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Alkyl Cyanates

VIII. The Formation of Alkyl Cyanates from Alkyl Halides and Silver Cyanate

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The products of the reaction between alkyl halides and silver cyanate in various solvents have been analysed by gas chromatography. No cyanates are formed from primary alkyl iodides, but isopropyl iodide and *sec*-butyl iodide yielded the corresponding cyanates and isocyanates in almost equal amounts. *tert*-Butyl bromide formed *tert*-butyl isocyanate, together with 2-methylpropene and cyanic acid, which indicates that unstable *tert*-butyl cyanate is also formed. Only isocyanates were formed from triphenylmethyl chloride and silver cyanate or from alkyl iodides or sulfates and potassium cyanate.

The formation of alkyl cyanates is generally promoted by solvents of high polarity. However, some of these, especially dimethyl sulfoxide, transform the alkyl cyanates in a manner which has not yet been cleared up.

Alkyl cyanates have until now been prepared in four different ways. Decomposition of alkoxy thiatriazoles gives, in good yields, both alkyl and aryl cyanates.[1,2] The reaction between cyanogen bromide or chloride and an alcoholate has been used in the preparation of various aryl cyanates;[3] this method has, however, failed in the case of aliphatic cyanates except with some highly sterically hindered compounds [4] and with a few halogen substituted cyanates.[3] Alkyl cyanates are formed in the reaction between *O*-alkyl thiocarbamates and metal oxides such as HgO and Ag_2O.[5] Recently, one of us reported that isobutyl cyanate is formed in 3 % yield by the reaction between "cyanic acid" (*i.e.* the tautomeric mixture of HOCN and HNCO) and diazoisobutane; the main product was isobutyl isocyanate.[6]

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However, several possibilities still exist which may lead to alkyl cyanates, one of these being the reaction between alkyl halides and metal cyanates. This reaction is a well known route to alkyl isocyanates. [7–10] It is usually performed by heating the reactants in a solvent, or mixed with sand, until the initiation of a more or less violent reaction. The resulting isocyanate has always been isolated by means of distillation, which means that any cyanate, which may have been present in the crude product, has been isomerised.

Little interest seems to have been paid to the fact that the cyanate ion is an ambident ion, *i.e.* it may attack an incoming electrophile with either of its electronegative atoms. In the reaction with an alkyl halide it may thus form both alkyl cyanates and isocyanates. Since any alkyl cyanate formed by this reaction is isomerised by the above mentioned procedure, we have reinvestigated the reaction under controlled conditions in order to optimise the yield of cyanate possibly formed.

According to general belief,[11] the isocyanate should be formed in a displacement reaction with S_N2 character:

$$RX + OCN^- \longrightarrow RNCO + X^-$$

The alkyl cyanate should be formed in a nucleophilic substitution reaction with S_N1 character:

$$R^+ + OCN^- \longrightarrow R{-}OCN$$

the cyanate ion attacking with its most electronegative atom.

The first order reaction is known to be promoted by such ions as Ag^+ and Hg^{2+}, and silver cyanate was therefore used as the nucleophilic agent. As alkyl halides the iodides were used since these favour the S_N1 reaction. Carbonium ion formation is favoured in polar solvents and we have thus investigated the reaction in solvents with different polarity. No solvents containing hydroxy- or amino groups were, of course, used since these are reactive toward both cyanates and isocyanates. Alkyl cyanates are somewhat more stable in solution when ether, methylene chloride, and carbon tetrachloride are used as solvents. However, it might be expected that the rate of isomerisation is affected by solvents with a high polarity.

By means of infrared spectroscopy, the possible isomerisation of a 5 % ethyl cyanate solution was studied with nitromethane, nitrobenzene, acetonitrile, and dimethyl sulfoxide as solvents. Dimethyl sulfoxide caused rapid disappearance of the absorption band at about 2260 cm^{-1}, characteristic of cyanates and isocyanates, in the course of less than 20 min. Only a slight diminution of this band was observed in the course of several hours with nitrobenzene and acetonitrile as solvents. No change was observed in the course of 24 h when ethyl cyanate was dissolved in nitromethane and thus this solvent was chosen for most of the following experiments.

Primary alkyl halides such as propyl iodide and butyl iodide reacted very slowly with silver cyanate at room temperature with nitromethane as solvent and only the isocyanates were formed. At 30°, isobutyl bromide behaves as might be expected of a primary halide, slowly forming only isobutyl isocyanate.

At 80°, the reaction path is different. AgBr was precipitated immediately and *tert*-butyl isocyanate only was formed indicating that the reaction proceeds as a multistep reaction *via* a carbonium ion. *tert*-Butyl cyanate is expected to be very unstable since even *sec*-alkyl cyanates are unstable at this temperature decomposing to cyanic acid [12] and alkene in the course of about 30 sec. Thus no cyanate would be identified even were it likely to be formed. The above formation of *tert*-butyl isocyanate has been observed earlier by Brauner.[13]

Isopropyl iodide reacted with silver cyanate in nitromethane solution in the course of 5 min with 50 % conversion. About 10 % isopropyl cyanate and slightly less isopropyl isocyanate was formed. With 25 min reaction time, the conversion was completed and 20 % cyanate along with 19 % isocyanate was isolated. The other reaction products were not identified.

sec-Butyl iodide was treated with silver cyanate in a variety of solvents. No cyanate and only little isocyanate could be isolated when the reaction was carried out in dimethyl sulfoxide. With nitrobenzene and acetonitrile as solvents, about 2 % cyanate was formed together with the isocyanate and a number of unidentified products. Very little cyanate and isocyanate were formed in acetone. With ether or with pentane as solvent both *sec*-butyl cyanate (4 %) and isocyanate (30 %) were formed. The best yields of the cyanate were obtained with nitromethane as solvent, from which 8 % *sec*-butyl cyanate and 8 % *sec*-butyl isocyanate could be obtained.

It is thus seen that more polar solvents give comparatively higher yields of cyanate provided that the solvent has no catalytic effect on the isomerisation of the cyanate. However, the highest total yields of cyanates and isocyanates were obtained in ether and pentane, presumably due to the inertness of these solvents.

When *tert*-butyl bromide was mixed with silver cyanate at 0°C in pentane solution, gas was evolved and a white precipitate was formed. From the gas-chromatogram, a yield of 70 % *tert*-butyl isocyanate was calculated but the gas-chromatogram showed two additional peaks corresponding to 2-methylpropene and to cyanic acid. The white precipitate was identified as cyamelide formed from cyanic acid. Cyanic acid cannot be formed from *tert*-butyl isocyanate and, as mentioned above, *tert*-butyl cyanate may presumably even at low temperatures decompose into cyanic acid and 2-methylpropene. Thus, the formation of unstable *tert*-butyl cyanate seems likely.

Triphenylmethyl chloride is known to partly ionize in polar solvents and, because the S_N1 reaction is favoured, formation of triphenyl cyanate was expected. In ether solution, the reaction was completed in 5 min at 0°C, but the reaction product was identified as triphenylmethyl isocyanate. The IR spectrum of this compound showed the very intense absorption at approximately 2260 cm^{-1} characteristic of isocyanates; no absorption near 1100 cm^{-1}, characteristic of cyanates, was present.

This result may be explained as a consequence of partial ionization of the initially formed cyanate into carbonium ions and cyanate ions:

$$R-OCN \rightleftharpoons R^+ + OCN^- \longrightarrow R-NCO$$

Some investigations on the reaction between alkyl iodides and potassium cyanate were carried out. As expected, only alkyl isocyanates were formed, slowly, at room temperature.

A well known preparation of ethyl isocyanate from potassium cyanate, diethyl sulfate, and potassium carbonate was re-examined. The product from this reaction, performed with and without potassium carbonate, yielded only ethyl isocyanate and no ethyl cyanate.

EXPERIMENTAL

The reaction products were analysed gas chromatographically on a "Perkin-Elmer 116" instrument using a nonpolar column, Perkin-Elmer "O column". Identification of the peaks in the chromatogram and calculation of the amounts of cyanate/isocyanate were performed by adding known amounts of the respective alkyl cyanates and isocyanates to the reaction mixture. The analyses were performed at temperatures between 42.5°C and 80°C, depending upon the molecular weight of the cyanates. Thus, trimerisation products and other non-volatile products do not appear in the chromatogram. The percentages of the volatile components are calculated on the basis of the amounts of alkyl halides used in the experiments.

Propyl iodide and silver cyanate. Propyl iodide (0.85 g) was stirred with silver cyanate (0.78 g) in nitromethane (7.5 ml) at room temperature. Propyl isocyanate was formed in 75 % yield in the course of 70 h. Propyl cyanate could not be detected.

Isobutyl bromide and silver cyanate. Isobutyl bromide (5.3 g) and silver cyanate (10.0 g) were stirred in acetonitrile (40 ml) at room temperature. After 30 min the gas chromatogram showed a complex mixture containing mainly isobutyl isocyanate and no isobutyl cyanate. No attempt was made to identify the other components. When the reaction was carried out at 80°C, the process was completed in the course of 2 min and the mixture was found to contain *tert*-butyl isocyanate and no isobutyl cyanate or isocyanate.

Isopropyl iodide and silver cyanate. Isopropyl iodide (1.7 g) and silver cyanate (2.0 g) were stirred in nitromethane (15 ml) at room temperature. In the course of 25 min, all iodide had disappeared and 20 % isopropyl cyanate with 19 % isopropyl isocyanate had been formed. Another volatile compound, with a somewhat longer retention time, was not identified.

sec-*Butyl iodide and silver cyanate.* *sec*-Butyl iodide (3.0 g) was stirred with silver cyanate (3.3 g) in acetonitrile (15 ml) at room temperature. As mentioned in a preceding paper,[12] *sec*-butyl cyanate decomposes on heating and could thus not be analysed gas-chromatographically at 60°C and 1.8 atm (as was possible with the higher and lower homologues). However, we have found it possible to perform the analysis at 42.5°C and at 2.5 atm. After a reaction time at 30 min, it was found that about 30 % *sec*-butyl iodide was unchanged and about 24 % *sec*-butyl isocyanate together with 2 % cyanate had been formed, the rest being trimerised, since only very small peaks of unidentified compounds appeared in the chromatogram. Similar experiments were carried out with ether, acetone, dimethyl sulfoxide, nitromethane, and pentane as solvents. With nitromethane as solvent, 8 % *sec*-butyl cyanate and 8 % *sec*-butyl isocyanate were formed, the other products being polymerisation products. In pentane, 4 % of the cyanate and 30 % of the isocyanate had been formed after 30 min, while 65 % was unchanged *sec*-butyl iodide. Thus, very little polymerisation occurred, possibly because of the nonpolarity of this solvent.

tert-*Butyl bromide and silver cyanate.* *tert*-Butyl bromide (1.8 g) was stirred with silver cyanate (2.5 g) in 15 ml of hexane (or pentane) at 0°C. Evolution of gas started after the formation of silver iodide and a white precipitate of cyamelide (identified by its infrared spectrum) and continued after the solution had been filtered. The gas chromatogram showed the presence of *tert*-butyl isocyanate, cyanic acid, and 2-methyl-propene as the only identifiable compounds. It was not possible to assign any of the peaks to the unknown *tert*-butyl cyanate, nor to exclude it by this method. However, the IR spectrum of the mixture did not exhibit the characteristic

absorption of alkyl cyanates near 1100 cm^{-1}. The same result was obtained when performing the reaction at different temperatures varying from 0°C to −78°C, and with reaction times from 5 min to 8 h.

Triphenylmethyl chloride and silver cyanate. In one experiment, 2.79 g (0.01 mole) of triphenylmethyl chloride was stirred with 6.0 g (0.04 mole) of silver cyanate in 75 ml of nitromethane. The reaction was rapid and the mixture was stirred at 0°C for 10 min. After filtration and evaporation of the nitromethane, an oil was isolated which solidified on scratching. M.p. 88−89° from heptane. The m.p. is in accordance with that given for triphenylmethyl isocyanate (85−87).[14] The infrared spectrum showed a strong absorption near 2260 cm^{-1} characteristic of isocyanates and no absorption near 1100 cm^{-1} characteristic of cyanates. The same result was obtained with decreasing reaction time and decreasing amount of silver cyanate.

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