Some Analytical Properties of 8-Hydroxyquinaldine

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SINCE the introduction of 8-hydroxyquinaldine as a precipitating reagent for metals (δ), only fragmentary additional data on its analytical applications have appeared (1, 3, 6, 7). Its major differences from the much better known 8-quinolinol are its failure to precipitate aluminum under any conditions so far investigated and the slightly higher pH necessary for the quantitative precipitation of other ions. Additional significant differences, particularly in reactions of analytical interest such as oxidation and bromination, would be anticipated from the aldehyde to ketone relationship (in the ammonia compounds) of 8quinolinol and 8-hydroxyquinaldine, since aldehydes are generally somewhat more reactive than ketones. The bromination of 8-hydroxyquinaldine and its reactions with some of the trivalent elements and heavy metals were therefore studied.

The limited availability of the reagent made it desirable to develop a more convenient synthesis and also methods of determining it and similar derivatives of 8-quinolinol.

PREPARATION OF REAGENT

A previously published procedure for making 8-hydroxyquinaldine (5) by the Doebner-Miller reaction of o-aminophenol with crotonaldehyde gives a 30 to 40% yield by a process requiring at least 2 days of work. [A better yield has been reported (4), but the product was isolated as the o-nitrophenol salt which cannot be used in analysis or conveniently converted to the free base.]

The following modification of the Doebner-Miller reaction gives a 35% yield of a satisfactorily pure product in about 4 hours' working time.

8-Hydroxyquinaldine Preparation. In a three-necked flask provided with condenser, stirrer, and dropping funnel are placed 27.5 grams (0.25 mole) of o-aminophenol, 100 ml. of concentrated hydrochloric acid, and 5 grams of arsenic pentoxide. The mixture is heated in an oil bath to an external temperature of 120° C. and 20 grams (0.29 mole) of crotonaldehyde are added rapidly through the dropping funnel. A reaction occurs which is finished after about 5 minutes. The mixture is steam distilled to remove volatile impurities, and then neutralized, while cooling, with a concentrated sodium hydroxide solution. On steam distillation 8-hydroxyquinaldine comes over. Two immediate recrystallizations from 70% ethyl alcohol give a product with a tan color but of high purity. Yield is 14 grams (35%).

In the course of about 25 runs of this reaction it was noted that the theoretical amount of arsenic pentoxide as an oxidizing agent caused considerable decomposition, but that a small amount materially improved the color of the final product. *o*-Nitrophenol as an oxidizing agent was not effective in this method. Immediate recrystallization is recommended, as the impure compound becomes very dark colored on standing.

A completely colorless product for use in the rest of this investigation was obtained by vacuum distillation (boiling point 145° C. at 15 mm.) before recrystallization. Melting point was 73.5-74° C.; n_D^{79} 1.5960.

DETERMINATION OF 8-HYDROXYQUINALDINE

Quantitative dibromination of 8-hydroxyquinaldine was readily obtained (Table I), whether the determination was performed by the addition of excess bromate-bromide solution with back-titration of the iodine liberated from potassium iodide or by direct potentiometric titration with standard bromate-bromide.

Application of this method to aryl-substituted 8-quinolinols gave low results, perhaps because of the electronegativity of these aryl substituents.

Attempts to determine 8-hydroxyquinaldine by titration with

iodine did not succeed because of incomplete and reversible iodination.

Bromometric Analysis. An excess of 1 to 2 ml. of 0.1 N potassium bromate in potassium bromide solution was added to the compound dissolved in 50 ml. of 6 N hydrochloric acid. The flask was stoppered and allowed to stand 5 minutes before adding 0.5 gram of potassium iodide. After 5 minutes the liberated iodine was titrated with 0.1 N thiosulfate using starch as indicator.

Potentiometrically the titration was performed by adding the standard bromate-bromide solution to the compound dissolved in hydrochloric acid until the potential break (about 120 mv.) was obtained. Platinum-calomel electrodes with a Beckman Model H-2 pH meter were used.

With most of the compounds analyzed the bromination product was sufficiently insoluble to precipitate during the titration, but this caused no interference.

| Table I. | Quantitative Bromination | of | Substituted | | | |
|---------------|--------------------------|----|-------------|--|--|--|
| 8-Quinolinols | | | | | | |

| Substituent | Wt. Taken, Gram | Wt. Found, Gram |
|----------------------------------|--------------------|------------------------|
| 2-CH: | 0 1280 | 0 1280 |
| - 0110 | 0.1071 | 0.1070 |
| | 0.0300 | 0,0499,0,0497,0,0496 |
| | 0.0250 | 0.0246, 0.0247 |
| | 0.0250^{a} | 0.0246 |
| | 0.0100^{a} | 0.0096, 0.0096, 0.0097 |
| | 0.0050^{a} | 0.0048 |
| 3-CH2 | 0.0693 | 0.0691 |
| | 0.0373 | 0.0373 |
| $2,3-(CH_3)_2$ | 0.0519 | 0.0523 |
| | 0.0439 | 0.0433 |
| $2-C_{2}H_{5}-3-CH_{3}$ | 0.1044 | 0.1048 |
| 2-Phenyl | 0.1086 | 0.1049 |
| 2-m-Tolyl | 0.1151 | 0.1068 |
| 2-p-Tolyl | 0.1238 | 0.1198 |
| ^a By potentiometric t | itration. | |

QUALITATIVE TESTS

The solubility of metals and their salts in molten 8-hydroxyquinaldine with the formation of the characteristic chelate colors and fluorescences was noted. At 100° C. compounds of the following ions (usually the chlorides, acetates, or nitrates were used) dissolved: magnesium, zinc, cupric, cobalt, nickel, lead, stannous, cadmium, zirconyl, uranyl, ferric, aluminum, and thorium. The solutions of zinc, cadmium, magnesium, and aluminum had a yellow fluorescence in ultraviolet light.

Since the alkali metals give fluorescent salts with 8-hydroxyquinaldine which cannot be chelates, the fluorescence obtained from dissolving aluminum compounds in molten 8-hydroxyquinaldine need not be regarded as indication of chelate formation.

Metallic zinc, copper, and aluminum could also be dissolved in molten 8-hydroxyquinaldine.

QUANTITATIVE TESTS

The quantitative behavior of 8-hydroxyquinaldine with magnesium, zinc, cupric, cobalt, nickel, manganese, ferric, and aluminum has been investigated (5, θ). As aluminum was the only one of the ions not precipitated, a study of other Group III and trivalent elements was made. Yttrium, lanthanum, gallium, indium, and scandium compounds all formed yellow fluorescent precipitated (Table II). Yttrium was apparently only partially precipitated and a similar difficulty has been noted for gallium elsewhere (3).

The scandium chelate carries a molecule of reagent of crystallization when dried at 105° C., a phenomenon recently noted

| Table | 8-Hydrox | yquinaldine | with |
|---|---|--|-----------------------|
| Ion | Wt. Taken, Gram | Wt. Found, Gram | Method of Analysis |
| In + + + | 0.0349 | $0.0352, 0.0354 \\ 0.0351$ | A B |
| Sc + + + | 0.0169 | $0.0171 \\ 0.0172, 0.0173$ | Ĉ D |
| Th + + + + | $0.0229 \\ 0.0402$ | 0.0230, 0.0232 0.0404 ± 0.0003^{a} | A A |
| UO2 + + | $\begin{array}{c} 0.0710 \\ 0.0562 \end{array}$ | 0.0711, 0.0711 0.0558, 0.0559 | E |
| Pb + + | $\begin{array}{c} 0.1125 \\ 0.0183 \\ 0.0244 \\ 0.0146 \\ 0.0122 \end{array}$ | 0.1124 0.0184 0.0245 0.0148 0.0124 | E A A A A |
| A. Dried to an B. Bromometry C. Ignited to c D. Weighed as E. Weighed as ^a 17 trials. | hydrous chelate a ic titration. xide. Sc(C10H8NO)a.C1 UO2(C10H8NO)a.C | at 105° C. ₀H₂NO. C10H₂NO. | |

Table II. Precipitation of Metals with

with the corresponding 8-quinolinol chelate (8). Other ions said to form chelates with 8-quinolinol containing reagent of crystallization are thorium and uranyl (9); with 8-hydroxyquinaldine uranyl ion apparently formed UO₂(C₁₀H₈NO)₂.C₁₀H₉NO, but thorium gave only a yellow precipitate of Th(C₁₀H₈NO)₄.

Bervllium and zirconyl ions were only partially precipitated (whether as basic salts containing 8-hydroxyquinaldine or as chelates was not determined) and unsatisfactory results were also obtained from mercuric compounds because they mercurated the quinoline ring instead of forming chelates.

In all the precipitations the techniques recommended for 8quinolinol were used (9). The minimum pH necessary for quantitative precipitations with 8-hydroxyquinaldine were generally slightly higher (0.5 to 2 units), the chelates were less satisfactory in filtering characteristics, and greater difficulty from coprecipitation of excess reagent was experienced.

Experimental Procedures. The solutions used were standard-ized against 8-quinolinol by the same methods used in the determinations with 8-hydroxyquinaldine.

INDIUM. Precipitation was performed from an acetate buffer

as described by Geilmann and Wrigge (2) for 8-quinolinol. URANYL. The reagent in acetic acid was added to a hot solu-tion of uranyl acetate. The pH was raised to 8 by adding dilute ammonium hydroxide and the precipitate digested for an hour at 70° C. before filtration. SCANDIUM. The same procedure recommended for 8-quin-

olinol (8) served.

THORIUM. The reagent in acetic acid solution was added in slight excess to a solution of thorium nitrate. Precipitation was obtained from the hot solution by adding ammonium acetate and then ammonium hydroxide until a slight excess of ammonia was detected by odor. The precipitate was digested at 70° C. for 1 hour, filtered, and washed with hot dilute amonia. LEAD. The procedure recommended for 8-quinolinol served

(9).

ACKNOWLEDGMENT

This work was supported by a grant from the Research Corp.

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RECEIVED for review November 23, 1951. Accepted January 21, 1952

Attainment of High Resolution in X-Ray Fluorescent Analysis

Simplification of X-Ray Fluorescent Analysis Procedures

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IN ANY quantitative analytical procedure employing x-ray fluorescent radiation as a measure of composition, the method is simplified if the intensity of characteristic radiation measured is resolved radiation emitted by only the element in question.

While the characteristic x-ray spectrum is much simpler than the optical spectrum, there are instances of importance where characteristic radiation from more than one element will have very similar wave lengths. This condition complicates the use of x-ray fluorescent analysis for these elements.

Birks and Brooks(2), who have encountered this difficulty, have suggested three methods of overcoming it. In their investigation of hafnium-zirconium and tantalum-niobium systems, they used (a) fine collimation to resolve the hafnium and zirconium lines, (b) comparison of the integrated intensity of an unresolved tantalum-niobium doublet with the integrated intensity of a resolved niobium line, and (c) lowering the x-ray tube voltage to excite the hafnium L spectrum without exciting the zirconium K spectrum.

The method they used to correct for lack of resolution of secondorder NbK α and TaL α radiation involved several intensity measurements at slightly different angles to establish the shape of the curue, followed by calculation of the area beneath the curve.

X-ray fluorescent analysis becomes a much simpler and more attractive method if the intensity can be measured at only one point.

Experimental work on molybdenum, niobium, tantalum, and tungsten mixtures has been done in this laboratory using a General Electric XRD-3 Fluorescent Analyzer. The technique used involved characteristic line intensity measurements at only the angle of maximum intensity. It was found that the $TaL\alpha_1$ and $WL\alpha_i$ lines were resolved from any second-order NbK α radiation.

The wave lengths of the tantalum and tungsten $L\alpha_1$ lines are 1.51885 and 1.4733 A., respectively. The wave lengths of the



Figure 1. Recording of Second-Order Niobium Ka Radiation