262

## XXXVIII.—Transformation of Urea into Cyanamide.

## By H. J. H. FENTON, M.A., Demonstrator of Chemistry in the University of Cambridge.

It is well known that cyanamide when treated with dilute acids takes up the elements of water, forming urea:  $CN_2H_2 + OH_2 = CON_2H_4$ . In fact, if the ordinary view with regard to the constitution of these bodies be accepted, cyanamide may be considered as the nitril of carbamic acid, of which urea is the amide :---

${ m NH}_2$	$\mathbf{NH}_2$
CONH <sub>2</sub>	ĊООН
Urea.	Carbamic Acid.
	NH2   CONH2 Urea.

Ammonium carbamate loses water, forming urea (Basaroff, Chem. Soc. J. [2], 6, 194), and thio-urea can be readily caused to part with the elements of hydrogen sulphide, giving cyanamide.

Drechsel has also obtained cyanamide by the action of moist carbon dioxide on ammelide, and the latter, it is stated, is met with among the products of the decomposition of urea by heat. But the direct dehydration of urea into cyanamide has not hitherto been effected (Drechsel, J. pr. Chem. [2], 11, 209).

Attempts were made in this direction by acting upon urea with phosphorus pentoxide, calcium chloride, and other ordinary dehydrating agents, but in none of these cases was any cyanamide produced. When, however, urea is gently heated with metallic sodium, a violent reaction takes place, and a large quantity of hydrogen is evolved, which takes fire and burns at the mouth of the vessel. The solid residue which remains dissolves almost completely in water, and the solution so obtained gives abundantly the characteristic reactions of cyanamide; namely, a bulky yellow precipitate with silver nitrate, nearly insoluble in cold ammonia, but readily soluble in dilute nitric acid, and a brownish-black precipitate with cupric salts.

In order to obtain the cyanamide from this solution (which must obviously contain it as the sodium derivative), ammonia in excess and silver nitrate were added, and the yellow precipitate obtained was thoroughly washed and dried, covered with ether, and subjected to the action of hydrogen sulphide.

The ethereal solution was filtered from silver sulphide, and evaporated at a gentle heat. The residue thus obtained had the characteristic property of remaining liquid until touched with a pointed body, when it immediately crystallised. The crystals were carefully dried over strong sulphuric acid, and analysed by a modifi-

## FENTON: TRANSFORMATION OF UREA INTO CYANAMIDE. 263

cation of Gottlieb's method, *i.e.*, weighed quantities of the substance were burnt in a vacuum with copper oxide, and the resulting carbon dioxide and nitrogen collected and measured in the ordinary way :--

0.0412 gram treated in this manner gave-

		Theory $(CN_2H_2)$ .
$\mathrm{CO}_2.\ldots.$	21.5 c.c. (corr.)	21·95 c.c.
Ν	21.28 "	21.95 "

0.0346 gram gave-

$\mathrm{CO}_2.\ldots.$	18 <sup>.</sup> 15 c.c.	18.43 c.c.
N	18.24 ,,	$18^{ ext{-}43}$ ,,

The formation of cyanamide in the above reaction may be represented by the equation—

$$2\text{CON}_{2}\text{H}_{4} + \text{Na}_{2} = 2\text{CN}_{2}\text{H}_{2} + 2\text{NaOH} + \text{H}_{2},$$

the cyanamide being then further acted upon by sodium, producing the disodium derivative CN<sub>2</sub>Na<sub>2</sub>.

It was natural from the above results, to expect that ammonium carbamate and ammonium carbonate would behave similarly when acted upon by metallic sodium---

$$\begin{array}{rcl} \mathrm{NH}_2 & - 2\mathrm{H}_2\mathrm{O} = \mathrm{CN}_2\mathrm{H}_2 \text{, and} \\ \mathrm{COONH}_4 & - 3\mathrm{H}_2\mathrm{O} = \mathrm{CN}_2\mathrm{H}_2. \end{array}$$

And such was found to be the case, a fairly good yield of cyanamide being obtained in each instance, although it is impossible to prevent considerable loss from volatilisation of the unaltered material, which is not the case to any extent with urea.

The above reactions afford very convenient methods for the preparation of cyanamide, especially the action of sodium upon urea, by which it is easy to prepare considerable quantities of cyanamide in a comparatively short time.

I am at present engaged in analysis of the yellow silver-derivative of cyanamide. The percentage of silver, in samples prepared under varying conditions, appears to be always intermediate between the values required by theory for  $CN_2HAg$  and  $CN_2Ag_2$ ; whilst the colour varies from a very pale-yellow to a bright canary-yellow, according to the manner in which the substance is prepared.