

CONCERNING MERCURATED ACETIC ACID*

By W. KITCHING† and P. R. WELLS‡

Some years ago in this Journal, we briefly described¹ the product of the reaction between mercuric acetate and acetic acid, and at that time suggested that the product was a polymer of mercurated acetic acid with $n \simeq 5$, i.e. $\text{CH}_3\text{CO}_2[\text{HgCH}_2\text{CO}_2]_n\text{H}$. In view of recent interest (e.g. see²) in the chemistry of α -metalated carbonyl compounds, and in particular the potential utility of heavy-atom derivatives of proteins for structural studies,³ we now wish to elaborate on our previous report, and present data fully confirming our previous postulates.

The infrared spectra (Nujol mulls) show strong broad bands at 1295 and 1575 cm^{-1} due to the carboxylate group. A broad band of medium intensity occurs at 1695 cm^{-1} in the carbonyl region, some 20 cm^{-1} higher than in bromomercuriacetic acid but similar to that (1690 cm^{-1}) found for chloromercuriacetic acid.⁴ The sharp bands of medium intensity at 1085 and 1110 cm^{-1} in the compound may be compared with those at 1075 and 1115 cm^{-1} in authentic bromomercuriacetic acid, and those at 1090 and 1150 cm^{-1} in chloromercuriacetaldehyde ($\text{ClHgCH}_2\text{CHO}$).‡ Such bands appear to have their origin either as an overtone of the fundamental Hg-C stretching frequency or as a $-\text{HgCH}_2-$ deformation mode.§ Whatever their origin they appear indicative of the $-\text{CH}_2\text{Hg}$ arrangement.

More detailed proton n.m.r. studies of mercurated acetic acid have proved particularly illuminating as to structural details and have permitted a rather good estimate of the molecular weight, impossible to determine by conventional methods due to poor solubility.

Mercurated acetic acid dissolves rather easily in aqueous solutions of KCl, NaOH, KBr, and also in KI and $\text{Na}_2\text{S}_2\text{O}_3$. The similarity of spectra of KCl and

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† Department of Chemistry, University of Queensland, Brisbane.

‡ The p.m.r. spectrum exhibited a triplet at 0.87 τ (J 5 c/s) for the aldehydic proton and a doublet at 8.20 τ (J 5 c/s) for the methylene protons. Carbonyl absorption occurred at 1640 cm^{-1} in the i.r.

§ In the spectrum of $\text{ClHgCH}_2\text{COOH}$ (DMSO solution) a band of medium intensity at 1100 cm^{-1} is discernible. The features of what may be an accompanying band at c. 1070 cm^{-1} are masked by solvent absorption.

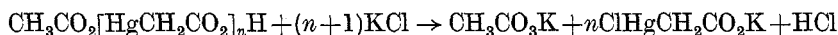
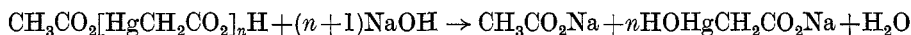
¹ Wells, P. R., and Kitching, W., *Aust. J. Chem.*, 1963, **16**, 508.

² Lutsenko, I. F., Foss, V. L., and Ivanova, I. L., *Dokl. Akad. Nauk. SSSR*, 1961, **141**, 1107, and subsequent papers.

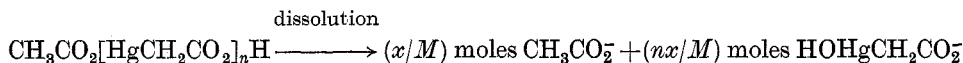
³ Tilander, B., Strandberg, B., and Fridborg, K., *J. molec. Biol.*, 1965, **12**, 740.

⁴ Tilander, B., *Ark. Kemi*, 1966, **25**, 467.

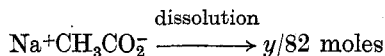
NaOH solutions indicate similar dissolution modes, almost certainly involving disintegration of the polymeric network.



Consider the system where added acetate ion is present.



where x is the weight and M the molecular weight.



where y is the weight and 82 the molecular weight.

Therefore

$$R = \frac{\text{methyl intensity}}{\text{methylene intensity}} = \frac{3(x/M + y/82)}{2(nx/M)} = \frac{3}{2nx}(x + My/82)$$

With no added acetate, i.e. $y = 0$, $R = 3/2n$, from which $n = 5.5$.

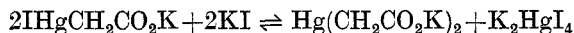
With known amounts of sodium acetate (0.3548 g) and mercurated acetic acid (0.4369 g),

$$\frac{\text{methyl intensity}}{\text{methylene intensity}} = \frac{61}{16.66}$$

from which $M = 1270$. This value agrees well with that calculated (1350) for $n = 5$.

The proton n.m.r. spectra of aqueous KCl and NaOH solutions are straightforward, showing signals for acetate (7.92 τ) and $-\text{CH}_2\text{Hg}-$ protons. This latter resonance occurs at 7.52 τ (NaOD) and 7.41 τ (KCl), in good agreement with values for $\text{BrHgCH}_2\text{COOH}$ (7.70 τ) and $\text{ClHgCH}_2\text{COOH}$ (7.60 τ). The values of $J(\text{CH}_2-^{199}\text{Hg})$ differ appreciably indicating dissimilar substituents on mercury.⁵ Thus in basic solution, $J = 265$ c/s, while in KCl solution, $J = 305$ c/s, essentially identical with that found for authentic $\text{ClHgCH}_2\text{CO}_2\text{H}$. Presumably the hydroxy- and chloro-mercurials are under scrutiny.

Dissolution of the compound in aqueous iodide and thiosulphate involve phenomena subsequent to polymeric disintegration. The spectrum of a KI/D₂O solution (Fig. 1) shows signals at 8.04 τ (J 167 c/s) and 8.14 τ (acetate). Such methylene protons are clearly different from those that exist in KCl/D₂O since $J(^{199}\text{Hg}-^1\text{H})$ (cf. 167 c/s with 305 c/s) and the resonance positions (cf. 8.04 τ and 7.41 τ) are dissimilar. KI is perhaps the best known symmetrizing agent, and the spectrum can be interpreted in terms of the following reaction:



⁵ See Wells, P. R., and Kitching, W., *Tetrahedron Lett.*, 1963, 1531.

The absence of a signal ascribable to $\text{IHgCH}_2\text{CO}_2\text{K}$ shows the above equilibrium to lie essentially completely to the right. The high-field shift of the resonance position and the reduction in $J(^{199}\text{Hg}-^1\text{H})$ are perfectly consistent with the above interpretation.^{6*}

In D_2O containing thiosulphate, mercurated acetic acid exhibits three unsplit resonances at 8.12τ (acetate), 8.03τ , and 7.49τ (J 257 c/s). The signal at 8.03τ agrees well with that for KI solution (8.03τ) and is ascribable to the dialkyl as before. The persistence of the signal for the monoalkyl mercurial in thiosulphate solution is consistent with the weaker symmetrizing power of thiosulphate.

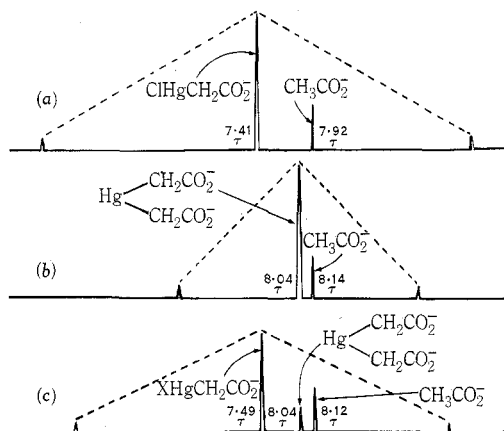


Fig. 1.—N.m.r. spectra of mercurated acetic acid in (a) $\text{KCl}/\text{D}_2\text{O}$; (b) $\text{KI}/\text{D}_2\text{O}$; (c) $\text{Na}_2\text{S}_2\text{O}_3/\text{D}_2\text{O}$. The HOD resonance has been omitted. The dashed lines locate the $^{199}\text{Hg}-^1\text{H}$ satellites.

This unequivocal demonstration of the structure of mercurated acetic acid appears to suggest strongly that polymeric arrangements of monomercurated repeat units are of general occurrence in compounds previously thought to be di- and tri-mercurated. Indeed, no sound piece of evidence has yet been produced to support di- and tri-mercuration at a carbon centre, and only scattered examples of *gem*-dimetallic compounds have appeared.⁷

Numerous mercury derivatives of aldehydes, ketones, and carboxylic acids have been prepared but the structures of few of the compounds have been determined. A detailed account may be located in Whitmore's⁸ monograph. It is clear that many of the proposed structures are incorrect, and a thorough reinvestigation of this area of aliphatic organomercury chemistry is required.

* For example, the change $\text{CH}_3\text{HgCl} \rightarrow (\text{CH}_3)_2\text{Hg}$ is accompanied by a high-field shift of 0.69 p.p.m. and a reduction in $J(^{199}\text{Hg}-\text{CH}_3)$ from 211 to 104 c/s, i.e. a factor of two. The change $\text{ClHgCH}_2\text{CO}_2\text{K} \rightarrow \text{Hg}(\text{CH}_2\text{CO}_2\text{K})_2$ in the present case leads to a resonance shift of 0.62 p.p.m. to high field and a reduction in J from 306 to 167 c/s, i.e. a factor of c. 1.8.

⁶ Wells, P. R., Kitching, W., and Henzell, R. F., *Tetrahedron Lett.*, 1964, 1029.

⁷ Matteson, D. S., and Shdo, J. G., *J. Am. chem. Soc.*, 1963, 85, 2684, footnote 1.

⁸ Whitmore, F. C., "Organic Compounds of Mercury." (Chemical Catalog Company: New York 1921.)