Recent Nuclear Magnetic Resonance Evidence for the Mercurinium Ion

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RECENTLY, some features in the 60 Mc./sec. ^{1}H n.m.r. spectrum of the $Hg(NO_3)_2$–D_2O–ethylene system were interpreted[1] in terms of the existence of an olefin–mercury(II) π-complex, *i.e.* mercurinium ion.[2,3] We now report that this interpretation is incorrect.

The evidence for the suggestion that the ethylene–mercury(II) π-complex co-exists with the σ-bonded mercurial, (I), rests upon the assignment of a set of 'triplet-like' peaks among the low-field (τ 6·3) half-spectrum of the σ-bonded mercurial, to an ethylene derivative with almost equivalent CH_2-groups equally coupled to ^{199}Hg with J 247 c./sec.

$HOCH_2{\cdot}CH_2{\cdot}HgX$ (I);

$XHgCH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}HgX$ (II)

Repetition of the experiments provided spectra essentially the same as in ref. 1, and the spectra of the corresponding $Hg(ClO_4)_2$ system showed no major differences in form, except that the intensity of the resonances, allegedly due to the π-complex, was comparatively greater (Figure, a, b). However, an integral curve established for both systems at 60 and 100 Mc./sec. that the intensities of the resonances at *ca.* τ 6·3 and 7·8 were the same, which disproves the former interpretation, since the τ 6·3 resonance should have been more intense by an amount corresponding to the concentration of the π-complex. This result suggests that, in addition to the 2-hydroxyethylmercury(II) species (I), there is another species present with methylene groups in very similar environments to those in (I) but that the difference, though small, is more pronounced for the lower field methylene group, *i.e.* the methylene group adjacent to oxygen. Besides the close agreement in chemical shifts, the similarity of the ^{199}Hg–^{1}H coupling constants [*cf.* J 238 c./sec. for $XHgCH_2{\cdot}\mathit{CH}_2OH$ and J 253 c./sec. (247 c./sec. in ref. 1) for the alleged π-complex] is indicative of methylene groups similarly located with respect to a mercury atom.†

Inspection of the *ca.* τ 6·3 resonance in Figure 1 shows clearly, that in addition to the resonance for $HO\mathit{CH}_2{\cdot}CH_2{\cdot}HgX$ (half of the A_2X_2 pattern),[4] the residual signals are not a 'triplet'‡ as claimed,[1] but a facsimile of the $HO\mathit{CH}_2{\cdot}CH_2{\cdot}HgX$ resonance pattern. The ^{199}Hg–^{1}H satellite pattern in the 100 Mc./sec. spectrum confirms this (Figure, c). Closer examination also reveals that the resolution in the pattern of $HO\mathit{CH}_2{\cdot}CH_2{\cdot}HgX$ (*i.e.* in the τ 6·3 pattern) is lacking in the higher-field resonance of $HOCH_2{\cdot}\mathit{CH}_2{\cdot}HgX$, and that these higher

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‡ Although the "triplet" resonance was ascribed to a special case of an A_2B_2 spin system, the surprising feature was that there was no indication that the A and B protons had different couplings with ^{199}Hg.

† The difference between 238 c./sec. and 253 c./sec. suggests a very modest change in environment. In general, we are disinclined to accept that comparisons of n.m.r. parameters of σ- and π-bonded platinum and mercury compounds, with presumably differing extents of σ- and π-bonding components, are at all meaningful.

field lines are broadened (quite clearly in the 100 Mc./sec. spectra), consistent with the presence of an underlying resonance, having almost the same chemical shift. The ^{199}Hg–^{1}H coupling constant for HOCH$_2$·*CH*$_2$·HgX (*J* 274 c./sec.) and that for the underlying species are extremely similar.

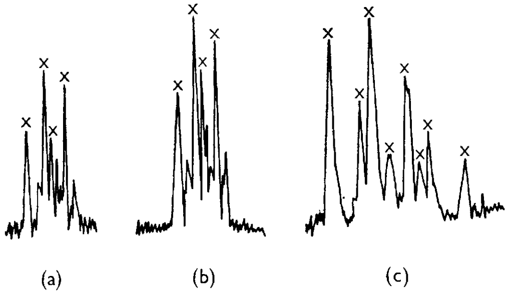

FIGURE (a) *Lower-field region* (ca. τ 6·3) *of the* 60 Mc./sec. *spectrum of the* $Hg(NO_3)_2$–D_2O–C_2H_4 *system*;

(b) *Lower-field regions of the* 60 Mc./sec. *spectrum of the* $Hg(ClO_4)_2$–D_2O–C_2H_4 *system, showing essential similarity to* (a);

(c) *The high-field* ^{199}Hg *satellite pattern of the* τ 6·2 *resonance in the* 100 Mc./sec. *spectrum of the* $Hg(ClO_4)_2$–D_2O–C_2H_4 *system.*

Related resonances in the resonance facsimiles are indicated.

Mercury(II) salts of strong acids [*e.g.* $Hg(ClO_4)_2$ and $Hg(NO_3)_2$] in aqueous solution, in the presence of ethylene, are well known to yield in addition to the hydroxyethyl-mercury species (I), ethers[2,3] of the type (II). (These may be isolated as the halides but are amorphous and generally difficult to manipulate.) Thus the chemistry§ of these systems and the ^{1}H n.m.r. data are consistent with the co-occurrence of (I) and (II). The observed chemical shifts for the mercurials in the region of τ 6·3 agree well with those for the related resonances in di-ethyl ether (τ 6·38) and ethanol (τ 6·30).

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§ Results reported[1] which seem to argue against, rather than for a mercurinium-ion description, are the insensitivity of the system to temperature, and the survival of the π-complex in the presence of KOH.

[1] Y. Saito and M. Matsuoa, *Chem. Comm.*, 1967, 961.
[2] See W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 35.
[3] J. Chatt, *Chem. Rev.*, 1951, **48**, 7.
[4] P. R. Wells and W. Kitching, *Tetrahedron Letters*, 1963, 1531.