Inorganic Syntheses, Volume V
Edited by Therald Moeller

CHAPTER IVA

See also:

12. CYANOGEN

$$4NaCN + 2CuSO_4 \rightarrow (CN)_2 + 2Na_2SO_4 + 2CuCN$$

SUBMITTED BY GEORGE J. JANZ*
CHECKED BY HENRY M. WOODBURN,† JAMES T. PECKA,† AND THOMAS J. DOLCE†

Cyanogen is most commonly prepared by adding an aqueous solution of sodium or potassium cyanide to an

---

* Rensselaer Polytechnic Institute, Troy, N.Y.

† The University of Buffalo, Buffalo, N.Y.

aqueous solution of copper(II) sulfate or chloride.[1-5] It is also obtained by the thermal decomposition of paracyanogen prepared by the reaction of alkali metal cyanides with phosphorus(V) chloride,[6] by the vapor-phase reaction between hydrogen cyanide and chlorine,[7] and by the dry distillation of mixtures of mercury(II) cyanide and mercury(II) chloride.[8] The wet procedure is convenient for laboratory operations and gives a product of high purity if certain precautions are taken.

Procedure

Caution. This synthesis must be carried out in a well-ventilated hood.

The apparatus (Fig. 6) consists of a 2-l. resin kettle, reaction vessel *A*, to which are attached a water-cooled condenser *B,* a mechanically operated stirrer *C* with mercury-seal connection *D,* a thermometer, and a 1-l. dropping funnel *E* equipped with a pressure-equalizing connection *F* and attached to a nitrogen cylinder through a water bubbler *G.* The cyanogen outlet *H* is attached in series to two bubblers containing acidified silver nitrate solution, to two drying towers packed with phosphorus(V) oxide, and to a 250-ml. glass trap *I* (Fig. 7) cooled to −80° with Dry Ice in chloroform and carbon tetrachloride.

Five hundred grams of powdered copper(II) sulfate 5-hydrate (2 mols) is placed in the reaction vessel, and the latter is attached to the remaining apparatus with the stirrer just under the top of the solid. A saturated solution of sodium cyanide* (500 ml.), which has been freshly prepared and filtered, is placed in the dropping funnel, and the pressure equalizer is attached. A slow stream of nitrogen is passed through the apparatus, and the sodium cyanide solution is added sufficiently slowly so that the temperature in the reaction vessel is maintained at 50

* The carbon dioxide content of the product is reduced by adding barium chloride to the cyanide solution and removing precipitated barium carbonate.

to 55°.* Cyanide addition is continued until the copper(II) ion is completely reduced.† The temperature of the reaction vessel is then increased to 70 to 75°, and the remaining cyanogen is swept into the trap *I* (Fig. 7) with

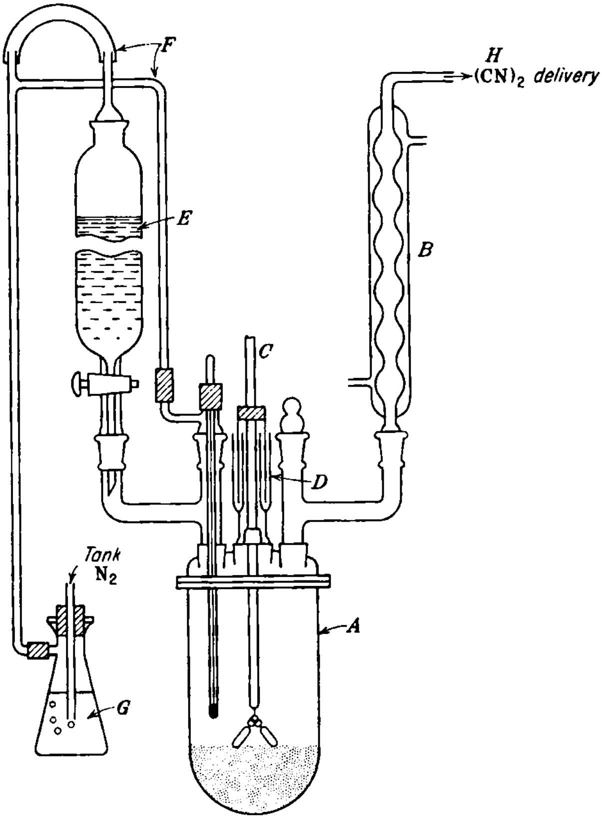

FIG. 6. Apparatus for the preparation of cyanogen.

---

* This optimum temperature range should be maintained by controlled addition of the cyanide solution and external cooling of the reaction vessel with a water bath if necessary. Initial heating to 55° before adding the cyanide decreases the yield. Addition of copper(II) sulfate to the cyanide also decreases the yield.

† If additional sodium cyanide solution is required, it should be introduced into the dropping funnel without interrupting the nitrogen flow. The checkers suggest a side arm with stopcock on the dropping funnel for this purpose.

nitrogen.[*] An excess of iron(II) sulfate is then added to the reaction vessel to remove all cyanide ion before the reaction vessel is washed out.

For storage, the cyanogen is transferred to a 500-ml. stainless-steel cylinder *J*[†] (Fig. 7) by connecting the trap *I* through a wash-bottle-top fitting attached to the cylinder by means of a rubber joint *L*, immersing the steel cylinder in a 2-l. beaker *M* containing Dry Ice, chloroform, and carbon tetrachloride at −80°, and slowly withdrawing the trap from its freezing bath. A slow stream of dry nitrogen

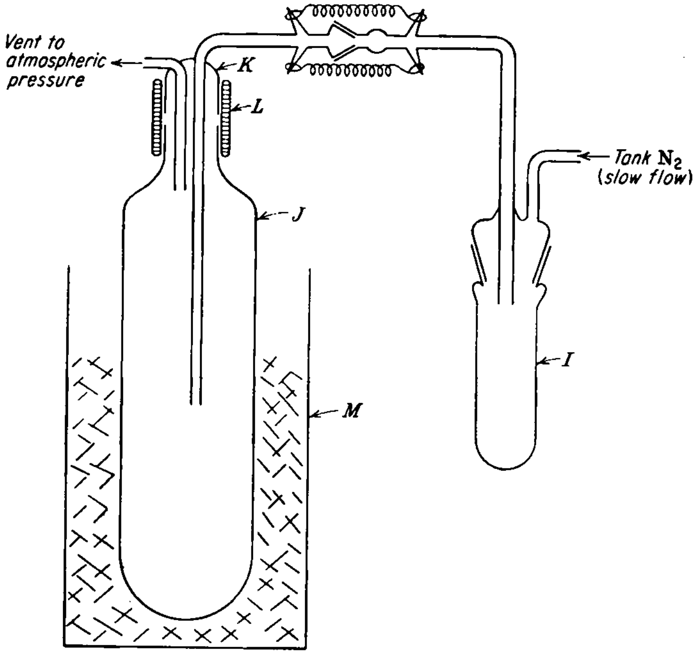

Fig. 7. Apparatus for the collection and storage of cyanogen.

---

[*] Addition of 12 *M* hydrochloric acid at the end of the reaction increases the yield by about 6%. However, so much silver nitrate is consumed in the scrubbers by the hydrogen chloride gas carried that this technique is not economically feasible.

[†] If the interior of the cylinder has been pickled in acid, washed, and thoroughly dried, cyanogen can be stored in it indefinitely without polymerization or decomposition.

is passed through the apparatus to facilitate the transfer. When distillation is complete, the cylinder is closed with a screw-type valve fitting and then allowed to warm to room temperature. Gas analysis[9,10] shows the product to be better than 89 mol per cent cyanogen. Carbon dioxide is invariably present as a result of initial carbonate impurities and of hydrolysis of cyanate ion formed from cyanogen and the alkaline cyanide solution. The yield of cyanogen is about 21 g. (41%).

Properties

Cyanogen is a colorless gas, condensing to a colorless liquid boiling at −21.17° and freezing at −27.9°. The heat of vaporization of the liquid is 5.778 kcal./mol, and the density at the boiling point is 0.9537. One volume of water dissolves about 4 volumes of the gas.

Cyanogen is the dinitrile of oxalic acid and yields first oxamide and then oxalic acid upon hydrolysis. A number of resonance forms contribute to the linear structure,[11] the measured bond distances[12] being C-N, 1.16 A. and C-C, 1.37 A. The heat of dissociation of the molecule to CN groups is variously reported from 77 to 145 kcal./mol.[13–15] The most probable value is around the upper limit.[16] Chemically, cyanogen resembles the halogens. Thus, with hydroxyl ion it yields cyanide and cyanate ions. Above 500° it polymerizes to insoluble paracyanogen, $(CN)_n$. Cyanogen is toxic, its physiological effect being comparable to that produced by hydrogen cyanide.

References

1. G. Jaquemin: *Compt. rend.*, **100,** 1005 (1885).
2. B. Ricca: *Ann. chim. appl.*, **16,** 83 (1926).
3. C. Noir and Tcheng-Datchang: *Compt. rend.*, **187,** 126 (1928).
4. G. Hahn and W. Leopold: *Ber.*, **68B,** 1974 (1935).
5. G. J. Janz, R. G. Asceah, and A. G. Keenan: *Can. J. Research,* **25B,** 272 (1947).
6. L. Bert: *Compt. rend.*, **222,** 1117 (1946).
7. B. S. Lacy, H. A. Bond, and W. S. Hinegardner: U.S. patent 2,399,361 (Apr. 30, 1946); *cf. C. A.*, **40,** 4744 (1946).

8. B. Ricca: *Ann. chim. appl.*, **16**, 89 (1926).
9. L. M. Dennis and M. L. Nichols: "Gas Analysis," p. 272, The Macmillan Company, New York, 1929.
10. E. G. Mahin: "Quantitative Analysis," 4th ed., p. 266, McGraw-Hill Book Company, Inc., New York, 1932.
11. L. O. Brockway: *Proc. Natl. Acad. Sci. U.S.*, **19**, 868 (1933).
12. L. Pauling, H. D. Springall, and K. J. Palmer: *J. Am. Chem. Soc.*, **61**, 927 (1939).
13. G. B. Kistiakowsky and H. Gershinowitz: *J. Chem. Phys.*, **1**, 432 (1933).
14. J. U. White: *ibid.*, **8**, 459 (1940).
15. N. C. Robertson and R. N. Pease: *ibid.*, **10**, 490 (1942).
16. H. D Springall: *Trans. Faraday Soc.*, **43**, 177 (1947).

13. ALLOPHANYL HYDRAZIDE

(1-Aminobiuret)

$$2NH_2CONH_2 + ClCOOR \rightarrow NH_2CONHCOOR + NH_2CONH_2\cdot HCl$$

$$NH_2CONHCOOR + N_2H_4 \rightarrow NH_2CONHCON_2H_3 + ROH$$

$$(R = CH_3 \text{ or } C_2H_5)$$

Submitted by Paul G. Gordon* and Ludwig F. Audrieth*
Checked by P. Lensi†

Allophanyl hydrazide has been prepared previously as the hydrochloride by the zinc–hydrochloric acid reduction of 1-nitrobiuret.[1] The new procedure[2,3] outlined here entails the hydrazinolysis of allophanic esters in alcoholic solution. Excellent yields (80 to 84%) of allophanyl hydrazide are obtainable with a minimum of difficulty using readily available starting materials. The methyl and ethyl allophanates are prepared from urea and the corresponding chlorocarbonic esters.[4]

---

* University of Illinois, Urbana, Ill. Experimental work was carried out under Ordnance Contract DA-11-022-ORD-33. Publication has been approved by the Office of Public Information of the Office of Chief of Ordnance.

† Chemical Research Division, Samuel Feltman Ammunition Laboratories, Picatinny Arsenal, Dover, N.J.