Collapse of Satellites in the ^{1}H Nuclear Magnetic Resonance Spectra of Dimethylmercury and Methylmercuric Iodide

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DIMETHYLMERCURY, unlike dimethylzinc and dimethylcadmium, does not readily participate in reactions in which methyl groups are exchanged from one metal to another,[1] but the formation of ethylmethylmercury from dimethylmercury and diethylmercury can be catalysed by the addition of aluminium chloride.[2]

In the absence of catalyst, the ^{1}H nuclear magnetic resonance (^{1}H n.m.r.) spectrum of dimethylmercury in benzene consisted of a sharp central peak, together with satellites due to the methyl groups bound and coupled to spin-half ^{199}Hg [17% abundant, J(HgH) = 102 c./sec.][3] The addition of 10 mole % aluminium chloride instantly collapsed the methyl spectrum to a single peak. Thus, aluminium chloride caused methyl groups to exchange from one mercury atom to another, with a pre-exchange life-time of less than 0·003 sec. ($1/\pi J$). The pre-exchange lifetime, τ, is the time required for all but 1/e (=0·368) of the methyl groups to have exchanged.

Catalysis by either aluminium chloride or methylaluminium dichloride was so effective that only a single peak could be observed at the lowest practical concentration of catalyst (10^{-2} M). The use of various mixtures of methylaluminium dichloride and dimethylaluminium chloride allowed the pre-exchange lifetime to be varied systematically about the value 3×10^{-3} sec. By first adding methylaluminium dichloride (up to 0·03 mmole‡) and then dimethylaluminium chloride (up to 0·07 mmole‡) to a solution of dimethylmercury (0·7 mole) in benzene (0·55 ml), the spectrum was steadily changed from a broad single peak (4·5 c./sec. width at half height) through to a sharp central peak (1·0 c./sec. width) with sharp satellites (1·4 c./sec. width) 102 c./sec. apart. The maximum observed width of the central peak was 10 c./sec. Computer-simulated spectra, obtained from solutions of the exchange-modified Bloch equations[4] for this system, predict that the width of the central line reaches a maximum of 10·5 c./sec. at a pre-exchange lifetime of 0·003 sec. One pair of experimental and calculated spectra are shown in Figure 1. The observed behaviour of the central line and satellites corresponds to a range of τ from about 0·001 sec. (satellites absent) to about 0·4 sec. (satellites present).§

The broadness or absence of ^{199}Hg satellites in the ^{1}H n.m.r. spectrum of methylmercuric iodide has usually been interpreted in terms of exchange of methyl groups between spin-half ^{199}Hg nuclei and spin-zero Hg nuclei.[5] Thus the spectrum should show a range of behaviour like that of dimethylmercury and, in particular, the ^{199}Hg satellites should appear if the exchange could be slowed down sufficiently, *e.g.*, by cooling. The ^{1}H n.m.r. spectrum of CH_3HgI (1·2 M) in pyridine has therefore been recorded as a function of temperature.

As the temperature was lowered satellites began to appear (symmetrically placed, width at half height ~15 c./sec. at 20°), and sharpened gradually

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‡ Calculated as monomer.

§ The methyl groups of the catalyst also participate in the general exchange, for the catalyst peak (see Figure 1) appeared and sharpened along with the satellites. The calculations neglected this contribution, so that the short lifetimes could be even shorter than estimated.

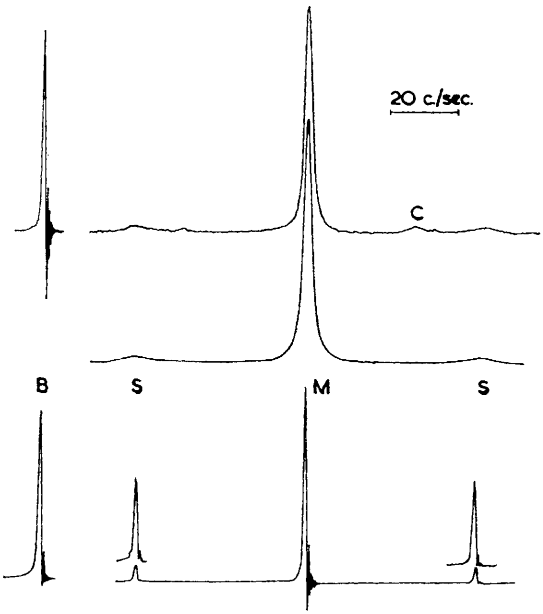

FIGURE 1. 60 *Mc./sec.* ^{1}H *n.m.r. spectra of dimethylmercury in benzene at* 40°, *showing catalysis of methyl exchange.* M, *main methyl peak*; S, ^{199}Hg *satellites*; B, *solvent benzene. Lower*: 1M-*dimethylmercury, with satellite separation* 102 *c./sec.* = J(*HgH*); *linewidths in c./sec.*: M 0·9; S, 1·1; B, 0·9. *Upper*: 1·2 M-*dimethylmercury with methylaluminium dichloride and dimethylaluminium chloride, each* 4·3 *mole* % (*calc. as monomer with respect to dimethylmercury*); C, *catalyst peak*; *linewidths in c./sec.*: M, 2·4; S, 8; B, 0·9. *Middle*: *Computed spectrum assuming methyl exchange with a pre-exchange lifetime of* 0·03 *sec.*

until at −35° their width (5 c./sec.) approached that of the central peak (1·1 c./sec.) and their separation was 205 c./sec. *Unlike the case of dimethylmercury,* however, the central line-width did not change at all over the temperature range −35° to 80°. (See Figure 2.) Spectra were computed on the assumption of methyl exchange among the three magnetic sites. Then, from a comparison of the satellite widths at low temperatures with the computed spectra, lifetimes were obtained and extrapolated on an Arrhenius plot to indicate a central line-width at 80° of about 6 c./sec. Further, the separation of the satellites varied rather more rapidly with their width than the computed spectra would allow; *e.g.*, at a satellite width of 13 c./sec., the experimental separation was 200·5 c./sec. (calc. 204·2 c./sec.).

Thus it seems as if the collapse of the satellites in methylmercuric iodide is not due to exchange of methyl groups. Without the assumption of methyl exchange it is possible to interpret the present results in terms of a chain of relaxation effects. The ^{1}H nuclear spectrum could be collapsed by transitions of the ^{199}Hg nucleus, and these may be determined mainly by a strong spin coupling with the rapidly relaxing ^{127}I nucleus.[6] This mechanism should have the temperature dependence observed. The results of Hatton, Schneider, and Siebrand[5] could now be re-interpreted in terms of halide exchange.

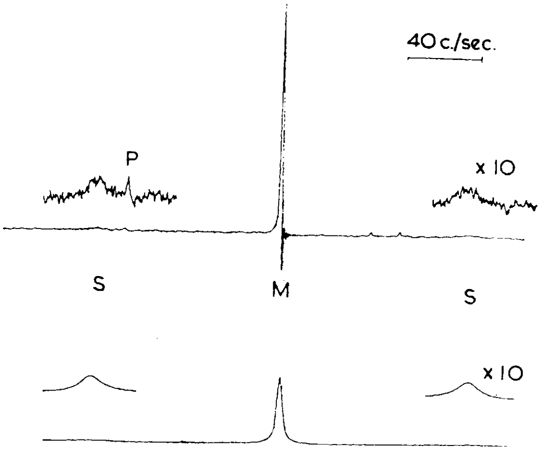

FIGURE 2. *Upper*: *Observed* 60 *Mc./sec.* ^{1}H *n.m.r. spectrum of methylmercuric iodide* (1·2 M) *in pyridine at* 5°; M, *main methyl peak*; S, ^{199}Hg *satellites*; P, *picoline impurity. Lower*: *Computed spectrum assuming methyl exchange with a pre-exchange lifetime of* 0·022 *sec. The experimental and calculated satellite widths are both* 14 *c./sec., but the central width is* 1·0 *c./sec. observed and* 3·4 *c./sec. calculated. The spectra are scaled to have the same integral.*

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[6] See, *e.g.*, A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, Oxford, 1961, pp. 309, 313.