On the Synthesis of Monobromocyanamamide

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Although dibromocyanamamide was prepared by Hesse $^1$ as early as 1896, the monobromoderivative was not prepared until 1922 by Gupta and Thorpe $^2$. They prepared monobromocyanamamide by partial debromination of dibromocyanamamide by means of dimethylamine:

$$\text{CBr}_3(\text{CN})\text{CONH}_2 + \text{C}_6\text{H}_5\text{N}-(\text{CH}_3)_2 \to \text{C}_6\text{H}_4\text{Br}-\text{N}-(\text{CH}_3)_2 + \text{CHBr(CN)CONH}_2$$

A solution of dibromocyanamamide and dimethylamine in benzene was kept at 80° for five hours. In this way monobromocyanamamide and p-bromoaniline were obtained in a yield of 55 per cent of the theoretical amount.

Dibromocyanamamide is obtained in a simple way by bromination of cyanamamide in aqueous solution in the presence of sodium acetate at low temperature. The dibromo-product separates during the reaction. Gupta and Thorpe stated, that all attempts to prepare monobromocyanamamide by direct bromination were fruitless.

However, a more careful study of the bromination reaction indicates, that the following three competitive reactions take place:

$$\text{CH}_2(\text{CN})\text{CONH}_2 + \text{Br}_2 \to \text{CHBr(CN)CONH}_2 + \text{HBr} \quad (1)$$
$$\text{CHBr(CN)CONH}_2 + \text{Br}_2 \to \text{CBr}_3(\text{CN})\text{CONH}_2 + \text{HBr} \quad (2)$$
$$\text{CH}_2(\text{CN})\text{CONH}_2 + \text{CBr}_3(\text{CN})\text{CONH}_2 \to 2 \text{CHBr(CN)CONH}_2 \quad (3)$$

At a low temperature the reactions (1) and (2) are very fast; reaction (3) is evidently slow. At a higher temperature, however, reaction (3) is also fast. On bromination of cyanamamide in the cold, the formation of the dibromoderivative is also favoured by the fact, that it is less soluble than the monobromoderivative and thus quickly separates from the solution. It is likely, that a bromination of cyanamamide at a high temperature would lead mainly to the monobromoderivative, when equimolar parts of amide and bromine are used.

The best method for preparing monobromocyanamamide is, however, to make use exclusively of reaction (3). Thus, on heating equimolar parts of cyanamamide and dibromocyanamamide in aqueous solution, a good yield of the monobromo-product is obtained.

Both mono- and dibromocyanamamide are quantitatively debrominated by an acidified potassium iodide solution:

$$\text{CHBr(CN)CONH}_2 + 2 \text{HJ} \to \text{CH}_2(\text{CN})\text{CONH}_2 + \text{J}_2 + \text{HBr}$$
$$\text{CBr}_3(\text{CN})\text{CONH}_2 + 4 \text{HJ} \to \text{CH}_2(\text{CN})\text{CONH}_2 + 2 \text{J}_2 + 2 \text{HBr}$$

These reactions are useful for the analytical determination of bromocyanamamides, since the liberated iodine can be titrated with sodium thiosulfate.

Experimental. 6.3 g (0.075 mole) of cyanamamide and 18.2 g (0.075 mole) of dibromocyanamamide were dissolved in 50 ml of hot water, and the solution was boiled for about two minutes, treated with some decolorizing charcoal and filtered hot. On cooling, monobromocyanamamide separated as white needles. Yield 20 g (80%). The product may be recrystallized from hot water or preferentially from alcohol. M.p. 121—122°.

0.1929 g: 23.30 ml 0.1018 N Na$_2$S$_2$O$_3$.
0.2008 g: 24.19 ml 0.1013 N HCl (Kjeldahl)
C$_4$H$_6$O$_2$N$_2$Br = 163.0. Calc. N 17.19, Br 49.03
Found = 17.09, = 49.12


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