

THE REACTION OF MERCURIC SALTS WITH ACETIC ACID*

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In the course of studies of the mercuration of aromatic compounds Brown and McGary¹ observed a slow apparent first-order reaction between mercuric acetate and the solvent acetic acid. Vollrath² also mentions the reaction and suggests that a mercurated acetic acid may be formed.

The product of this reaction can be obtained by removal of the acetic acid, or by the reaction of mercuric nitrate with aqueous acetic acid, when it is obtained as a white amorphous precipitate. Its high melting point ($> 255^{\circ}\text{C}$ decomp.) and low solubility in all organic solvents except hot glacial acetic acid suggest the product has a polymeric structure. It is different from 2-acetoxymercuriacetic acid which was prepared from 2-bromomercuriethanol by permanganate oxidation followed by reaction with silver acetate.

The product shows infrared absorption in Nujol characteristic of the acetate anion ($1290, 1580\text{ cm}^{-1}$) as observed in the spectra of mercuric acetate and methylmercuric acetate. There is a second absorption band in the carbonyl region at 1695 cm^{-1} that might be expected for an undissociated polymeric carboxylate. The product dissolves readily in dilute nitric acid, dilute sodium hydroxide, and aqueous potassium chloride, bromide, and cyanide. Bromine and iodine rapidly cleave the product yielding the mercuric halide. Hydrogen sulphide gives an immediate precipitate of mercuric sulphide (utilized for analysis), indicating that the compound is not of the mercarbide type (cf. Whitmore³). The product can be titrated in acetic acid solution by means of thiocyanate to an end-point indicating one C-Hg bond per Hg atom.

Proton magnetic resonance spectra in D_2O containing NaOD (c. 2.8N) and in D_2O containing KCl are very similar, both showing two singlets. One singlet is at 7.92τ in both solutions due to the methyl group of an acetate anion (identified by addition of sodium acetate). The second singlet is at 7.52τ in NaOD solution ($\text{HOHgCH}_2\text{CO}_2^-$) and at 7.27τ in KCl solution ($\text{ClHgCH}_2\text{CO}_2^-$). These are in good agreement with the resonance position of 7.4τ predicted for $\text{AcOHgCH}_2\text{CO}_2\text{H}$ from the spectrum of methylmercuric acetate and the shift expected due to the carboxyl group.

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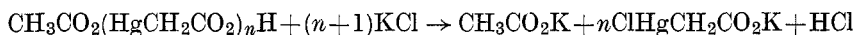
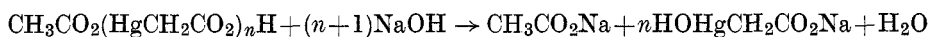
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¹ Brown, H. C., and McGary, C. W. (1955).—*J. Amer. Chem. Soc.* **77**: 2306.

² Vollrath, R. E. (1940).—*J. Amer. Chem. Soc.* **62**: 1310.

³ Whitmore, F. C. (1921).—"Organic Compounds of Mercury." pp. 50-59. (Chemical Catalog: New York.)

The following mode of dissolution is indicated:



From the relative areas of the methyl and methylene peaks n is estimated to be about 5. (A correction has been made for the isotopic composition of mercury.)

The analytical percentage (Found: C, 10.4; H, 1.1; Hg, 74.5, 74.3%) may be compared with those calculated for various low molecular weight polymeric salts of mercurated acetic acid.

Calculated for $\text{CH}_3\text{CO}_2(\text{HgCH}_2\text{CO}_2)_n\text{H}$

n	C	H	Hg
4	10.97	1.09	73.31%
5	10.65	1.03	74.12%
6	10.43	0.99	74.67%

These values are in satisfactory agreement with the suggested structure having n between 5 and 6. (Low solubility prevented the determination of molecular weight by the freezing point method.)

This simple mercuration of acetic acid is a very slow reaction (first-order rate constant $1.4 \times 10^{-5} \text{ sec}^{-1}$ at 95°C) unlike the rapid and often complex mercuration of aliphatic compounds that can enolize, e.g. acetone. We are investigating this reaction whose mechanism may be of the extremely rare S_E2 type.