

The ^1H Nuclear Magnetic Resonance Spectra of Methylmercury Compounds

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WHEREAS the ^1H n.m.r. spectra of $\text{Me}^{199}\text{HgX}$, observed as satellites in the spectra of methylmercury compounds, appear as sharp doublets for most X groups, very broad peaks have been reported^{1,2} when X = I. Some broadening is also reported when X = Br and SCN.¹ It has been suggested that this phenomenon has its origin in a rapid exchange of methyl groups between the 17% of ^{199}Hg present and the other mercury isotopes, whose methyl groups are responsible for the main peak in the spectrum. This is presumably a bimolecular process whose rate will be concentration dependent and will increase with temperature. Furthermore, the mean lifetime of methyl groups in the remaining 83% of the mercury compound will be only about five times as great as that for the ^{199}Hg species, so that the broadening of the satellites of MeHgI should be matched by smaller broadening of the main peak.

Some results obtained by resonance measurements at 100 Mc./sec. and 60 Mc./sec. on pyridine solutions of methylmercury iodide are given in Table 1.

The satellite line-widths measured at 60 Mc./sec., although very crude, suggest no marked temperature dependence. Indeed the increase in width would correspond to a bimolecular process having an activation energy less than 2 kcal. mole⁻¹. The spectra obtained at 100 Mc./sec. indicate that there is no concentration dependence of the satellite line-widths except when the solution is saturated and that the main peak is not detectably broadened (tetramethylsilane yields a peak of similar width). It seems clear that methyl group exchange is not responsible for the line broadening.

In the case of the methylmercury iodide, a line-broadening mechanism specifically associated with the ^{199}Hg species can be envisaged, arising from coupling between ^{199}Hg and the quadrupole of ^{127}I . A rough assessment of this factor suggests that an effect of the observed magnitude can be calculated.³ A similar mechanism might be operative in the case of the bromide arising from ^{79}Br and/or ^{81}Br although for this compound some other factor increasing the natural line-width by a small amount may be responsible. It would be difficult,

TABLE 1. Methylmercury iodide in pyridine solution

	100 Mc./sec.; $\sim 35^\circ$			60 Mc./sec.	
			Sat'd soln.	$\sim 35^\circ$	$\sim 72^\circ$
Mole fraction MeHgI	0.08	0.13		0.24	0.24
Chemical shift (τ)	8.96 ± 0.002	8.94 ± 0.002	8.925 ± 0.01	8.92 ± 0.01	—
$J(^{199}\text{Hg}-^1\text{H})$ (c./sec.) ..	203 ± 2	200 ± 1	204 ± 2	199 ± 2	~ 196
Main peak width (c./sec.) ..	1.0	1.0	—	—	—
Satellite width (c./sec.) ..	11.0 ± 0.5	10.7 ± 0.5	17 ± 2	20—25	24—27

TABLE 2. Methylmercury compounds in pyridine solution; present results

	MeHgCl	MeHgBr	MeHgSCN	MeHgI
Mole fraction	0.05	0.105	0.13	0.08
Chemical shift (τ)	9.07 ± 0.006	9.01 ± 0.008	9.08 ± 0.01	8.96 ± 0.004
$J(^{199}\text{Hg}-^1\text{H})$ (c./sec.) ..	215.4 ± 0.6	211.0 ± 1.1	210.5 ± 0.5	203 ± 2
Main peak width (c./sec.) ..	0.8	1.4	0.5	1.0
Satellite width (c./sec.) ..	0.8	1.3	0.5	11.0 ± 0.5

Results from ref. 1. (5 moles %)

Chemical shift (τ) ^a	(9.07)	(9.02)	(9.03)	(8.96)
$J(^{199}\text{Hg}-^1\text{H})$ (c./sec.) ..	215.2	212.0	208.0	200.0
Main peak width (c./sec.) ..	< 1	< 1	< 1	< 1
Satellite width (c./sec.) ..	< 1	2	5	16

^a Chemical shifts relative to C_6H_{12} converted into τ -values by assuming 9.07 for methylmercury chloride.

however, to account for a substantial line broadening in the thiocyanate case on grounds other than methyl group exchange.

We have re-examined the ^1H n.m.r. spectrum of pyridine solutions of methylmercury thiocyanate employing carefully purified samples prepared either from methylmercury chloride and sodium thiocyanate or from dimethylmercury and mercuric thiocyanate. Our results from 100 Mc./sec. measurements are compared in Table 2 with the results of ref. 1.

It seems that pure samples of methylmercury

thiocyanate in pyridine solution show no indications of satellite line-broadening. The same is true for solutions in benzene and in dioxan. The result reported in ref. 1 was obtained using material prepared from methylmercury iodide and could be accounted for if the sample contained iodide.

In summary the ^1H n.m.r. spectra of methylmercury compounds show no evidence of methyl group exchange. Methylmercury iodide may be unique in giving broad satellite resonances arising from a specific interaction between ^{199}Hg and ^{127}I .

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¹ J. V. Hatton, W. G. Schneider, and W. Siebrand, *J. Chem. Phys.*, 1963, **29**, 1330.

² P. R. Wells and W. Kitching, *Tetrahedron Letters*, 1963, 1531.

³ P. C. Lauterbur and P. R. Wells, to be published.