[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

PREPARATION OF SOME ORGANO-MERCURIC NITRATES, AND A METHOD OF ANALYSIS FOR MERCURY APPLICABLE TO DILUTE SOLUTIONS OF SUCH COMPOUNDS

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In continuing the studies on the "electron-sharing ability of organic radicals,"[1] a series of organo-mercuric derivatives has been prepared and carefully purified for the measurements of physical constants which will be reported later. It was found necessary to develop a method of analysis for the determination of the organo-mercuric compounds when present in dilute aqueous solutions. This method depends upon the liberation of mercury from its organic linkage by refluxing with aqueous bromine and later precipitating and weighing the mercury as the sulfide. The method has also been applied to the determination of mercury in the pure organo-mercuric derivative. In the presence of iodides, a double precipitation of the sulfide is necessary.

The type compounds $RHgNO_3$ were prepared by treating the corresponding halides in a suitable solvent with silver nitrate. The butyl- and benzylmercuric nitrates have not been previously reported; the melting points and statements regarding the stability of the methyl- and ethylmercuric nitrates are corrected.

Experimental

Methylmercuric Nitrate.—To a weighed quantity of silver nitrate a slight excess of methylmercuric iodide is added and shaken in ethyl alcohol until the filtrate gives no test for silver ions. The solution is diluted with water, warmed and filtered with suction and evaporated over a water-bath in a current of air. The product is recrystallized twice from water by concentrating the solution until a crystalline mush is obtained and then removing the mother liquor by pressing between filter papers. The crystals are dried *in vacuo*. The product is white, stable in light, strongly deliquescent, and causes painful blisters if applied to the skin. Samples have been kept for two years without becoming discolored.

The melting point, unlike that given in the literature,[2] is 59°, obtained in two independent preparations and constant through successive recrystallizations.

Anal. Calcd. for CH_3HgNO_3: Hg, 72.26. Found: Hg, 72.24, 72.72.

The conductivity in water checks the values reported by Maynard and Howard,[3] though they gave no melting point.

Ethylmercuric nitrate was prepared in the same way as the methyl compound, is less soluble and recrystallizes more easily, giving a better yield. The melting point, not reported by Strecker,[2] who first prepared it, is 87°.

Anal. Calcd. for $C_2H_5HgNO_3$: Hg, 68.79. Found: Hg, 68.85, 68.42.

The solubility in water at 25° is 6.96 g. per liter.

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[1] Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).

[2] Strecker, *Ann.*, **92**, 79 (1854).

[3] Maynard and Howard, *J. Chem. Soc.*, **123**, 960 (1923).

Butylmercuric nitrate was prepared from the bromide and silver nitrate. It was found to be very unstable until carefully recrystallized from ether. It was never obtained entirely colorless, and always decomposed slightly on standing for several months; m. p. 39.5–40°.

Anal. Calcd. for $C_4H_9HgNO_3$: C, 15.02; H, 2.84; N, 4.38. Found: C, 14.80; H, 2.89; N, 4.44.

The solubility in water at 25° is 0.956 g. per liter.

Benzylmercuric nitrate is best prepared by mixing a solution of benzylmercuric chloride in ether with silver nitrate in alcohol. After shaking for an hour, the silver chloride is filtered off and the solvent evaporated at as low a temperature as possible *in vacuo*. In this way, 11.35 g. of benzylmercuric chloride and 5.89 g. of silver nitrate gave 4.95 g. of silver chloride (theoretical, 4.97 g.). The resulting benzylmercuric nitrate was a gray crystalline mass. Recrystallized from ether, it gave large, pure white, rhombic needles; m. p. 90–91° with decomp.

Anal. Calcd. for $C_6H_5CH_2HgNO_3$: Hg, 56.71. Found: Hg, 56.64, 57.05.

The solubility in water at 25° is 0.93 g. per liter. In spite of all care in preparation, the compound slowly decomposes and after several months appears dark, though still crystalline.

Method of Analysis for Mercury in Organo-mercuric Halides and Nitrates.—In analyzing a solid compound, sufficient sample to give 0.25 g. of mercuric sulfide is covered with 100 cc. of water and treated with 5 cc. of bromine. The flask is heated gently and finally boiled to remove the excess of bromine. The last traces of bromine are removed by a few drops of sodium bisulfite solution[4] and the mercury is determined by the usual method. In case the organic radical forms oily bromination products, as occurs with many aromatic mercury derivatives, these may be removed by filtering through a paper filter.

The success of this method of decomposing organic compounds of mercury is indicated by the data in Table I. The method has been found equally successful in analyzing very dilute solutions of these compounds.

The quantitative precipitation of mercury as the sulfide is difficult when iodides are present.[5] This difficulty can be eliminated by applying the double precipitation method used by Scott[6] in separating mercuric sulfide from lead sulfide. In this method the precipitated mercuric sulfide is dissolved in potassium acid sulfide solution and reprecipitated by adding a solution of ammonium nitrate, boiling gently to expel most of the liberated ammonia. This second precipitate is then filtered onto a Gooch crucible and treated in the usual way.

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[4] Contrary to statements in textbooks, sulfur dioxide has not been found to reduce mercury in solution. A slight excess of sodium bisulfite in these acid solutions causes no trouble.

[5] Dunning and Farinholt, This Journal, **51**, 807 (1929), report the necessity of removing iodine. Reinders, *Z. physik. Chem.*, **32**, 498 (1900), considers digestion of the precipitated mercuric sulfide with ammonium chloride solution as sufficient to remove this difficulty.

[6] Scott, "Standard Methods of Chemical Analysis," 4th ed., **1927**, p. 310.

TABLE I

ANALYTICAL DATA

Compound	Sample, g.	HgS found, g.	HgS calcd., g.
C_4H_9HgBr	0.2283	0.1580	0.1574
C_4H_9HgBr	.2551	.1763	.1758
CH_3HgNO_3	.3504	.2935	.2936
CH_3HgNO_3	.2736	.2307	.2292
$C_2H_5HgNO_3$	.1428	.1140	.1139
$C_2H_5HgNO_3$	.1573	.1248	.1255
$C_6H_5CH_2HgNO_3$	.1614	.1060	.1062
$C_6H_5CH_2HgNO_3$	.1693	.1120	.1114
o-$ClC_6H_4CH_2HgBr$[a]	.5000	.2859	.2865
	.5000	.2873	.2865
o-$ClC_6H_4CH_2HgAc$[a]	.3000	.1822	.1813
	.3000	.1817	.1813
(*o*-$ClC_6H_4CH_2)_2Hg$[a]	.5000	.2565	.2576
	.5000	.2581	.2576
o-$ClC_6H_4CH_2HgCl$[b]	.2000	.1282	.1287
	.2000	.1287	.1287
$C_6H_5(CH_2)_2HgBr$[c]	.3574	.2158	.2157
	.4412	.2676	.2662

[a] Analyzed by F. E. Ware. [b] By E. H. C. Fang. [c] By Florence Hooper.

In analyzing 0.025 molal mercuric iodide solutions that were 0.05 molal in potassium iodide, the first precipitate when weighed was found to be approximately 4% too heavy while, when reprecipitated, the weight both with mercuric iodide and with methylmercuric iodide was found to agree within 0.1% with the calculated values.

Summary

1. The purification of methyl- and ethylmercuric nitrates is described and the melting points of these compounds are corrected.

2. Butyl- and benzylmercuric nitrates are described.

3. A rapid method of analysis for mercury in the type compounds RHg-X is described which is satisfactory even in the presence of iodides.

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