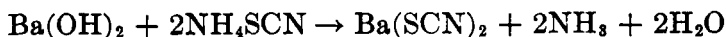


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5. BARIUM THIOCYANATE



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Barium thiocyanate was first prepared by Berzelius, who roasted barium hexacyanoferrate(II) with sulfur.¹ It has also been obtained by reaction of barium carbonate with a solution of thiocyanic acid,² by conversion of ammonium thiocyanate through the copper(I) thiocyanate by consecutive reactions with copper(I) chloride and barium hydroxide,³ by treatment of Prussian blue with barium sulfide,⁴ and by reaction of barium sulfide, sulfur, and cyanamide.⁵ The procedure described below makes possible the preparation of barium thiocyanate in any desired quantity from barium hydroxide and ammonium thiocyanate as starting materials. The 3-hydrate,⁶⁻⁸ which is obtained first, is dehydrated readily to yield anhydrous barium thiocyanate.

Procedure

Seventy-six grams (1 mol) of ammonium thiocyanate and 158 g. (0.5 mol) of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are placed in a 500-ml. round-bottomed flask and shaken until the mass liquefies. The solution is boiled until ammonia is no longer evolved, the evaporated water being replaced at intervals. The mixture must now be alkaline to phenolphthalein. If necessary, more barium hydroxide is added, and the process repeated. At this point the solution usually contains a precipitate, which may range from white to dark gray in color. The solution is filtered through a sintered-glass Büchner funnel; if such a funnel is not available, the filter

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paper must be precoated with just enough kieselguhr, Celite 521, or Filter-Cel, to form a continuous mat.*

To the filtrate is added 6 *N* sulfuric acid until the solution is only faintly alkaline to litmus (just colorless to phenolphthalein); the remainder of the barium hydroxide is neutralized with carbon dioxide. The solution is heated to boiling to remove any barium hydrogen carbonate that may have formed. It is preferable, but not absolutely necessary, to digest the mixture overnight on a steam bath. The solution is filtered through paper precoated as before, the filtrate is heated to boiling, 0.5 g. of activated charcoal is added, and the solution is filtered again.

The final filtrate is concentrated until the boiling point rises to 125°, but no higher. The solution is allowed to cool to room temperature and is then placed in an ice bath. The crystals of the 3-hydrate that form are collected on a Büchner funnel.† The product is dried in air. Yield, approximately 115 g. (75 per cent). *Anal.* Calcd. for $\text{Ba}(\text{SCN})_2$: SCN, 45.76. Found: SCN, 46.04.

Properties

Barium thiocyanate is a white solid that is very soluble in water but has a very steep temperature-solubility gradient. This solid is also soluble in acetone, methanol, ethanol, methylamine and ethylamine, moderately soluble in isopropylamine and dimethylamine, but insoluble in trimethylamine.⁶ The anhydrous salt is very hygroscopic. Crystallization from water yields the 3-hydrate as well-formed, needle-shaped crystals. Double salts are formed with the thiocyanates of the alkali and other alkaline earth metals.⁸

* If larger quantities than those specified are to be prepared, a glass filter cloth is very convenient.

† The filtrate may be concentrated further to effect some increase in yield. (If larger quantities are to be prepared, the recovery process can be repeated several times and the yield increased accordingly. For preparations on the scale described here, however, more than one such repetition is not worth the time involved.)

The reaction mixture used in this procedure may find application in freezing mixtures because of its high negative heat of reaction. Barium thiocyanate has been used in the dye and color printing industries and as a dispersing agent for cellulose. It can be converted readily by treatment with a dilute sulfuric acid to give dilute solutions of thiocyanic acid, or into the thiocyanates of other metals by precipitation of barium sulfate.

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