extract was acidified with hydrochloric acid and evaporated to dryness. The determinations were then made on the water solutions of these residues without removing the calcium. With the exception of the sodium potassium tartrate, the sodium content of each substance was also determined by the gravimetric magnesium uranyl acetate method as a check on the accuracy of the results.

The above results were considered to be satisfactory evidence of the usefulness of the method. It should be mentioned that these values were obtained in a fraction of the time that would be required to obtain the sodium content of such materials by any of the older methods. This volumetric procedure has certain advantages not possessed even by the gravimetric magnesium uranyl acetate method. There is no need, for example, to free the original solution from insoluble and inert suspended matter when using the volumetric method. The error arising from the determination of sodium in the presence of barium when using a reagent containing considerable sulfate is then eliminated for this same reason. Perhaps the greatest practical advantage of this volumetric procedure lies in the fact that sodium may be determined in the presence of small amounts of phosphates without their preliminary removal before proceeding to the sodium determination.

Summary

A rapid volumetric method for the determination of sodium has been described based upon its precipitation as sodium magnesium uranyl acetate and the titration of the uranium content of the precipitate by means of a standard phosphate solution.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

ADDITION COMPOUNDS OF COPPER HALIDES AND SILVER NITRATE WITH BENZYL SULFIDE[1]

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RECEIVED NOVEMBER 12, 1929 PUBLISHED APRIL 7, 1930

Introduction.—The previously known addition compounds of benzyl sulfide and inorganic metal salts are few in number. Löndahl[2] prepared and analyzed $PtCl_2 \cdot 2(C_7H_7)_2S$, $PtBr_2 \cdot 2(C_7H_7)_2S$, $PtI_2 \cdot 2(C_7H_7)_2S$, $Pt(OH)NO_2 \cdot 2(C_7H_7)_2S$, $Pt(NO_2)_2 \cdot 2(C_7H_7)_2S$ and $PtCl_4 \cdot 2(C_7H_7)_2S$. Herrmann[3] obtained two compounds of the composition $AuCl_2 \cdot (C_7H_7)_2S$ and $AuCl \cdot (C_7H_7)_2S$, and Smith[4] prepared the gold halide compounds $AuBr_2 \cdot (C_7H_7)_2S$,

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[1] Thesis presented to the Graduate School of the University of Washington, in partial fulfilment of the requirements for the degree of Master of Science.

[2] H. Löndahl, *J. prakt. Chem.*, [2] **38**, 521 (1888).

[3] F. Herrmann, *Ber.*, **38**, 2813 (1905).

[4] G. McP. Smith, THIS JOURNAL, **44**, 1769 (1922).

$AuBr\cdot(C_7H_7)_2S$, $AuI_2\cdot(C_7H_7)_2S$ and $AuClI\cdot(C_7H_7)S$. Also, Forster, Cooper and Yarrow[5] obtained from ferric chloride and benzyl sulfide, in ether, a product that proved to be $FeCl_2\cdot(C_7H_7)_2S$.

The purpose of this study was to prepare and study similar compounds with copper and silver halides, silver nitrate and salts of cadmium.

A. Copper Halides.—Since cupric chloride and bromide, and cuprous chloride, bromide and iodide were all found to yield compounds of the type $CuX\cdot 2S(C_7H_7)_2$, it will suffice to describe a general method for their preparation.

The copper halide was mixed with benzyl sulfide[6] in the proportion of $1CuX_2$ to $4(C_7H_7)_2S$, or $1Cu_2X_2$ to $8(C_7H_7)_2S$, and the mixture dissolved in the least possible amount of gently boiling acetone. In the case of the cupric salts, either in acetone or alcohol, the solutions rapidly faded in color with the evolution of a sharp penetrating odor, due to the oxidation of benzyl sulfide to the sulfoxide, by the cupric halide, as previously noted by Herrmann[3] in the case of gold chloride. In the case of a cuprous salt it was necessary to allow the mixture to stand overnight in acetone in order to complete the reaction. In all cases a portion of the product usually separated in the form of lustrous fine white needles, but upon the addition of a little more acetone and warming, these redissolved and the solution could be decanted or filtered from a small amount of sludge. The needles were then crystallized from the acetone solution, usually by partial evaporation and cooling. They were washed with a very little cold acetone and dried between layers of filter paper. Upon analysis they were found to be of the type $CuX\cdot 2S(C_7H_7)_2$.

The $CuCl\cdot 2S(C_7H_7)_2$ melts at 98.3° and decomposes about a degree higher, the $CuBr\cdot 2S(C_7H_7)_2$ melts at 87.5–87.8°, and the $CuI\cdot 2S(C_7H_7)_2$ melts at 63.5°.

Upon redissolving these compounds in either acetone or alcohol, the separation in small quantity of an insoluble white or cream-colored substance was noted, which upon analysis was found to consist of the corresponding cuprous halide. For this reason the addition compounds are best recrystallized from small amounts of the solvent, in the presence of a small quantity of benzyl sulfide. In this way the dissociation may be prevented.

All three of these compounds are insoluble in water. Dissolved in acetone, in the presence of sufficient benzyl sulfide to prevent the precipitation of cuprous halide, they were found to yield precipitates with hydrogen sulfide but only a fraction of the copper could be thus precipitated.

For analysis, the addition compounds were best decomposed by the oxi-

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[5] Forster, Cooper and Yarrow, *J. Chem. Soc.*, **111**, 809 (1917).

[6] The benzyl sulfide was prepared from alcoholic solutions of potassium sulfide and benzyl chloride, according to Märcker [*Ann.*, **136**, 88 (1865)]. The product was purified by recrystallization from alcohol.

dation of a small weighed sample in a porcelain casserole with concentrated sulfuric and nitric acids; but it was found necessary alternately to concentrate the sulfuric acid by evaporation and to add the nitric acid from ten to fifteen times. The resulting cupric sulfate was treated with potassium iodide and the liberated iodine titrated with standard sodium thiosulfate solution.

TABLE I

ANALYTICAL DATA

No.	From	Sample, g.	$Na_2S_2O_3$ soln., g.[a]	Cu in sample, g.	Calcd. % of copper in
1	Cupric chloride	0.2130	4.15	12.11	$CuCl \cdot 2(C_7H_7)_2S$
1	Cuprous chloride	.2907	5.60	11.97	12.05
2	Cupric bromide	.2563	4.58	11.11	$CuBr \cdot 2(C_7H_7)_2S$
2	Cuprous bromide	.3358	5.97	11.05	11.11
3	Cuprous iodide 1	.2108	3.44	10.14	$CuI \cdot 2(C_7H_7)_2S$
3	Cuprous iodide 2	.1315	2.21	10.44	10.21

[a] Copper equivalent of $Na_2S_2O_3$ solution, 0.006216 g. per cc.

B. **Silver Nitrate.**—In attempting to prepare addition compounds of silver halides with benzyl sulfide in a manner similar to that used by Sheppard and Hudson[7] with silver halides and thiosinamine, mixtures of benzyl sulfide and potassium chloride, bromide and iodide, respectively, were put in alcohol and an alcoholic solution of silver nitrate added to each. The proportions were $1AgNO_3$ to $1KX + 4(C_7H_7)_2S$. The mixtures were allowed to stand overnight and were found to have yielded a compact, pasty white solid on the bottom of the beaker. The precipitates so formed were washed by decantation with alcohol to dissolve any excess benzyl sulfide and then with water to remove any excess potassium salt. On drying between filter papers, each precipitate constituted a white powder melting at 105.5°, showing that the product from each solution was the same—evidently from the silver nitrate and the benzyl sulfide present in each case. For this reason silver nitrate and benzyl sulfide were then mixed in the proportions of $1AgNO_3$ to $4(C_7H_7)_2S$ and dissolved in alcohol. After standing overnight, a white pasty solid was present. This was washed with small amounts of alcohol and dried between filter papers, yielding a white powder which also melted at 105.5°. This confirmed the conclusion previously drawn that the reaction was between benzyl sulfide and the silver nitrate. This substance could not be recrystallized from alcohol, because brown metallic silver separated as the solid went into solution. It was therefore, quickly washed with small amounts of cold alcohol and dried between filter papers.

The addition compound of silver nitrate and benzyl sulfide was analyzed by simply igniting the sample in porcelain over a Bunsen flame and weighing the residue of silver. A very small flame was used at first, in order to

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[7] Sheppard and Hudson, THIS JOURNAL, **49,** 1814 (1927).

prevent spattering, but after the sample had thoroughly charred and was no longer liquid, the flame was turned on full with plenty of air to accomplish oxidation.

Anal. Subs., 0.1306: Ag, 0.0237. Calcd. for $AgNO_3 \cdot 2(C_7H_7)_2S$: Ag, 18.28. Found: Ag, 18.15.

C. Other Attempts.—Besides the unsuccessful attempts to prepare addition compounds of benzyl sulfide and silver halides, referred to in the above, attempts were also made to prepare them directly from the silver halides and benzyl sulfide, in the presence of alcohol. The results were negative.

Each of the cadmium halides was also mixed with benzyl sulfide in varying proportions and dissolved in alcohol and in acetone, but in no instance was a new product obtained.

Summary

1. The following new addition compounds of cuprous halides and silver nitrate with benzyl sulfide have been prepared and described: $CuCl \cdot 2(C_7H_7)_2S$, $CuBr \cdot 2(C_7H_7)_2S$, $CuI \cdot 2(C_7H_7)_2S$ and $AgNO_3 \cdot 2(C_7H_7)_2S$.

2. The addition compounds of cuprous halides with benzyl sulfide in alcohol or acetone solution have been shown to be in equilibrium with benzyl sulfide and the cuprous halide as indicated by the equation

$$CuX \cdot 2(C_7H_7)_2S, \rightleftharpoons CuX + 2(C_7H_7)_2S$$

3. Similar attempts to prepare addition compounds of benzyl sulfide with silver halides and with cadmium halides met with failure.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. IX. THE ELECTRIC MOMENTS OF CERTAIN SUBSTITUTED PHENOLS AND THEIR RELATION TO THE STEREOCHEMISTRY OF THE OXYGEN ATOM

BY JOHN WARREN WILLIAMS AND JOHN M. FOGELBERG

RECEIVED NOVEMBER 14, 1929 PUBLISHED APRIL 7, 1930

Introduction

Studies of electric moment data are beginning to give considerable information concerning the structure of molecules. It has, for example, been quite definitely established that the four valences of the carbon atom are directed toward the corners of a regular tetrahedron.[1,2] The structures of the simple polar molecules, water and ammonia, as deduced from infra-red

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[1] (a) Williams, *Physik. Z.*, **29**, 683 (1928); (b) *Z. physik. Chem.*, **138A**, 75 (1928); (c) *Chemical Reviews*, **6**, 589 (1929).

[2] Höjendahl, "Studies of Dipole Moment," Dissertation, Copenhagen, **1928**.