[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

METHYL AND ETHYL AMMONIUM-MERCURIC BROMIDES

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Woodward and Alsberg[1] have pointed out the fact that tertiary alkyl amines in 0.1 *N* concentration are readily precipitated as tri-alkyl ammonium-mercuric iodides by the addition of Mayer's reagent (potassium mercuric iodide) and have used this fact as a basis for the separation of tertiary from the primary and secondary amines. As a sequel to this research, Jamieson and Wherry[2] have prepared and described a series of methyl and ethyl ammonium-mercuric iodides, and have further extended the method to the crystallographic identification of the addition products, a procedure now commonly used in this Bureau as a confirmatory analytical step in the separation of amines. Barker and Porter[3] have also contributed to the subject by a description of a number of the higher homologous quaternary ammonium-mercuric iodides.

The present work was undertaken at the suggestion of Dr. Edgar T. Wherry, Crystallographer of the Bureau of Chemistry, in order to complete the series of alkyl ammonium-mercuric halides and to determine the feasibility of using the alkyl substituted bromides in place of the corresponding iodides for the separation and identification of alkyl amines.

Unfortunately, the extreme solubility of all the alkyl ammonium-mercuric bromides in common solvents precludes their use in determining amines. While the iodides usually are formed by addition of 1 molecule of alkyl ammonium bromide to 1 of metal bromide, the bromides tend to combine in the ratio of 1 to 2.

Numerous experimental difficulties were encountered in making the substances described. Preliminary attempts to make them in alcohol-acetone solution from alkyl halide, metal bromide and amine hydrochloride resulted in indefinite mixtures of alkyl ammonium-mercuric chlorides and bromides.

The compounds were finally obtained by the use of the hydrobromide of the amine in alcoholic solution according to the following equation: $R_2NH.HBr + RBr + HgBr_2 \longrightarrow R_3NHBr.HgBr_2 + HBr$. Concentration of the alcoholic solution gave crystals which, in a few cases, were suitable for crystallographic measurement.[4]

Experimental Part

1,2-Dimethylammonium-mercuric Bromide, $(CH_3)_2NH_2Br.2HgBr_2$.—Thirty-five g. of mercuric bromide suspended in 300 cc. of absolute ethyl alcohol was treated with ab-

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[1] Woodward and Alsberg, *J. Biol. Chem.*, **46**, 1 (1921).

[2] Jamieson and Wherry, THIS JOURNAL, **42**, 136 (1920).

[3] Barker and Porter, *J. Chem. Soc.*, **117**, 1303 (1920).

[4] Reserved for publication by Dr. E. T. Wherry.

solute alcoholic solutions containing 9 g. of methyl bromide and methylamine hydrobromide equivalent to 3 g. of the amine. The mercuric bromide dissolved completely. The solvent was evaporated by an air blast until crystals appeared, which were separated and dissolved in a few drops of alcohol. After this solution had stood for about a week crystals again separated. These were removed and dried between filter papers, and obtained as white crystals, soluble in all organic solvents, m. p., 171–172°. The corresponding chloride has been described by Topsoe.[5]

Analyses. Subs., 0.3031: HgS, 0.1667. Subs., 0.3202: 0.1 *N* acid (Kjeldahl), 3.8 cc.[6] Calc. for $C_2H_8NBr_5Hg_2$: Hg, 47.37; N, 1.65. Found: Hg, 47.41; N, 1.66.

1,2-Diethylammonium-mercuric Bromide, $(C_2H_5)_2NH_2Br.2HgBr_2$.—This compound was obtained as was the preceding one, from 40 g. of mercuric bromide, 15 g. of ethyl bromide and an alcoholic solution of ethylamine hydrobromide equivalent to 3 g. of free amine. The product was recrystallized and obtained as heavy, brilliant, white, plate-like crystals; m. p., 158°.

Analyses. Subs., 0.3933: HgS, 0.2101. Subs., 0.3621: 0.1 *N* acid (Kjeldahl), 4.3 cc. Calc. for $C_4H_{12}NBr_5Hg_2$: Hg, 45.85; N, 1.60. Found: Hg, 46.06; N, 1.66.

1,1-Trimethylammonium-mercuric Bromide, $(CH_3)_3NHBr.HgBr_2$.—Repeated attempts were made to obtain this compound in condition for crystallographic measurement. On standing the crystals became red, probably because of surface decomposition. The substance softened at 100° and melted to a clear liquid at 102°.

Analyses. Subs., 0.3475: HgS, 0.1641. Subs., 0.4868: 0.1 *N* acid, 10.35 cc. Calc. for $C_3H_{10}NBr_3Hg$: Hg, 40.82; N, 2.79. Found: Hg, 40.71; N, 2.98.

1,2-Triethylammonium-mercuric Bromide, $(C_2H_5)_3NHBr.2HgBr_2$.—This compound was obtained by the usual procedure. It melts to a yellow oil at 124–125°. The corresponding chloride has been described by Topsoe.[5]

Analyses. Subs., 0.5042: HgS, 0.2816. Calc. for $C_6H_{16}NBr_5Hg_2$: Hg, 47.63. Found: 48.15.

1,1-Tetra-ethylammonium-mercuric Bromide, $(C_2H_5)_4NBr.HgBr_2$.—Alcoholic solutions of the constituents when mixed and concentrated in the usual way give white crystals; m. p., 72°.

Analyses. Subs., 0.2153: AgBr, 0.2118. Subs., 0.4273: HgS, 0.1748. Calc. for $C_8H_{20}NBr_3Hg$: Br, 42.00; Hg, 35.15. Found: Br, 41.88; Hg, 35.28.

Summary

Several methyl and ethyl ammonium-mercuric bromides have been prepared and described.

The alkyl ammonium-mercuric bromides are far more soluble in organic solvents than the corresponding chlorides and iodides.

The presence of chloride ion (as from an amine hydrochloride) decreases the solubility, but gives products containing both chloride and bromide.

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[5] Topsoe, *Oversigt Danske Videnskab. Selskabs. Forh.*, and *Autz. Beidschr. Krystall.*, **8**, 246 (1882).

[6] Mercury was determined by Jamieson's method (Ref. 2) except that the compounds were first decomposed by dil. sulfuric acid, as direct addition of sodium sulfide caused reduction to metallic mercury. For the nitrogen results the author is indebted to Messrs. Ellis and Jenkins of the Nitrogen Laboratory of this Bureau.