_4$ is frequently used to generate stable organometallic hydrides for analysis, *e.g.* $(C_4H_9)_3SnH$ from $(C_4H_9)_3Sn^+$ in various environmental matrices [6]. However, the reaction of CH_3HgCl with $NaBH_4$ is thought to proceed as follows (eqn. (1)) in aqueous methanol [7]

$$4RHgCl + NaBH_4 + 4OH^- \rightarrow 4RH + 4Hg + 4Cl^- + Na^+ + H_2BO_3^- + H_2O \quad (1)$$

We now present evidence that CH_3HgH can, in fact, be generated in aqueous solution by $NaBH_4$. This can be purged with helium, condensed in a cold trap and distilled out for atomic absorption (AA) detection of the mercury or it can be transported directly after generation through a capillary GLC column and then subjected to AA or MS detection. We present direct MS and NMR evidence for the existence of CH_3HgH and CH_3HgD. *

2. Results and discussion

Several related forms of apparatus have been used. The first is a capillary GLC system linked by a transfer line to an AA instrument used as detector. AA detection is via a quartz cell at 660°C. Alternatively, a GLC–MS system may be used. CH_3HgH was also obtained by a purge and trap system. The volatilized CH_3HgH is trapped at liquid nitrogen temperature in a glass U-tube. The trap is electrothermally heated and the CH_3HgH volatilizes and is detected by atomization in a quartz cell in the beam of an AA spectrometer. Purge and trap derivatization was carried out on solu-

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* Since this paper was submitted for publication independent evidence for the existence of CH_3HgH has appeared (M. B. Filippell, F. Baldi, F. E. Brinckman and G. J. Olson, *Environ. Sci. Technol.*, *26* (1992) 1457.

0022-328X/93/$6.00

tions containing about 50 ng of CH_3HgCl per 50 cm^3 H_2O (1 ppb); in this system the recovery of CH_3HgH from CH_3HgCl was 60%. Purge and trap AA, or GLC–AA methodologies allow specification of the substance being analysed to the extent of confirmation of the presence of mercury and retention time data. The GLC–AA transfer line methodology was used for solutions of CH_3HgCl at the 1000 ppb level. However, only MS data can provide complete identification.

The clearest evidence for the existence of CH_3HgH comes from the mass spectra. The spectrum of the proposed CH_3HgH shows no peaks centred on *m/e* 252 or 232, *i.e.* it is not a spectrum of underivatized CH_3HgCl or $(CH_3)_2Hg$. A spectrum of CH_3HgCl or $(CH_3)_2Hg$ shows the expected CH_3Hg^+ pattern centred on *m/e* 217, *viz.*, the expected mercury isotopes in CH_3Hg^+ with a maximum value of *m/e* 219 for $CH_3{}^{204}Hg$. CH_3HgCl derivatized with $NaBH_4$ shows peaks we assign to CH_3HgH clustered around *m/e* 216 and 218 consisting of CH_3Hg^+ and CH_3HgH, with a maximum value of *m/e* 220 for $CH_3{}^{204}HgH$. CH_3HgCl derivatized with $NaBD_4$ shows peaks clustered around *m/e* 217 and 219 with a maximum value at *m/e* 221 for $CH_3{}^{204}HgD$. Figure 1 (A–C) illustrates these arguments clearly. The same follows from the $^{204}Hg^+$, $^{204}HgH^+$ and $^{204}HgD^+$ peaks in the MS at *m/e* 204, 205 and 206 respectively. Appropriate mixtures are found for $^{204}Hg^+$ with $^{204}HgH^+$ and $^{204}HgD^+$ respectively.

2.1. NMR spectroscopy

The argument from ^1H NMR is also compelling. Standard NMR spectral details for CH_3HgCl, CH_3HgBr, CH_3HgI and $(CH_3)_2Hg$ are presented in Table 1.

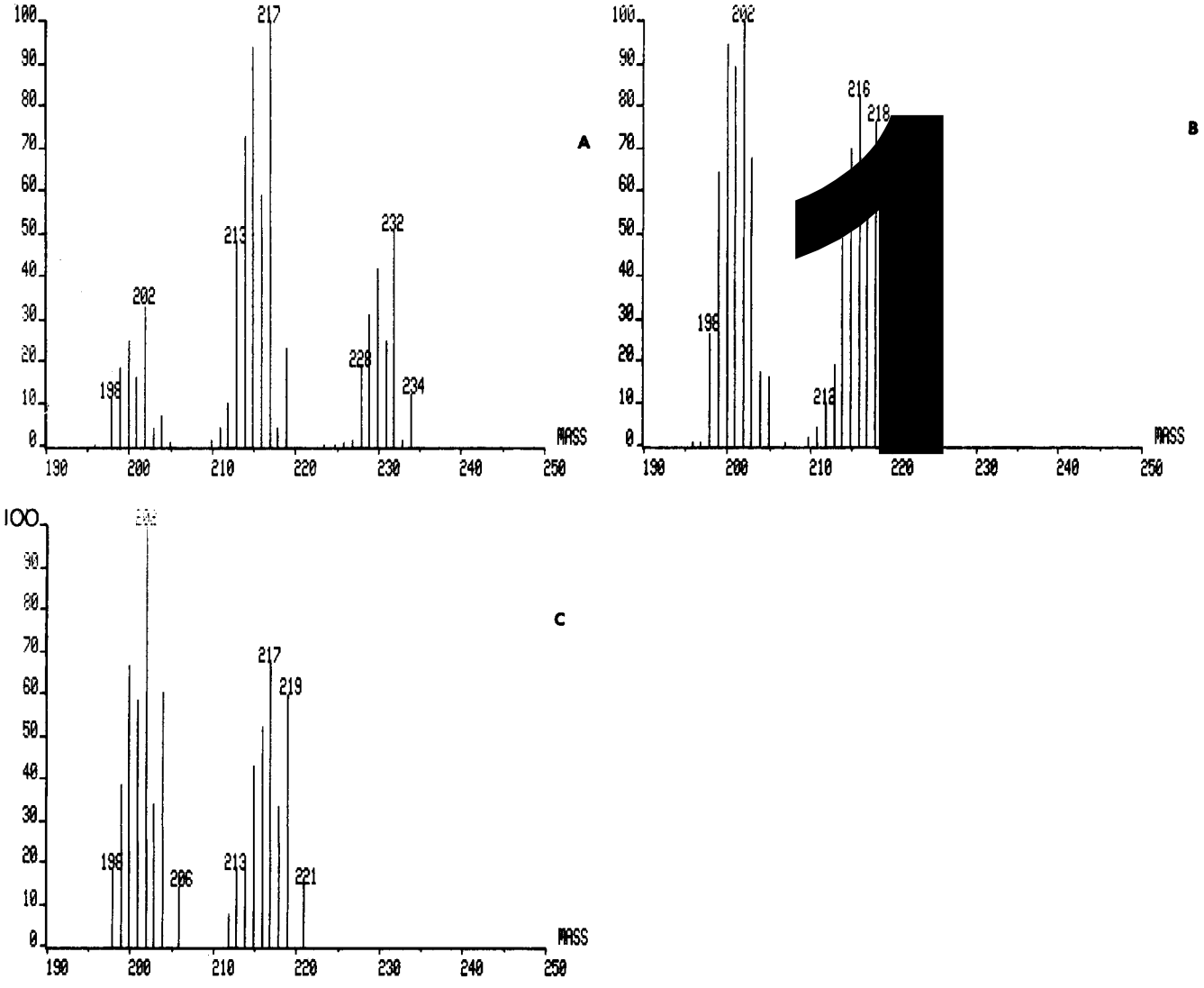

Fig. 1. Mass spectra of CH_3Hg^+ (A), CH_3HgH (B), and CH_3HgD (C).

TABLE 1. ^{1}H NMR data

Species	$\zeta(CH_3HgX)$	$J(C^{199}Hg-CH_3)$	$J(CH_3HgH/D)$
CH_3HgCl	1.16	203	–
CH_3HgBr	1.20	195	–
CH_3HgI	1.25	182	–
$(CH_3)_2Hg$	0.31	102	–
CH_3HgH	0.10	102	4.2
CH_3HgD	0.09	103	6.7

When CH_3HgH is generated into a benzene–D_6 layer or via a purge and trap system, and then subjected to NMR, we observe peaks centred at $\delta = 0.10$ ppm that we assign to CH_3HgH. CH_3HgD gives peaks centred at $\delta = 0.09$ ppm. These latter peaks clearly do not belong to CH_3HgCl, CH_3HgBr, CH_3HgI or $(CH_3)_2Hg$. The coupling constants to methyl from the ^{199}Hg isotope (17.0% abundance, $I = \frac{1}{2}$) are in the expected regions for such coupling, and the integrated area ratios of the ^{199}Hg isotope peaks are in accord with the known values. We did not detect any ^{201}Hg coupling with CH_3 ($I = 3/2$).

The CH_3HgH peak at $\delta = 0.10$ has a ^{199}Hg coupling (doublet) of $J = 102$ Hz, and CH_3HgD gives a similar doublet with $J = 103$ Hz. The CH_3HgD peak is a triplet with a small coupling constant ($J = 6.7$ Hz), in accordance with $I = 1$ for deuterium.

The CH_3HgH peak is a doublet ($J = 4.2$ Hz) owing to coupling with the hydrogen attached to mercury. We would therefore expect to see a quartet assignable to CH_3HgH in the NMR spectrum, and such a quartet is found at $\zeta = 17.2$ ppm ($J = 4.4$). Spin decoupling was carried out by irradiation at the frequency corresponding to the doublet (2890.044 Hz); the quartet collapsed into a singlet. Following irradiation at a frequency corresponding to the quartet (7168.07 Hz) the doublet collapsed into a singlet. Hence the doublet and quartet are coupled. The doublet peak is assignable to a methyl bonded to mercury on the grounds of the above-described coupling with ^{199}Hg. The following solutions in benzene–D_6 do *not* show a quartet at 17.2 ppm; CH_3HgD, CH_3HgOH and $NaBD_4$. Hence we conclude that the peak at 17.2 ppm arises from hydrogen bonded to mercury. During the time of the NMR experiments there is evidence of some decomposition of CH_3HgH to $(CH_3)_2Hg$, but the $(CH_3)_2Hg$ peaks do not obscure those of CH_3HgH. Clearly the position assigned to the CH_3HgH peak at 17.2 ppm suggests unusual complexation or bridging processes or other solution effects, but the basic chemical entity must involve the CH_3HgH grouping. Had the species in question been CH_3HgOH, formed by hydrolysis, then CH_3HgD would also have given the same spectrum as CH_3HgH.

2.2. Conclusion

We believe that our results show that CH_3HgH can be formed and transported.

3. Experimental details

3.1. Reagents

CH_3HgCl and $HgCl_2$ were purchased from commercial sources. They were not purified further. Solvents were spectroscopic grade. $NaBH_4$ and $NaBD_4$ were obtained from Aldrich. They were not purified further.

3.2. Apparatus

3.2.1. Capillary GLC–AA system

The GLC apparatus was a Perkin-Elmer F17 linked by a capillary column-transfer line to a Perkin-Elmer 3100 AA equipped with a quartz furnace cell in the light path. The building and arrangement of the quartz furnace cell for the AA has been fully described elsewhere [6]. The GLC was modified in the present work to take a capillary column.

The stainless steel transfer line was of length 1 m heated by 10.1 m of 28 SWG Nichrome wire. The inner diameter of the stainless steel tube was 1.1 mm (0.043 inch). A length of the capillary column (1 m) was uncoiled and threaded down the transfer line where it was directly coupled to the quartz furnace using a 6.4 mm to 1.6 mm Swagelock adaptor. By this means continuous chromatographic integrity from GLC to AA furnace was achieved. The capillary column ended 5 cm short of the furnace, before the air input.

Conditions for GLC–AA were as follows. Nitrogen was used as the carrier gas. Flow rates were determined by a bubble flow meter attached to the furnace end of the transfer line. Flow rates were as follows: air (13 $cm^3\ min^{-1}$) and hydrogen (varied at 250, 167, 94, 15 and 0 $cm^3\ min^{-1}$). The maximum sensitivity was obtained with zero hydrogen flow, but some air was required. The quartz furnace temperature was varied from room temperature to 880°C in 110°C steps. The optimum temperature was 660°C. The injector temperature of the GLC was 60°C, the oven temperature 50°C, and the capillary-transfer line was at 60°C.

Peaks were recorded on a Kipp and Zonen Chart Recorder (10 mm min^{-1}, 200 mV f.s.d.). The quartz cell in the AA was previously rinsed in a bath containing 40% hydrofluoric acid. The spectral line used was at 253.6 nm (slit 0.7 nm) from a hollow cathode lamp operated at 6 mV continuous mode. Following hydride generation derivatization (Section 3.2.3) the retention time for CH_3HgH with this apparatus, and under these conditions, was 2.16 min.

3.2.2. Purge and trap method

Derivatization of samples by $NaBH_4$ was followed by cold trapping prior to quartz furnace AA detection and has been described in detail by one of us previously [8,9]. Briefly, volatile hydride derivatives were produced from 50 cm^3 of milliQ water containing the mercury compound(s) using a 5% aqueous solution of $NaBH_4$ (1 cm^3) and these were purged from the aqueous solution and headspace with helium. The volatile derivatives were trapped at liquid nitrogen temperature in a 45 cm U-trap packed with 60/80 mesh chromosorb G-NAW coated with 3% SP2100. The trap is then warmed using a 0.5 mm diameter Nichrome wire, the species separate according to volatility and are detected in a quartz cell aligned in the beam of a Perkin-Elmer 5000 AA instrument with a background corrector. The carrier gas was helium–hydrogen (200 cm^3 min^{-1}) and oxygen (20 cm^3 min^{-1}) entered just prior to the entrance to the cell. The species were measured at 0.7 mm slit width using an EDL source at 253.6 nm.

Calibration curves were constructed for methyl mercury chloride, after hydride generation, at levels between 10 and 60 ng added to 50 cm^3 of water. The system in practical use will detect amounts of mercury species smaller than 0.20 ng at the quartz cell. The retention time was 1.34 min. The calibration curves demonstrate that CH_3HgH is stable for at least this period of time.

3.2.3. Conditions for GLC–MS

Mass spectra were obtained using a Hewlett Packard 5890 gas chromatograph fitted with a 12 m SE54 capillary column (Altech) interfaced to a VG Mass Lab Trio-3, triple quadruple mass spectrometer [10]. Helium gas pressure was 7 psi (5×10^4 Nm^{-2}).

The hydride generation analysis was performed by adding 1 cm^3 $NaBH_4$ (0.4%) to 10 cm^3 of a 100 ppm solution of MeHgCl in pH4 buffer. The resulting mass spectra of the headspace confirm the presence of MeHgH with a retention time of 1.9 min at a GLC column (SE54 Altech) temperature of 50°C and injection temperature of 60°C.

The MS work was carried out to confirm that the derivatization method produced the expected products which could only be generically identified by GLC–AA. The MS work confirmed the expected identities.

3.2.4. NMR

The work was carried out using a Bruker 250 mHz instrument. The compounds were generated from 500 cm^3 of aqueous 1000 ppm CH_3HgCl solution at pH 4 by injection of 1 cm^3 of 4% $NaBH_4$ or $NaBD_4$. The solution was contained in a 500 cm^3 graduated flask. This solution extended into the neck of the flask. On top of this aqueous solution was placed a 5 cm^3 aliquot of benzene-d_6 (Aldrich). After derivatization the solution was left for 15 min without shaking. Using a Pasteur pipette 0.5 cm^3 of the benzene-d_6 was taken and transferred to an NMR machine after drying over $MgSO_4$ for 15 min.

Spectra were also obtained from samples produced by the purge and trap method above. A 100 cm^3 aliquot of the 1000 ppm CH_3HgCl solution was placed in the derivatization vessel and purged with helium gas at 100 cm^3 min^{-1}. Then 5 cm^3 of an aqueous solution containing 0.4 g of $NaBH_4$ was added using a 10 cm^3 syringe. Purging was continued for 15 min with the products being swept into the liquid nitrogen cooled U-tube. The U-tube was then heated with continuation of purging and the vapour products led through a 5 cm^3 aliquot of benzene-d_6 in a sample tube using PTFE tubing. The products contained in the benzene-d_6 were subject to NMR analysis.

3.2.5. Conditions of hydride generation for GLC–AA

Aqueous standard solutions of CH_3HgCl were prepared in pH 4 buffer solution (BDH) and 10 cm aliquots analysed via the headspace method in 20 cm^3 PTFE-faced butyl septa-sealed crimp-on vials, via the addition (injection) of 1 cm^3 of 0.4% $NaBH_4$. The optimum line for derivatization was found to be 50 min for the undisturbed solution. After this time samples (1 cm^3) were removed for analysis using a gas tight syringe.

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