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Cyanamide Derivatives. Part 99.* Electrolytic Oxidation of Cyanamide

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Cyanamide was electrochemically oxidized with a platinum anode in aqueous potassium hydroxide. Electrolysis was carried out at 1.30 V *vs.* SCE of anode potential. Oxidation products consist of several unknown 1,2,3,5-tetrazine compounds and known linear cyano compounds.

A number of studies have been performed on the catalytic and electrolytic reduction of cyanamide, but only one paper dealing with the oxidation of cyanamide was published by Calcagni and Lazzari.[1] They electrolyzed cyanamide in aqueous sulfuric acid but gave no details except for the formation of nitric and nitrous acids.

Cyanamide is considerably stable in strongly alkaline and acidic solutions because it is an amphoteric compound, while it is easily converted into dicyandiamide by dimerization and into urea by hydration in weakly alkaline and acidic solutions, respectively. Potassium hydroxide was used as an electrolyte in this work. The advantage of a strongly alkaline electrolyte is not only that cyanamide can be stabilized but also that its anionic form ($NC\text{–}NH^-$ or $NC\text{–}N^{2-}$) favorable to migration to an anode surface can be formed.

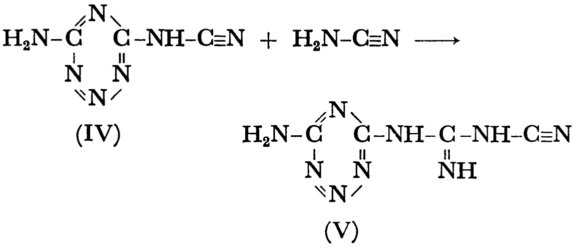
Results and Discussion

Cyanamide was electrolyzed with a platinum anode in 2 M potassium hydroxide. Several products were isolated from the anolyte neutralized with hydrochloric acid or carbon dioxide.

Of the products, dicyanoimine(I), cyanourea(II), and dicyandiamide(III) are known compounds and were identified with authentic samples, while the structures of VII and VIII could not been confirmed. Cyanic acid in the form of potassium salt was also confirmed IR-spectroscopically without being isolated. On the other hand, 4-amino-6-cyanamino-1,2,3,5-tetrazine (IV), 4-amino-6-cyanoguanidino-1,2,3,5-tetrazine(V), and 4-ureido-6-cyanoguanidino-1,2,3,5-tetrazine(VI) are new compounds with a rare 1,2,3,5-tetrazine ring.[2] Their structures were confirmed as follows.

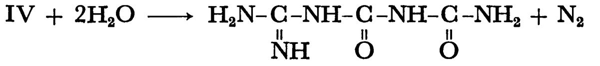
The potassium salts of these compounds exhibited the absorption for C≡N and cyclic –N=N–N– groups at 2160—2190 and 1200—1300 cm^{-1},[3] respectively.

IV was converted into V by addition of cyanamide in aqueous potassium carbonate.



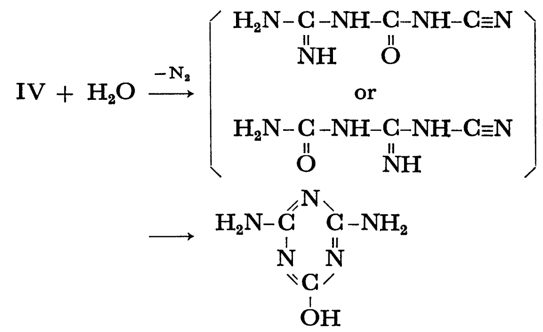
(IV) (V)

Amidinobiuret and nitrogen were formed in 73 and 80% yields, respectively, when IV was warmed at 40 °C in dilute sulfuric or hydrochloric acid. Neither carbon dioxide nor ammonia was detected. IV also decomposed slowly,

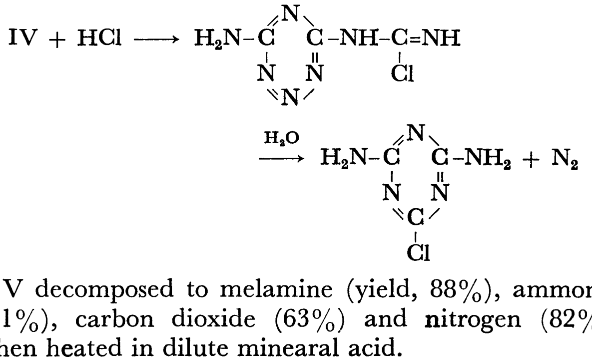


$$\text{IV} + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{N-}\underset{\substack{\| \\ \text{NH}}}{\text{C}}\text{-NH-}\underset{\substack{\| \\ \text{O}}}{\text{C}}\text{-NH-}\underset{\substack{\| \\ \text{O}}}{\text{C}}\text{-NH}_2 + \text{N}_2$$

accompanied by evolution of nitrogen in aqueous potassium hydroxide at room temperature, and finally giving ammeline in a 45% yield after being left to stand for 24 h. The decomposition seems to involve cyanoamidinourea or cyanocarbamoylguanidine as an intermediate.[4]



In order to obtain the free acid of IV, hydrogen chloride gas was introduced into a dry acetone solution of potassium salt of IV. The resulting precipitate was not the desired free acid but the hydrochloride of a base which gave 2,4-diamino-6-chloro-1,3,5-triazine by treatment with water. The basic intermediate exhibited no absorption for –C≡N group. It is presumed to be 4-amino-6-(iminochloromethyl)amino-1,2,3,5-tetrazine on the basis of its elemental analysis.



V decomposed to melamine (yield, 88%), ammonia (91%), carbon dioxide (63%) and nitrogen (82%), when heated in dilute minearal acid.

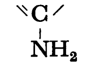


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Table 1. Properties of products

Compounds (Formula)	IR spectrum cm^{-1}	UV spectrum λ_{max} (log ε) nm in CH$_3$OH	in H$_2$O	in 2×10^{-3} M KOH	D.p. °C	Appearance
IV($C_3H_2N_7K$)	3360, 3130, 2190 1645, 1550, 1451 1270, 1196, 1018	320 (4.34)			171	Pale yellow fine needles
V($C_4H_4N_9K$)	3350, 3160, 2180 1675, 1630, 1525 1230, 986		335 (4.43)	334 (4.43) 205 (3.77)	225	Yellow needles
V($C_4H_5N_9$)	3300, 3150, 2210 1660, 1588, 1414 1245, 1012, 930	333 (4.24) 306 (4.22)		336 (4.27) 226 (4.00)	130[a]	Yellow powder
VI($C_5H_4N_{10}OK_2$)	3350, 3150, 2160 1610, 1510, 1272 1190, 1080, 982		340 (4.52)	340 (4.53) 214 (4.00)	217	Yellow granules
VII($C_3H_2N_7O_2K$)	3450, 3330, 2180 1650. 1314, 1281 1155, 995		301 (4.34)		131	Yellow needles
VIII(?)	3400, 3170, 2160 1700, 1596, 1355 1230, 1089, 948		299 (—)		162	White powder

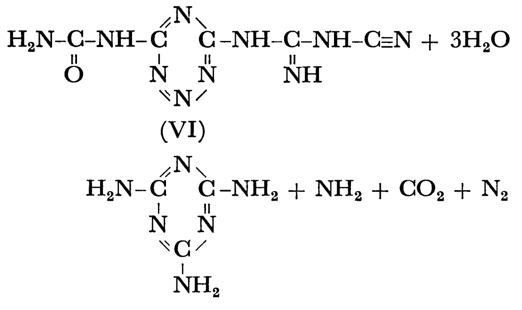
a) Explosive.

Table 2. Results of electrolysis of cyanamide

Neutralizing reagent of anolyte	Yield of products g (%)									Recovered cyanamide[f]
	I[b]	II	III	IV[c]	V[c]	VI[d]	VII	VIII	N_2[e]	g (%)
HCl	0.72 (8)	+	—	0.84 (19)	0.04 (1)	—	+	+	5	0.18 (1)
CO_2	0.70 (8)	+	+	0.20 (5)	1.11 (26)	0.35 (7)	—	+	5	0.45 (2)

a) 0.101 F of electricity was passed through an anolyte containing 4.20 g (0.10 mol) of cyanamide.
b) Monoammonium salt. c) Monopotassium salt. d) Dipotassium salt. e) ml under 1 atm at 0 °C.
f) Disilver salt.

VI also decomposed to melamine (yield, 80%), ammonia, carbon dioxide and nitrogen under similar conditions.



(VI)

No detailed mechanism could be established for hydrolytic decompositions of IV, V and VI. However, the above results might bring some reliable information for determination of the structures of these compounds. At least the formation of amidinobiuret and 2,4-diamino-6-chloro-1,3,5-triazine suggests the existence of the skeletons of N–$\underset{\underset{N}{|}}{C}$–N–C–N–C≡N and N–C–N–$\underset{\underset{N}{|}}{C}$–N–C≡N, respectively. The evolution of nitrogen in the course of decomposition also suggests that a –N=N– bond is involved in IV. The most probable structure of IV is thus represented as shown above. It is further supported by the fact that the decomposition of V derived from IV is reasonable from a stoichiometric aspect.

Only V could be successfully converted into the corresponding free acid. Although the free acid gave no molecular peak even in a high resolution mass spectrum measured carefully because of its thermolability, the spectrum indicated a N_3^+ fragment at m/e 42.0109 (pattern coefficient, 26%; calcd m/e 42.0125). This is an evidence for the existence of the –N=N–N– group. The highest m/e value of peak in the spectrum was 151.0601 (pattern coefficient, 15%) corresponding to a $C_4H_5N_7^+$ fragment (calcd m/e 151.0606) formed by elimination of N_2 from a molecule ($C_4H_5N_9$). The properties and the amounts of the products are listed in Tables 1 and 2, respectively.

The distribution of products derived from an anolyte neutralized with hydrochloric acid differs from that derived from the one neutralized with carbon dioxide. This suggests that an unstable intermediate may be left active in an anolyte even after electrolysis.

Experimental

Electrolytic Cell and Procedure. An H-type cell divided with a sintered glass diaphragm was used. Both anode and cathode were platinum plates (3×4 cm). 75 ml of 2 M potassium hydroxide was used as anolyte and catholyte. 4.20 g (0.10 mol) of cyanamide was added to the anolyte and electricity was supplied. The anode potential and the temperature of anolyte were maintained at 1.30 V *vs.* SCE (an initial anodic current density, 20 amp/dm²) and below 10 °C, respectively, during electrolysis. When the anodic current density lowered to 2 amp/dm^2 after 3.5 h, electricity was turned off. The amount of passed electricity was 1.01 F/mol.

Separation of Products. After electrolysis, the anolyte was neutralized to pH 8—9 with carbon dioxide and then evaporated to dryness under reduced pressure at below 20 °C.[5] The residue was extracted with 150 ml of acetone. When the insoluble solid in acetone was treated with 50 ml of water, the crude monopotassium salt of V, which was purified by recrystallization from water, was left as a yellow solid. Found: C, 22.11; H, 2.18; N, 58.70%. Calcd for $C_4H_4N_9K$: C, 22.11; H, 1.86; N, 58.63%. The aqueous solution was neutralized to pH 6.5 with hydrochloric acid and 400 ml of ethanol was added. The resulting precipitate (potassium hydrogen carbonate) was filtered off and the filtrate was evaporated to dryness. When the residue was treated with 10 ml of water, dipotassium salt of VI, which was recrystallized from a small amount of water, was left as a yellow solid. Found: C, 20.29; H, 1.28; N, 47.63%. Calcd for $C_5H_4N_{10}OK_2$: C, 20.13; H, 1.35; N, 46.95%. 50 ml of ethanol was added to the aqueous solution and the resulting precipitate (potassium carbonate) was filtered off. After aqueous ammonia was added to the filtrate, it was evaporated to dryness. When the residue was extracted with 10 ml of acetone, monoammonium salt of II was left as a white solid. The ammonium salt was dissolved in dilute hydrochloric acid and the solution was evaporated to dryness. The residue was treated with ethanol in order to remove ammonium chloride. When the ethanolic solution was again evaporated to dryness, the free acid of II, which was recrystallized from ethanol, was left as a white solid. When the acetone solution was evaporated to dryness, ammonium salt of I, recrystallized from a mixture of acetone and ether, was left as white needles.

On the other hand, when the acetone solution prepared at the first stage was concentrated to one-third of its original volume, a small amount of VIII, which was recrystallized from acetone, crystallized out of the solution as white powder. Found: C, 16.62; H, 1.22; N, 49.24%. The structure of VIII could not be determined. The acetone solution was evapoated to dryness and the residue was extracted with ether. The ether extract was again evaporated to dryness and the residue was dissolved in dilute ammonia. When an aqueous solution of silver nitrate was added to the ammoniacal solution, disilver salt of recovered cyanamide precipitated as yellow powder. When the insoluble solid in ether was extracted with 10 ml of cold water, III, which was recrystallized from hot water, was left as a white solid. The aqueous solution was evaporated to dryness and the residue was again dissolved in 100 ml of acetone. When 20 ml of ether was added to the acetone solution, monopotassium salt of IV crystallized out of the solution as pale yellow needles. IV was purified by recrystallization from acetone containing a small amount of ether. Found: C, 20.23; H, 1.06; N, 55.94%. Calcd for $C_3H_2N_7K$: C, 20.56; H, 1.15; N, 55.97%.

In the case where an original anolyte was neutralized to pH 6.4—6.8 with dilute hydrochloric acid, the products were separated by a similar method to the above.

Decomposition of IV in Acidic Solution. 0.35 g (2 mmol) of potassium salt of IV, a small glass ampoule containing 2 ml of concentrated hydrochloric acid, and 50 ml of water were placed in a flask connected with a gas burette. The flask was heated at 40 °C and then the ampoule was broken with a magnet hammer. 36 ml (yield, 80%) of nitrogen generated for 30 min. The reaction mixture was evaporated to dryness and then was dissolved in dilute ammonia. When a saturated solution of ammonium picrate was added to the ammoniacal solution, 0.35 g (yield, 65%) of potassium picrate crystallized out of the solution. When the mother liquor was acidified with acetic acid, 0.55 g (yield, 73%) of amidinobiuret picrate crystallized out of the solution.

Decomposition of IV in Alkaline Solution. 0.35 g (2 mmol) of potassium salt of IV and 20 ml of 2M potassium hydroxide were placed in a flask similar to that described above. 20 ml (yield, 45%) of nitrogen generated for 24 h. 0.11 g (yield, 45%) of ammeline crystallized out of the solution, when the reaction mixture was neutralized with acetic acid.

Decomposition of IV with Hydrogen Chloride in Acetone. Dry hydrogen chloride gas was introduced into 50 ml of an acetone solution containing 0.075 g (0.43 mmol) of potassium salt of IV at 0 °C. After the resulting potassium chloride had been filtered off, the reaction mixture was evaporated to dryness. 0.067 g (yield, 75%) of white residue, which could not be purified, was presumed to be 4-amino-6-(iminochloromethyl)amino-1,2,3,5-tetrazine monohydrochloride. Found: C, 17.87; H, 2.11; N, 46.95; Cl, 32.44%. Calcd for $C_3H_5N_7Cl_2$: C, 17.16; H, 2.40; N, 46.68; Cl, 33.76%. This residue was converted into 2,4-diamino-6-chloro-1,3,5-triazine by treatment with water.

Decomposition of V in Acidic Solution. 0.49 g (2.2 mmol) of V was dissolved in 30 ml of cold 0.5M hydrochloric acid. The reaction mixture was heated at 75 °C for 1 h. The gas evolved consisted of 41 ml (yield, 82%) of nitrogen and 32 ml (yield, 63%) of carbon dioxide. When the reaction mixture was cooled in an ice bath, 0.32 g (yield, 88%) of melamine hydrochloride precipitated. The amount of ammonium chloride in the mother liquor was estimated to be 2.04 mmol (yield, 91%) by the hypobromite method.

Decomposition of VI in Acidic Solution. 0.24 g (0.8 mmol) of dipotassium salt of VI was decomposed by a similar procedure to that in the case of V. 0.10 g (yield, 80%) of melamine hydrochloride and 0.60 mmol (yield, 75%) of ammonia were obtained from the reaction mixture. The gaseous product consisted of nitrogen and carbon dioxide, but their volumes were not measured.

Free Acid of V. 0.27 g (yield, 58%) of the free acid of V precipitated as yellow powder, when 2 ml of 2M hydrochloric acid was added to 5 ml of cold aqueous solution containing 0.57 g (2.6 mmol) of potassium salt of V. The free acid was purified by recrystallization from water. Found: C, 26.63; H, 2.75; N, 69.12%. Calcd for $C_4H_5N_9$: C, 26.82; H, 2.81; N, 70.37%.

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4) Yu. I. Mushkin and A. I. Finkel'stein, *Zh. Org. Khim.* **3**, 507 (1967).

5) Evaporation of the solution was carried out under such conditions in order to avoid the decomposition of the compounds.