ZINC AND MAGNESIUM COBALTINITRITES FOR QUALITATIVE DETECTION OF POTASSIUM

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The methods for qualitative detection of sodium and potassium ions are not too satisfactory, owing to the solubility of the salts in question. The most delicate tests for these ions seem to be the use of sodium hexanitritocobaltate for potassium and of zinc or magnesium uranyl acetate for sodium[1]. If these reagents are used, however, a separate portion must be used for each test because of the introduction of sodium ions in testing for potassium. Furthermore, if potassium is present, it must be at least partially removed before testing for sodium on account of the similar solubilities of the potassium and sodium salts formed with either zinc or magnesium uranyl acetate.

It seemed desirable to develop a reagent for the detection of potassium which would retain the sensitivity of sodium cobaltinitrite, but which would not introduce the sodium ion and would leave the solution in the best form for the detection of the sodium ion. The use of zinc or magnesium uranyl acetates for the detection of sodium suggested the use of zinc or magnesium cobaltinitrite.

Previous work indicated that such compounds could be formed, because unstable solutions containing cobaltinitrite are formed when the gas from the action of concentrated nitric acid on metallic copper is passed through a mixture of the acetates of cobalt and either zinc or magnesium[2]. When such solutions were treated with the gas formed by the action of dilute sulfuric acid on sodium nitrite, the amount of cobaltinitrite varied greatly and for no apparent reason[3].

EXPERIMENTAL

A solution was made up which was one molar in zinc acetate and two thirds molar in cobalt acetate. Because of the lack of uniformity of the gas resulting from the reduction of nitric acid by copper, nitrogen dioxide was prepared by the action of nitric acid on sodium nitrite. The gas thus formed was passed through the mixture of acetates. Calculations indicated that 0.47 mols or 32.43 grams of sodium nitrite would be required to form enough nitrogen dioxide to convert the cobalt in 100 milliliters of this solution entirely to cobaltinitrite.

One hundred milliliters of the mixed acetates was placed in a gas wash bottle, over glass beads, and the nitrogen dioxide was then bubbled through the solution. Different amounts of sodium nitrite were used, varying from 0.47 mols to four times that amount. As the amount of sodium nitrite used was increased, the amount of cobaltinitrite formed increased fairly regularly until 3.75 times the calculated amount was used, and then fell off sharply with four times the amount of nitrite. In all cases, much of the gas seemed to pass through the solution without being absorbed. In all cases, twenty milliliters of the resulting solution was diluted to 100 milliliters, precipitated by the addition of an excess of potassium chloride solution, filtered, washed and dried at 110° C. If the precipitate was filtered off within an hour of precipitation, more precipitate formed in the filtrate. When several samples were precipitated at the same time and allowed to stand for differing lengths of time before filtration, the precipitate usually, but not always, increased very distinctly in amount with length of time of standing in the mother

[1] Kolthoff, I. M., *Z anal Chem.*, 70, 397 (1927).
[2] Adams, Hall and Bailey, Ind. Eng. Chem., Anal. Ed., 7, 310 (1935).
[3] Lippincott, Ann, Unpublished work, 1945, MacMurray College.

TABLE 1

Wt. $NaNO_2$	Mols $NaNO_2$	Weight of potassium precipitate
32.43	0.47	0.0693, 0.0860
48.64	(1.5) (0.47)	0.4151, 0.4117
81.08	(2.5) (0.47)	1.0482, 1.2093, 1.3241, 1.3239
113.50	(3.5) (0.47)	1.1035, 0.9857, 0.9813, 1.2268 1.3094, 1.2795, 1.5782
121.60	(3.75) (0.47)	1.2331, 1.4630, 1.4409, 1.5727
129.72	(4.0) (0.47)	0.1570, 0.1580

liquid, up to sixty hours. In a number of instances the precipitate became dark on heating, and in one case, nitrogen dioxide was observed coming from the drying precipitate. If in the formation of the complex, all the cobalt had been changed to cobaltinitrite, the precipitates from these twenty milliliter portions should have weighed 6.03 grams, assuming the precipitate to be $K_3Co(NO_2)_6$. The largest amount actually secured was 1.58 grams. The results are summarized in Table I.

For the determination of the composition of the precipitate formed with potassium chloride, one hundred milliliters of the mixed acetates of cobalt and zinc was treated with the gas made by adding nitric acid to 121.6 grams of sodium nitrite. Excess of potassium chloride solution was then added and the mixture allowed to stand over night. It was then filtered, washed, and dried at 110° C. Samples were analyzed electrolytically for cobalt[4], showing 13.94 percent and for potassium as the perchlorate[5], showing 23.44 percent, an atomic ratio of 2.53. Qualitative tests for zinc were negative. The percentages of cobalt and potassium in $K_3Co\ (NO_2)_6$ are 13.01 and 25.93 respectively.

In the same way, a cobaltinitrite was prepared by the action of nitrogen dioxide on a mixture of cobalt and magnesium acetates. This was precipitated with potassium chloride and the resulting precipitate was analyzed as above for both potassium and cobalt. The precipitate was 23.26% potassium and 13.39% cobalt. Qualitative tests for magnesium were negative. The atomic ratio found was 2.62.

To compare the stability of the two solutions, 200 milliliters of solutions which were two thirds molar in cobalt acetate and molar in either zinc or magnesium acetates were treated with the gas secured from 170 grams of sodium nitrite. This proportion of nitrite was somewhat less than that previously found to yield the greatest amount of complex, as it was desired to avoid the effect of decomposition caused by too great an amount of gas. The complex was formed in both cases; almost twice as much was formed in the magnesium solution as in the zinc solution, but still less than a third of what would have resulted had all the cobalt been converted to the nitrite complex. The solutions were kept in bottles covered with watch glasses to allow NO_2 to escape, and analyzed daily. Although the magnesium solution was more concentrated at first, neither showed any sign of cobaltinitrite after five days although both gave slight but distinct precipitates with potassium chloride after four days. A solution of sodium cobaltinitrite was found under the same conditions to give an immediate precipitate with potassium chloride after two weeks.

CONCLUSIONS

1. Cobaltinitrite is formed by passing oxides of nitrogen through a mixture of acetates of cobalt and either zinc or magnesium. The most uniform results are obtained when the gas is secured from the action of nitric acid on sodium nitrite. A sufficiently great amount of gas results in a decrease in the yield.

[4] Scott, *Standard Methods of Chemical Analysis*, N. H. Furman, editor, p. 312, Fifth edition, D. Van Nostrand Co.
[5] *Idem*, p. 870.

2. Analysis of the potassium precipitate does not conform closely to what seem to be the most likely compositions, but $K_3Co(NO_2)_6$ seems the most probable.

3. The magnesium salt seems to be more readily formed than the zinc salt but is not appreciably more stable.

4. Solutions of cobaltinitrite made by passing oxides of nitrogen through mixtures of cobalt actetate with either zinc or magnesium acetates are distinctly less stable than that made by adding acetic acid to a mixture of sodium nitrite and cobalt acetate.