LXIX.—*Studies on Hydrogen Cyanide. Part I. Mercuric Methyl Cyanide and the Alleged Isomerides of Hydrogen Cyanide.*

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ENKLAAR (*Rec. trav. chim.*, 1923, **42**, 1000; 1925, **44**, 889; 1926, **45**, 414), having on the basis of the Drude theory developed a theory of optical dispersion in which dispersion electrons are correlated with valency electrons, and having measured the dispersion of hydrogen cyanide, nitriles, and carbylamines, found evidence for the view that hydrogen cyanide behaves optically as a 50% mixture of HCN and HNC, or as though the hydrogen atom were bound equally to the atoms of carbon and nitrogen. Nevertheless, he regards as improbable the view that ordinary hydrogen cyanide consists of a 50% mixture of isomerides, since he claims to have isolated these isomerides as separate individuals and to have shown that one of them (considered to be HNC) is stable and the other, HCN, unstable. In view of its importance in connexion with the problem of the constitution of hydrogen cyanide, it seemed desirable to repeat the experiments upon which this claim was based.

Enklaar recognised the isomerides solely by their reaction with mercuric methyl hydroxide, in which two mercuric methyl cyanides of different melting points were formed, *viz.*, that melting at 90·5°, regarded as the derivative of the stable acid HNC, and that melting at 60°, corresponding to the " labile " acid HCN. Gaseous hydrogen cyanide generated by various simple reactions is said to yield in some cases the former, in others the latter derivative, thus indicating the separate existence of two isomeric forms of the gas. Further, the derivative of lower melting point is obtained from the reaction between mercuric methyl iodide and silver cyanide, and also by the spontaneous transformation of the form melting at the higher temperature when it is kept for several months at about 6°.

The Alleged Isomerides of Hydrogen Cyanide.—Enklaar found that (*a*) silver cyanide, alone or, better, in potassium cyanide solution, and (*b*) a solution of mercuric cyanide, when slightly decomposed by a small quantity of hydrogen sulphide yielded gaseous hydrogen cyanide, which, when led directly into aqueous mercuric methyl hydroxide, always gave the derivative of low melting point. In a later paper (*loc. cit.*, 1925), however, he reports a product similarly obtained as melting at 89·5°, without remarking on the inconsistency.

He also found that the hydrogen cyanide first evolved from an acidified solution of sodium ferrocyanide is " stable " (yielding the high-melting derivative), whereas that evolved after a few minutes' boiling is " labile " (yielding the low-melting derivative). Again, the hydrogen cyanide distilled from acidified solutions of potassium cyanide was unaccountably sometimes stable, sometimes labile, yielding a mercuric methyl cyanide melting as often at the higher as at the lower temperature. The claim is also made that the derivative obtained by distilling hydrogen cyanide from a system that is not free from water has a slightly lower melting point than that of the derivative produced by hydrogen cyanide distilled from an anhydrous system, the presence of water thus causing a certain amount of conversion of the stable into the labile acid. No attention is directed to a contradiction of this in the same paper (*loc. cit.*, 1925).

A repetition of these experiments has shown that mercuric methyl cyanide, produced directly from the pure base and hydrogen cyanide (whatever its origin), invariably melts, not at 90·5°, but at 93° without further purification, and the same substance obtained from mercuric methyl iodide and silver cyanide melts at 93° after purification. In a careful study of this substance no evidence has been found for the separate existence of a form melting at 60°. It suffers no change on keeping.

The variation in melting point of Enklaar's derivatives might be due to the use of impure substances. He employed mercuric methyl hydroxide melting at various temperatures between 92° and 97°. The pure base melts at 106°, cannot be purified from alcohol as attempted by Enklaar, and decomposes fairly rapidly on keeping; also it detonates when subjected to analysis by the ordinary combustion method (Hinkel and Angel, J., 1927, 1948), but Enklaar appears to have found no such difficulty. The melting point of mercuric methyl cyanide is greatly influenced by the presence of traces of moisture or solvents.

It might be objected that the processes of purification of the mercuric methyl cyanide obtained from the iodide and silver cyanide (the product from pure acid and pure base needed no purification) could convert any low-melting derivative into the high-melting form, and that Enklaar was right in avoiding purification. But when impurity is likely to be present (probably mercuric methyl iodide) no valid conclusions can be drawn from the melting point. Further, by this reaction an initial unpurified product could be obtained having a melting point only a few degrees below that of the pure high-melting derivative.

EXPERIMENTAL.

For the preparation of mercuric methyl cyanide directly from base and acid, the hydrogen cyanide was obtained, not only by the reactions referred to above, but also from a stock of the pure anhydrous substance prepared by dropping a concentrated solution of sodium cyanide into 65% sulphuric acid, the distillate being dehydrated by treatment with anhydrous sodium sulphate, followed by repeated distillation and treatment with phosphorus pentoxide extending over many months. Its boiling point was 25·7°/760 mm.

The mercuric methyl iodide employed melted at 145° and the hydroxide at 106°. Both were prepared and purified as described by Hinkel and Angel (*loc. cit.*).

Preparation of Mercuric Methyl Cyanide.—5 G. of mercuric methyl iodide in 25 c.c. of absolute alcohol were shaken at room temperature for 3 hours with 2·1 g. (a slight excess) of powdered silver cyanide. After the silver iodide and silver cyanide had been separated and the alcohol evaporated in a vacuum, white crystals remained, melting (not sharply) at 85°. (Enklaar, who gives no details, obtained by this method a product melting a little above 60°, rarely lower, which he considered to be the isomeride of the compound of higher melting point.) The product, after being twice dissolved in the minimum amount of boiling ether and precipitated by the gradual addition of light petroleum (b. p. 40—60°), and dried in a vacuum, melted sharply at 93°. A repetition of this process, using instead of ethyl alcohol (*a*) ether dried by sodium, (*b*) methyl alcohol, gave a product melting at 93° after purification. A preparation in the presence of a large excess of silver cyanide melted without any purification at 89° (after previous softening). The impurity is probably mercuric methyl iodide.

The preparation was also carried out by the use of a slight excess of mercuric methyl iodide, the mixture being boiled for 2 hours. The mercuric methyl iodide was separated by treatment with boiling water, in which it is practically insoluble. After purification as before, the product melted at 93° (Found : N, by Kjeldahl method, 5·75. C_2H_3NHg requires N, 5·78%).

The Properties of Mercuric Methyl Cyanide.—The only information in the literature on this substance is that given by Enklaar. The substance is readily soluble in water, methyl or ethyl alcohol, anhydrous hydrogen cyanide, and benzene, and fairly readily soluble in ether, from which it may be precipitated by the addition of light petroleum (b. p. 40—60°). It crystallises in colourless, lustrous, acicular plates with a faint smell of garlic, somewhat resembling that of the base. No change of melting point occurs (1) after heating the melt at 100° for several minutes, (2) after keeping at 0° for several days, and (3) after keeping at room temperature for 9 months. This may be contrasted with Enklaar's statement that the compound of higher melting point, on keeping for several months at about 6°, changes largely into the form of lower melting point.

The aqueous solution resembles that of mercuric cyanide in being neutral to indicators even after boiling for 10 minutes (compare other mercuric methyl salts, Maynard and Howard, J., 1923, **123**, 960). The behaviour of mercuric methyl cyanide with methyl iodide is precisely similar to that of mercuric cyanide and silver cyanide, a double compound being first formed which breaks down into methyl carbylamine at a higher temperature. With dry hydrogen chloride, mercuric methyl cyanide, dissolved in dry ether, slowly forms white crystals of mercuric methyl chloride. In aqueous solution hydrochloric acid precipitates the same substance, silver nitrate precipitates silver cyanide, and hydrogen sulphide mercuric methyl sulphide. Caustic potash, ammonia, and potassium iodide give no apparent reaction. Dilute sulphuric acid readily liberates hydrogen cyanide (according to Enklaar, this does not occur).

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