[CONTRIBUTION FROM THE GOVERNMENT COLLEGE CHEMICAL LABORATORIES]

ACTION OF SULFURIC ACID ON THIOCYANATES

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Thiocyanic acid can be prepared by the action of dilute sulfuric acid on alkali thiocyanates, with subsequent distillation under reduced pressure, collecting the distillate in a receiver kept in a freezing mixture.[1] At ordinary room temperature HSCN polymerizes to $(HCNS)_2$ and $(HCNS)_3$. With dilute sulfuric acid persulfocyanic acid, $H_2C_2N_2S_3$, is obtained. Decomposition with sulfuric acid is represented as

$$\text{(Dilute sulfuric acid) } 2HSCN + 2H_2O \longrightarrow 2NH_3 + CS_2 + CO_2$$
$$\text{(Strong sulfuric acid) } HCNS + H_2O \longrightarrow COS + NH_3$$

Persulfate and other oxidizing agents, according to Pawlewsky[2] and Goppelsroeder,[3] with thiocyanates yield $C_3N_3S_3H$. Concentrated sulfuric acid[1c] acts vigorously with solid thiocyanates and evolves acrid vapors consisting of formic acid, sulfur dioxide and carbon dioxide, and sulfur separates out.

While estimating the composition of the precipitate formed by treating ammonium thiocyanate solutions with sulfuric acid, it has been noticed that the composition of the precipitate varies according to the strength of ammonium thiocyanate and sulfuric acid solutions used. It has also been noticed that the stronger the sulfuric acid used, the lower became the sulfur content of the precipitate. The reaction of concentrated sulfuric acid on thiocyanates described by Allen does not seem to take place when solid ammonium thiocyanate is treated with concentrated sulfuric acid in the cold.

Anal. Calcd. for $H_2C_2N_2S_3$: C, 16; H, 1.3; N, 18.7; S, 64.0. Calcd. for $C_3N_3S_3H$: C, 20.6; H, 0.6; N, 24.0; S, 54.9.

Experimental

The composition of the precipitates obtained by using solutions of different strengths of ammonium thiocyanate and sulfuric acid was found to vary as follows—C, 13.01 to 17.6; H, 0.9 to 2.8; N, 18.4 to 21.3; S, 57.0 to 65.5.

The precipitate obtained by using a saturated solution of ammonium thiocyanate and 20% sulfuric acid in equal quantities gave the following results—C, 15.9 to 15.95; H, 1.01 to 1.1; N, 19.0 to 20.3; S, 62.5 to 65.5.

The precipitate obtained by treating solid ammonium thiocyanate

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[1] (a) Kalason, *J. prakt. Chem.*, II, **36**, 57 (1887); (b) *ibid.*, **38**, 383 (1888); (c) Allen, "Technical Analysis," Vol. VII, p. 544.

[2] Pawlewsky, *Ber.*, **33**, 164 (1903).

[3] Goppelsroeder, *J. Chem. Soc.* (Abstracts), **48**, 109 (1885).

with 50% sulfuric acid with gentle heating gave as analytical results—C, 16.4 to 16.5; H, 0.76 to 1.1; N, 19.2 to 20.0; S, 57.0 to 57.0.

Some of the precipitates were found to leave a little residue on combustion (mostly of iron oxide).

When solid ammonium thiocyanate was treated with concentrated sulfuric acid in the cold, a white precipitate was formed which was not sulfur. It dissolved after a few days, producing a sirupy liquid which did not give the characteristic red coloration with ferric chloride.

Concentrated hydrochloric acid produced a yellowish-white precipitate. It dissolved in water and the solution became turbid on heating.

All attempts to obtain these precipitates in a pure state have failed.

The acids used were Kahlbaum's pure reagents.

Discussion.—The analytical results show that the precipitates obtained by treating ammonium thiocyanate with sulfuric acid are generally mixtures of varying composition, depending on the strength of ammonium thiocyanate and sulfuric acid used. A study of the sulfur and carbon results shows that sulfuric acid has a variable oxidizing influence on thiocyanates, depending on the strength of acid used.

This work has been carried out at the Government College Chemical Laboratories, Lahore, India. Thanks are due to Dr. Dunnicliff for suggesting the problem.

Conclusions

1. The thiocyanate–sulfuric acid precipitates are generally mixtures.
2. There seem to be two factors which influence the formation of the precipitate: the strengths of (a) the ammonium thiocyanate solution and (b) of the sulfuric acid.
3. Sulfuric acid, besides its hydrolyzing effect, appears to have an oxidizing influence on thiocyanates; the stronger the acid the more marked is the effect.

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