more rapid. Dilution with water tended to effect a partial reversal, but this procedure could not be repeated as in the case of nitric acid. When the acid used was 6 molar sulfuric, precipitation resulted, followed by rapid conversion to a clear crystalloidal solution on addition of more acid and no reversibility with water could be effected.

Summary

The reactivity of an organic anion with basic thorium chloride hydrosols depends not only on the number of combining groups present, but on their relative positions, and the closer the combining groups are to each other, the more active is the anion.

Hydroxy organic anions reverse the charge of basic thorium chloride (cationic) micelles producing aniono thoreate micelles. Peptization of hydrous thorium dioxide by the potassium salts of these anions also results in the production of hydrosols containing negatively charged micelles.

Concentrated nitric acid reverses the charge of basic thorium chloride micelles producing short-lived nitrato thoreate micelles.

The order of deolation of basic thorium chloride sols and subsequent formation of the crystalloidal state with concentrated inorganic acids has been found to be sulfuric > hydrochloric > nitric.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF GEORGIA]

A New Organic Reagent for Cadmium

BY ALFRED W. SCOTT AND ELEANOR G. ADAMS

Introduction

The lack of a specific easily recognizable test for cadmium ion in the presence of cupric ion has given rise to many difficulties, especially in elementary classes in qualitative analysis. Copper is usually converted into the cyanide complex or precipitated as the sulfide. The cyanide separation is dangerous for inexperienced students, and the cadmium sulfide precipitated by the second method is often masked by traces of impurities. This investigation was undertaken in an attempt to prepare a new organic reagent which would be specific for cadmium ion, characterized by a colored precipitate, sensitive to fairly low concentrations of the metallic ion and not too easily affected by interfering ions.

Several new organic compounds containing sulfur were prepared by combining organic radicals which are present in reagents that have been found useful in detecting cadmium ions. These were tested as analytical reagents with nitrate solutions of the cations met in qualitative analysis. The most effective precipitant prepared was 1-(2-quinolyl)-4-allyl thiosemicarbazide. A saturated solution of this reagent in 50% alcohol, in the presence of potassium iodide, gave a yellow precipitate with cadmium ion as dilute as one part in a million. Cadmium was detected in the presence of copper (in the absence of ammonia and sulfate) by the addition of potassium iodide solution, thiosemicarbazide solution, and ammonium hydroxide; cadmium gave a yellow precipitate, while copper gave a blue solution.

Experimental

Materials.—Allyl isothiocyanate, 2-aminoresorcinol hydrochloride (practical), 2-amino-4-nitrophenol, and 2-quinolylhydrazine, all were from Eastman Kodak Company.

$C_3H_5NHCSNHC_6H_3(OH)_2$, **N-Allyl-N′-2,6-dihydroxyphenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-aminoresorcinol hydrochloride in 95% alcohol. The brown needles from alcohol–ether decomposed at 230°. This compound is too insoluble in water for use as a precipitant.

$C_3H_5NHCSNHC_6H_3(OH)(NO_2)$, **N-Allyl-N′-2-hydroxy-5-nitrophenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-amino-4-nitrophenol in ether. The orange-red needles, melting at 122°, are soluble in alcohol, and somewhat soluble in water and in chloroform. The saturated water solution of this reagent added to nitrate solutions of the cations gave precipitates only with cadmium, copper, iron and nickel, the first three being yellow and the last white. The use of a 1% solution of the reagent in alcohol makes the precipitation of cadmium more complete and more sensitive, but care must be taken that excess reagent itself does not precipitate because of its slight solubility in water.

$C_3H_5NHCSNHNHC_9H_6N$, **1-(2-Quinolyl)-4-allyl-thiosemicarbazide,** was prepared from 10 cc. of allyl isothiocyanate and 16 g. of crystalline 2-quinolylhydrazine in ether; yield 20 g. Slow recrystallization from ether gave colorless crystals, melting at 158°, fairly soluble in ether alcohol, and benzene, slightly soluble in cold water. The molecular weight of the thiosemicarbazide was estimated by the Rast camphor method to be approximately 258. Element analyses proved the presence of C, H, N and S.

Anal. Calcd. for $C_{13}H_{14}N_4S$: C, 60.47; H, 5.43; N, 21.72. Found: C, 59.69; H, 5.41; N, 21.77.

The saturated solution of this reagent in 50% ethyl alcohol (0.05 g. per 100 cc.) added to normal nitrate solutions of the cations gave yellow precipitates with cadmium, zinc, and mercurous mercury, and brown precipitates with copper, nickel, cobalt, and silver. The presence of various anions (chloride, bromide, iodide, sulfate, cyanate, and thiocyanate) was found to affect the completeness of precipitation and the appearance of the precipitate to some extent. The most satisfactory test was secured in the presence of iodide ions, when a bright greenish-yellow precipitate was formed even with traces of cadmium ions. This precipitate contained cadmium, nitrogen, sulfur, potassium and iodine.

The sensitivity of the cadmium thiosemicarbazide iodide precipitation was tested by adding 1 cc. of 50% aqueous alcohol (saturated with the thiosemicarbazide and with potassium iodide) to 10 cc. each of solutions containing respectively, 1, 0.05 and 0.01 mg. of cadmium ion.

$Cd(NO_3)_2 \cdot 4H_2O$, g./l.	Cd^{++}	Effect
0.278	1/10,000	Filterable precipitate
.0139	1/200,000	Filterable precipitate
.00278	1/1,000,000	Opalescence; precipitate after two minutes

The detection of cadmium ions in the presence of copper ions was accomplished by a modification of the above procedure, in the absence of the ions of zinc, nickel and cobalt. Interfering ammonia and sulfate, if present, were removed by boiling off ammonia and precipitating the sulfate with barium chloride. To this solution was added saturated potassium iodide solution and brown copper iodide precipitated. Without filtering, the addition of saturated thiosemicarbazide solution (50% alcohol) precipitated the yellow cadmium thiosemicarbazide iodide complex. Upon addition of ammonium hydroxide the copper salt dissolved but not the cadmium complex. Thus a blue solution indicated copper, while a yellow precipitate indicated cadimum.

Summary

1. N-Allyl-N′-2,6-dihydroxyphenyl thiourea and N-allyl-N-2-hydroxy-5-nitrophenyl thiourea were prepared and tested as analytical reagents.

2. 1-(2-Quinolyl)-4-allyl thiosemicarbazide was prepared. It is a sensitive precipitant for the cadmium ion, and a good qualitative reagent for cadmium in the presence of copper.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Activity Coefficients of Sulfuric Acid in Anhydrous Ethyl Alcohol from Electromotive Force Data

BY A. W. SCHOLL,[1] A. WITT HUTCHISON AND G. C. CHANDLEE

In continuation of the work in this Laboratory on the properties of non-aqueous solutions it was thought that a study of the activity coefficients of sulfuric acid in ethyl alcohol solutions would be of interest. Data were obtained by the electromotive force method using the cell H_2, H_2SO_4, Hg_2SO_4s, Hg. Activity coefficients were calculated from these data by the use of the Debye–Hückel first approximation and also by the use of the extended equation of Gronwall, La Mer and Sandved.

Experimental

All electromotive force measurements were made with a Leeds and Northrup type K potentiometer by the null method. A Weston standard cell was used as a reference. It was checked from time to time during the course of the experiments against several other cells of the same type recently calibrated at the Bureau of Standards. A type R galvanometer was used as an indicating instrument. All lead wires and the standard cell were shielded.

The thermostat was maintained at a temperature of 25 ± 0.01°. The cells were placed in a copper tank, filled with oil, suspended in the thermostat water.

The cells were of the H type and were made by connecting two Pyrex test-tubes by means of a short piece of Pyrex tubing. A piece of 7-mm. tubing was sealed to the bottom of each test-tube and bent so that it became parallel to the tube. One tube then became the mercury–mercurous sulfate half-cell, and connection was made to it by means of a platinum wire dipping into the mercury. The test-tubes were fitted with well ground, gas tight, glass stoppers. Through the one stopper two tubes were sealed into the ends of which platinum wires were sealed to serve as the platinum electrodes. Hydrogen was bubbled in through the bottom of the hydrogen half cell and escaped from the top through an alcohol trap. It was saturated with alcohol by bubbling it through a wash bottle, immersed in the thermostat, containing the solution being measured.

The more concentrated solutions were prepared by the addition of sulfuric acid from a weight pipet to a weighed

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[1] From a thesis presented by A. W. Scholl in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.