

Alkyl Cyanates

IX. Addition-Elimination Reactions of Ethyl Cyanate

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In continuation of the preceding paper¹ on chemical reactions of alkyl cyanates some reactions are reported in which the cyanate adds a foreign molecule to the C≡N triple bond with the formation of an addition compound which may subsequently decompose giving either the starting cyanate or a more stable CN-containing molecule.

It has been stated¹ that diethyl imidocarbonate, (EtO)₂C=NH, is formed by the action of ethanolic sodium ethoxide on ethyl cyanate. Diethyl imidocarbonate is formed also by the reaction of cyanogen halides with ethanolic sodium ethoxide^{2,3} and it seems likely that ethyl cyanate is also involved in this reaction since Grigat and Pütter⁴ were able to detect ethyl cyanate as a product from the reaction of cyanogen chloride with ethanol in the presence of a base. However, the base is not necessarily needed for the reaction to take place since we have found that ethanol vapour and cyanogen bromide vapour react in the inlet system of a mass spectrometer** forming ethyl cyanate which can be identified by its mass spectrum. Details of the mass spectra of alkyl cyanates are given in another paper.⁵

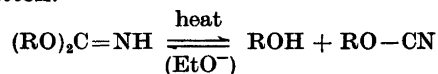
Houben⁶ tried to prepare ethyl cyanate by the decomposition of diethyl imidocarbonate but obtained ethanolic solutions of triethyl cyanurate and triethyl isocyanurate only. We have now found that ethyl cyanate is in fact formed on heating diethyl imidocarbonate to 200–250°C, and it could be identified by its mass spectrum⁵ when the decomposition was allowed to take place in the heated inlet line (the part of the inlet system connecting the leak with the ion source) of the mass spectrometer. Simultaneously, a mass spectrum of ethanol appeared.

Similarly, ethyl propyl imidocarbonate which is prepared by the addition of propanol to ethyl cyanate, splits off both ethyl cyanate and propyl cyanate

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** At 40°C and 10⁻² mm Hg.

when the compound is heated in the mass spectrometer. By this procedure, a little dipropyl imidocarbonate is also formed by gas phase addition of propanol to some of the propyl cyanate formed. Thus, the following reaction sequence may be written:



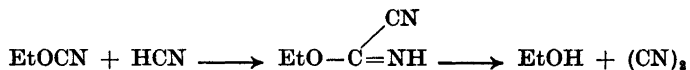
The reaction is similar to the one described by Grigat and Pütter⁷ in which a thiol adds to an aryl cyanate forming a thio imidoester which decomposes into a thiocyanate and a phenol.

This reaction also takes place between alkyl cyanates and thiols and we have verified this point by mixing ethyl cyanate and propanethiol in the reservoir of the mass spectrometer. When the compounds were heated in the inlet line there appeared new peaks in the spectrum corresponding to the formation of an addition compound, $\text{EtO}-\text{C}(=\text{NH})-\text{SPr}$, and propyl thiocyanate, $\text{Pr}-\text{SCN}$.

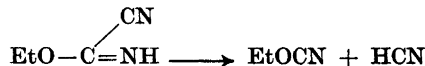
In a similar manner, hydrogen cyanide adds to ethyl cyanate forming ethyl cyanoimidofornate (ethyl imidonitrilo-oxalate), $\text{EtO}-\text{C}(\text{CN})=\text{NH}$, when ethyl cyanate is added to a *conc.* solution of potassium cyanide in water at 0°C, or better when dry hydrogen cyanide gas is led to an ethereal solution of ethyl cyanate with pyridine added as a basic catalyst. In the first reaction some urethan is also formed as the result of the base-catalyzed addition of water to the cyanate.¹

Nef² prepared ethyl cyanoimidofornate by the action of chlorine on a solution of potassium cyanide in ethanol-water. This reaction seems now to be best explained by the formation of cyanogen chloride and then ethyl cyanate.

The ethyl cyanoimidofornate so formed is unstable and decomposes at room temperature into ethanol and cyanogen:



These were identified by introduction of the decomposition products into a mass spectrometer. When the imidoester was heated in the inlet line, additional small peaks corresponding to the formation of some ethyl cyanate appeared:



Recently Martin⁸ reported the reaction between an aryl cyanate and potassium cyanide in acetone-water giving cyanogen. However, Martin did not isolate the intermediate imidoester.

EXPERIMENTAL

The mass spectral analyses were carried out with an Atlas CH4 mass spectrometer. The all-metal inlet system was maintained at 40° and the ionization chamber at 250°C. An electron current of 35 μA and an ionizing potential of 70 eV were applied.

*Diethyl imidocarbonate*¹ was introduced in the mass spectrometer and the mass spectrum was recorded. The imidoesters examined gave rise to small but easily detectable molecular ions. When the temperature of the inlet line was raised to 200–250°C, there appeared new peaks at m/e 56 (CH_2OCN^+) and m/e 71 ($\text{C}_2\text{H}_5\text{OCN}^+$) which are indicative of the presence of ethyl cyanate.⁵ When the spectrum so obtained was corrected for the presence of undecomposed diethyl imidocarbonate and ethanol, a spectrum typical of heated ethyl cyanate resulted. As mentioned in the preceding paper,⁵ ethyl cyanate is transformed partly into ethyl isocyanate, cyanic acid, and ethylene when the sample is heated in the inlet line of the mass spectrometer. The amount of cyanate present can be measured by the ratio of the peaks at m/e 56 and m/e 71. In pure ethyl cyanate this ratio is 1.68. In ethyl isocyanate the ratio is 1.33.⁵ When ethyl cyanate is heated in the inlet line, the ratio changes to 1.44. In the spectrum obtained on heating diethyl imidocarbonate to 200–250°C in the inlet line, the m/e 56: m/e 71 ratio is 1.5, indicating the presence of a mixture of ethyl cyanate and ethyl isocyanate. The ratios mentioned are highly reproducible, although the mass spectra of alkyl cyanates are as a whole somewhat variable.⁵

Ethyl propyl imidocarbonate was prepared by the method previously described.¹ Yield 56%. B.p. 56–58°C at 15 mm Hg. The compound was identified by its infrared and mass spectra. When it was heated in the mass spectrometer, new peaks at m/e 56, 70, 71, 84, 85, and 145 appeared. These correspond to the formation of ethyl and propyl cyanate⁵ and dipropyl imidocarbonate.

Ethyl cyanoimidoformate. a) Ethyl cyanate (0.50 g), dissolved in 10 ml of dry ether, was added to a solution of 10 g of potassium cyanide in 20 ml of water at 0°C in the course of $\frac{1}{2}$ h. The water layer was removed, extracted with 10 ml of ether and the combined ether layers dried with sodium sulfate at 0°C for $\frac{1}{2}$ h. After filtering the sodium sulfate, the ether was removed *in vacuo* and ethyl cyanoimidoformate distilled at 40–42°C at 20 mm Hg (lit.² 42°C). Yield 0.21 g = 30%.

b) Ethyl cyanate (1.00 g) was dissolved in 10 ml of dry ether and placed in a flask at –5°C. The flask was kept dry with calcium chloride tubes. Dry hydrogen cyanide gas was passed into the solution for 10 min at a temperature of –5 to 0°C. Two drops of pyridine were then added and the addition of hydrogen cyanide continued for 10 min. After standing for $\frac{1}{2}$ h the ether was removed *in vacuo* and the ethyl cyanoimidoformate distilled as above. Yield 1.35 g = 98%. The compound was identified by its infrared and mass spectra. It can be stored without decomposition at –80°C. At temperatures above 0°C slow decomposition occurs.

When the decomposition products were introduced in a mass spectrometer a typical ethanol spectrum and an intense peak at m/e 52 ($(\text{CN})_2^+$) appeared. When the cyanoimidoformate was heated in the inlet line of the mass spectrometer additional small peaks at m/e 56 and m/e 71 appeared. These may be due to the formation of ethyl cyanate.

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