

Alkyl Cyanates

V. The Existence of Cyanic Acid, HO-CN

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During our work with alkyl cyanates¹⁻⁵ the classical problem of the possible existence and stability of the true cyanic acid, HO-C≡N, attracted our attention.

Although it has been proved (see below) that the acid usually referred to as "cyanic acid" consists mainly of isocyanic acid, HN=C=O, it was still an unsolved question whether it also contains some cyanic acid, HO-C≡N, possibly in tautomeric equilibrium with isocyanic acid.

An early experiment in this field, which is closely related to our work, was performed by Palazzo and Carapello⁶ who reacted "cyanic acid" with diazomethane and diazoethane. They reported that the reaction products were mainly methyl and ethyl isocyanate, corresponding to the formula HN=C=O for the acid.

Later, Goubeau⁷ investigated the Raman spectrum of liquid "cyanic acid" and concluded that the compound consisted of isocyanic acid; the presence of small amounts (< 5%) of cyanic acid could, however, not be excluded.

Werner and Grey⁸ investigated the polymerisation of "cyanic acid" at different temperatures and obtained mixtures of cyanuric acid and cyamelide, the ratios being dependent on the polymerisation temperature. They explained this variation by a tautomeric equilibrium.

Later investigators have studied the structure of gaseous, liquid, or solid "cyanic acid" by X-ray, infrared, and microwave methods⁹⁻¹¹ and all concluded that their observations could be explained on the assumption that only HN=C=O molecules were present. They did not, however, search for a minor proportion of HO-C≡N molecules.

Previously "cyanic acid" was prepared by the thermal decomposition of cyanuric acid, which yields impure reaction products. Therefore, we elaborated a new

procedure wherein finely powdered sodium cyanate was treated with gaseous hydrogen chloride. The reaction product was analysed by mass spectrometry and was found to contain only carbon dioxide as an impurity.

The reaction product, dissolved in methylene chloride at -80°C, was rapidly brought to room temperature and the infrared spectrum recorded. The fresh solution gave a spectrum different from the spectrum of the same solution aged at room temperature. After about one hour, the ratios of the spectral intensities did not vary but the total intensity decreased slowly as a white precipitate was formed.

We also obtained infrared spectra, at -80°C, of the concentrated solution and of the undiluted acid. These spectra did not exhibit any variation with time in the course of some hours.

We are, at present, not able to draw any well-founded conclusions regarding a possible tautomeric equilibrium between HO-C≡N and HN=C=O from the above mentioned experiments. However, the following experiments prove that the crude "cyanic acid" contains small amounts of HO-C≡N.

The reaction with diazoisobutane was selected in our further search for cyanic acid since it had previously been shown³ that isobutyl cyanate is comparatively stable. Diazoisobutane, dissolved in methylene chloride, was added to a solution of "cyanic acid" in methylene chloride until a faint yellow colour of diazoisobutane persisted. The reaction mixture was analysed by gas chromatography and appeared complex (about 14 components). The main component was isobutyl isocyanate, but an almost negligible peak corresponded to the retention time for authentic isobutyl cyanate. The component giving rise to this peak was collected and its identity with isobutyl cyanate was substantiated by recording its infrared spectrum (CCl₄ solution, micro cavity cell), which was found to be identical with that found for authentic isobutyl cyanate.⁴ The relative amounts (isocyanate/cyanate) were about (100/3).

By varying the age of the "cyanic acid" solution between 0 and 15 min and varying the reaction temperature between -80°C and +30°C, we found some variation of the relative amounts and, at present, this phenomenon is being studied more closely.

The existence of $\text{HO}-\text{C}\equiv\text{N}$ is not proved definitely by the above experiments since an ionic reaction mechanism, e.g. an autoprotolysis $2\text{HNCO}\rightleftharpoons\text{HNCOH}^+ + \text{OCN}^-$, might give both a cyanate and an isocyanate even if no HOCN molecules were present. We therefore carried out reactions between gaseous diazoisobutane and gaseous "cyanic acid". The gas chromatograms were identically the same as obtained from the reactions in methylene chloride solution. We believe that this suggests the existence of $\text{HO}-\text{C}\equiv\text{N}$ molecules both in the gas phase and in solution.

The relative yields, however, of isobutyl cyanate and isobutyl isocyanate are not simply related to the relative amounts of the two acids, since the yields are dependent on the rates of the reaction $\text{HOCN}\rightleftharpoons\text{HNCO}$, and on the individual reaction rates between the two acids and the diazo compound. Further work is in progress to directly determine the relative amounts of HOCN and HNCO in "cyanic acid".

Experimental. Preparation of "cyanic acid".

Gaseous hydrogen chloride and nitrogen were led through two calibrated flow meters, the flow rates being 22 ml/min and 20 ml/min, respectively. After mixing, the gases were led to the reaction tube, packed as follows: A glass tube, 25 cm long and 0.5 cm inner diameter, with inside indentations one cm from one end to prevent moving of material, was fitted with a piece of quartz wool and loosely filled with sodium cyanate (it should be mentioned that potassium cyanate does not react with hydrogen chloride under these circumstances). The sodium cyanate was finely ground in a mortar. The tube was knocked energetically (important in order to avoid channels) on the table until no further packing was possible. The tube was then provided with another piece of quartz wool.

During the reaction a warm (ca. 70°C) zone moving along the tube was observed during the "cyanic acid" production. When exit gas mixture was tested with silver nitrate, no hydrogen chloride was found to be present until the zone had moved to the end of the tube (after ca. 10 min). The gas, collected before the appearance of hydrogen chloride, was found by mass spectrometry to contain only carbon dioxide as an impurity.

Reaction of "cyanic acid" with diazoisobutane. Gaseous "cyanic acid" in admixture with nitrogen and carbon dioxide was led directly

from the described reaction tube to a methylene chloride solution of diazoisobutane (prepared from 2.90 g of *N*-nitroso-*N*-isobutyl urea, using 10 ml of methylene chloride as solvent). The mixture was, in various experiments, kept at temperatures between -80°C and 30°C. The addition was stopped when the colour of diazoisobutane had just disappeared.

In other experiments, "cyanic acid" was absorbed in methylene chloride. After ageing for some time this solution was added, drop by drop, to a solution of diazoisobutane, or *vice versa*.

The gas chromatograms showed a complex mixture containing about 14 components, all mixtures being nearly identical, showing only a variation in height of some of the peaks. The main component was isobutyl isocyanate which made up 1-2% of the solution. The identity was confirmed by means of infrared spectroscopy on a collected sample. A small peak, identified by means of infrared and mass spectrometry to represent isobutyl cyanate, was present in 2.5 to 3.9% relative to the isobutyl isocyanate peak. The other peaks have not yet been identified.

The gas chromatographic analyses were carried out on a Perkin-Elmer 116 instrument, using a two meter O-column at 80°C with helium as carrier gas. The flow rate was 117 ml/min. The retention times were 6.0 min and 14.0 min for isobutyl isocyanate and isobutyl cyanate, respectively.

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