ISOCYANIC ACID

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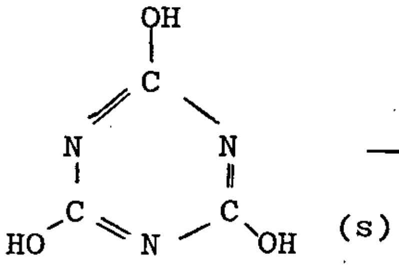
CHAPTER 1

INTRODUCTION

Compounds of the cyanate pseudo-halide group, -CNO, have been known for a long time and many molecular, organic cyanates find important applications in the plastics industry. In 1846, Liebig and Wöhler[1] showed that a compound having the molecular formula corresponding to that of the parent hydrogen pseudo-halide, HCNO, could be prepared by heating cyanuric acid, as in (1).



$$\longrightarrow \quad 3\ \mathrm{HCNO}_{(g)} \qquad (1)$$

It has since been shown that "cyanic acid" is often formed when compounds containing the amide group are heated, particularly in the industrially important processes involving carbamide[2] (urea), $H_2N.CO.NH_2$, and azodicarbonamide[3], $H_2N.CO.N{=}N.CONH_2$. However, because the "cyanic acid" is so reactive, particularly in its readiness to repolymerise, and difficult to keep, investigation of its properties has been fragmentary. Much of our knowledge is incomplete.

There has been much controversy concerning the molecular structure of HCNO. It is now generally accepted that the substance consists in the majority, if not in entirety, of molecules having the structure H-N=C=O. Thus, the substance is nowadays referred to as "isocyanic acid", the name "cyanic acid" being reserved for the previously supposed structure, H-O-C≡N. However, evidence has been put forward both for and against the existence of the tautomeric equilibrium in (2).

$$\mathrm{HOCN} \rightleftharpoons \mathrm{HNCO} \qquad (2)$$

The name "isocyanic acid" will be normally used throughout this thesis.

The polymerisation of isocyanic acid produces a mixture of the cyclic trimer, cyanuric acid, and cyamelide, whose structure is still not fully understood, but is thought to be of the long-chain type. There is still uncertainty over the mechanism of the polymerization and why the relative amounts of the two polymers change with temperature. Controversy over the mechanism of hydrolysis of isocyanic acid is not resolved and there is a general lack of knowledge of its reactivity in other circumstances. There is need for a review and critical appraisal of present knowledge about isocyanic acid as a preface to further work. This thesis sets out to provide such a review.

CHAPTER 2

Preparation and storage of isocyanic acid

A surprisingly wide range of methods of preparation have been used. Some involve the production of more or less pure isocyanic acid, gaseous or liquid, while others involve in situ production in a suitable solution. The former method is necessary for gas-phase experiments, but the latter has the advantage that polymerisation of isocyanic acid should be forestalled. Attempts to purify the isocyanic acid are not made in all cases.

2.1 Depolymerisation of cyanuric acid. This method was first used in 1846 by Liebig and Wöhler[1]. The method was developed to give a purer product and better yield by Linhard[4] and Herzberg and Reid[5]. Solid cyanuric acid, when heated, tended to sublime without reaction. The vapour had to be further heated to effect depolymerisation. Linhard warned against reheating the sublimate, as this produced large amounts of hydrocyanic acid. He overcame the problems caused by sublimation of cyanuric acid by using a one-metre long glass tube. The exit end having first been brought to red-heat, the tube was pushed through an electric tube-furnace at a rate matching that at which solid was being used up. A stream of dry nitrogen swept products into a receiver.

Herzberg and Reid modified the method as follows:

i) Preliminary heating of the cyanuric acid, in vacuo, to 200°C was necessary to remove water. Failure to observe this precaution led to the formation of some ammonia during the depolymerisation.

ii) The depolymerisation was carried out in vacuo.

The cyanuric acid was vapourised slowly at a relatively low temperature (450°C) and then the gas stream was passed through a hotter tube furnace (700°C) to effect depolymerisation.

iii) The bulk of the HNCO was collected in a trap at -80°C and the CO_2, which formed in "appreciable quantities", was passed on to a second, guard trap cooled by liquid nitrogen. This reduced the fractionation time and gave a purer product.

Linhard, and Herzberg and Reid, further purified HNCO as follows: HCN was removed by oxidation with silver oxide and a final drying with phosphorus (V) oxide was employed. The HNCO was then distilled from a bath at -30°C. Herzberg and Reid considered their product to be better than 99.5% pure. Linhard warned that isocyanic acid produced from commercial cyanuric acid regularly polymerised explosively at -30°C when attempts were made to distil it. The problem was obviated by double crystallization of the cyanuric acid from hot water.

Schmidt[6] recently measured the pressures of cyanuric acid vapour at various temperatures in the range 295-360°C. He confirmed that cyanuric acid must first be vapourised and then the depolymerisation takes place in the gas phase. Schmidt also measured the densities of cyanuric acid vapour at various temperatures (see Chapter 5) and calculated values of the equilibrium constant, Kp, for (3).

$$(HNCO)_{3\,(g)} \rightleftharpoons 3HNCO_{(g)} \qquad (3)$$

If the total pressure is 1 atm, then in terms of partial pressures,

$$P_{HNCO} = 1 - P_{(HNCO)_3}$$

and

$$Kp = \frac{(1 - P_{(HNCO)_3})^3}{P\ (HNCO)_3} = 74.3 \text{ atm}^2 \text{ at } 434^\circ C$$

(The value of Kp is from Table 1, Chapter 3).

Solving this equation gives $P_{(HNCO)_3} = 0.013$ atm

and $P_{HNCO} = 0.987$ atm

This means that, at 434°C, conversion to isocyanic acid is 98.7% complete. A substantially higher temperature, like that used by Herzberg and Reid, is unlikely to increase the yield to any useful extent, because at such a temperature dissociation of HNCO itself starts to become significant. The pyrolysis of HNCO, in the temperature range 550-700°C and at pressures between 5 and 20 mm of Hg, has been studied by Back and Childs[7]. The process is complex, CO, N_2, H_2, HCN and CO_2 being all obtained as products. (See Chapter 6). The reaction was found to be very slow at 500°C, but complete within ten minutes at 700°C. Herzberg and Reid[5], using 700°C to effect depolymerisation of cyanuric acid, obtained CO_2 in "appreciable quantities", but Smith and Jonassen[8], using 450°C, obtained only 3% CO_2, together with a "very small" amount of HCN and a trace of H_2O. Smith and Jonassen found that raising the temperature between 450 and 500°C produced markedly increased amounts of CO_2. A temperature of about 450°C seems the optimum for production of isocyanic acid from cyanuric acid vapour.

Other workers[9], using a similar method, dissolved the liquid HNCO in the cold trap in ether. Solutions were filtered to remove suspended cyanuric acid and cyamelide.

2.2 <u>Acidification of an alkali cyanate</u>. A variety of acids have been used and various methods for isolation of HNCO and for in situ generation have been described.

Smith and Jonassen[8] heated a mixture of potassium cyanate and potassium hydrogen sulphate. "Large amounts" of CO_2 were also produced and, because of this, they considered the method to be inferior to the depolymerisation of cyanuric acid. (See 2.1 above). However, Groving and Holm[10], who treated finely powdered sodium cyanate with dry hydrogen chloride, found this method gave fewer impurities than the depolymerisation of cyanuric acid.

In the method of Groving and Holm, metered flows of HCl and N_2 were mixed before flowing through a glass tube evenly packed with sodium cyanate which had been finely ground. They found that potassium cyanate did not react. During the reaction, a warm zone (about 70°C) moved along the tube. When the exit gas was tested with silver nitrate, no HCl was detected until the warm zone had moved to the far end of the tube, which took about ten minutes. Gas was collected before the appearance of HCl. Mass spectroscopy showed CO_2 to be the only impurity. The HNCO was dissolved in dichloromethane at -80°C. Oertel, Holtschmidt and Zenner[11], in a patent, claimed 85-95% yields of HNCO by similar methods, in which HCl was passed into suspensions of alkali metal cyanates in inert organic liquids.

Werner and Gray[12] described a method of generating HNCO in situ. Either dry HCl was passed into a suspension of KOCN in the molten reagent (a urethane in this case) or KOCN was added to a solution of the urethane in an anhydrous solvent (e.g. ether, dioxan) which had been saturated with HCl. Cummins[13] patented a similar method, in which NaOCN was added to an aqueous solution containing the reagent (RR$'^{S}$.C:NOH) and KCl. The mixture was then brought to pH3.

Bailey and co-workers[14] favoured the use of glacial acetic acid as solvent for the in situ generation of HNCO, while Nagayama et al patented[15] a process in which trichloroacetic acid in hexane was added to a warm mixture of NaOCN in hexane and the HNCO gas bubbled through a hexane solution of a reagent.

In earlier work than that cited in ref.11, Werner and Fearon[16] prepared HNCO from KOCN and nitric acid at 0°C.

2.3 Methods employing urea or its derivatives. Schiltknecht[2] has shown that, in the thermal decomposition of urea at normal pressure, the primary process is formation of isocyanic acid and ammonia only, as in (4).

$$H_2N.CO,NH_{2(s)} \rightleftharpoons HNCO_{(g)} + NH_{3(g)} \qquad (4)$$

The reaction offers a potential method of obtaining pure HNCO at a temperature of 200°C or less, if recombination with ammonia, as in (5)[2], can be prevented.

$$xHNCO + yNH_3 \longrightarrow \text{-CO-NH-CO-NH-CO-NH-} + yH_2O \qquad (5)$$

This might be achieved by mixing with the urea something like anhydrous copper (II) sulphate, zinc chloride or citric acid to "mop-up" the ammonia. It is found[32] that when mixtures of urea and anhydrous copper sulphate are heated, the mixture froths and a dark blue solid results. The yield of HNCO might be reduced by secondary reactions, like (6), (7) and (8).

$$HNCO + H_2N.CO.NH_2 \longrightarrow H_2N.CO.NH.CO.NH_2 \qquad (6)$$

$$3HNCO \rightleftharpoons C_3N_3(OH)_3 \qquad (7)$$

$$HNCO + H_2O \rightleftharpoons CO_2 + NH_3 \qquad (8)$$

However, as Schiltknecht[2] points out, the biuret formed in (6) decomposes rapidly above 200°C to give HNCO and ammonia. The other reactions can be forestalled by sweeping reaction products into a cold trap by a stream of nitrogen or use of a vacuum pump.

Urea is used as raw material in Verstegen's patented method[17], but is vapourised before heating at 350-500°C. It seems likely that cyanuric acid is formed first and then depolymerised. However, in the patented methods of Takahashi and Ozaki[18] and Schmidt et al[19], more moderate temperatures are used. The apparatus is designed to allow removal of ammonia and an inert gas stream is used to sweep out and dilute HNCO.

Davis and Blanchard[20] recommend an aqueous solution of nitrourea as a source of HNCO. Decomposition occurs when the solution is heated, according to (9).

$$NH_2.CO.NH.NO_{2(aq)} \longrightarrow HNCO_{(aq)} + NH_2NO_{2(aq)} \qquad (9)$$

The decomposition is accelerated when bases are present, but is inhibited by acids. The nitramide formed decomposes to give nitrogen (I) oxide, as in (10), so the solution is easily purified.

$$NH_2NO_{2(aq)} \longrightarrow N_2O_{(g)} + H_2O_{(l)} \qquad (10)$$

The method is clearly useful for in situ generation of HNCO in aqueous solutions of reagents.

According to a patent[21] by Roberts and Christmann, HNCO can be made by passing urea, biuret or cyanuric acid into a molten alkali metal cyanate at 325-600°C.

2.4 Methods employing carbamic acid derivatives. A Stauffer Chemical Co. patent[22] describes the removal of hydrogen halide from a carbamoyl halide, as in (11).

$$H_2N.COX \longrightarrow HNCO + HX \qquad (11)$$

The reagent used must have basic properties sufficient to remove HX, but not so strong as to promote polymerisation of

HNCO. Lewis bases are suitable, especially ethers as when reaction is complete and the mixture is distilled, a main fraction is obtained which consists of a complex of HNCO with the ether.

The pyrolysis of alkyl carbamates is described in a patent by Godfrey[23]. This takes place according to (12).

$$NH_2.COO.R \longrightarrow HNCO + ROH \qquad (12)$$

The alkyl carbamate is vapourised and heated at about 400°C and the pyrolysis products swept by nitrogen into a cold trap. The pyrolysate is fractionated at -40 to -20°C in vacuo to give HNCO.

2.5 <u>Other methods</u>. Laude used a solution of potassium manganate (VII) in concentrated ammonia, with a copper powder catalyst, to oxidise carbon[24] and a large number of carbon compounds[25]. Up to thirty hours' reaction time was needed and the yields of HNCO were not good.

Fossē[26] had earlier used a similar method, oxidising methanoic or oxalic acid amides. Fossē, de Graeve and Thomas[27] also described the action of phosgene on ammonia, but again yields of HNCO were not good.

2.6 <u>Storage of isocyanic acid</u>. At ambient temperature and above, isocyanic acid polymerises at an appreciable rate (see Ref. 8 and Chapter 5.3). Because of this, it cannot be stored at such temperature, either in the gas phase[5,8] or in concentrated solutions in organic solvents[10,28], although Nelson[28] found that dilute solutions (10^{-2} to 10^{-3} mol/dm^3) in tetrachloromethane showed no deterioration over 2-3 days. Michael and Hibbert[29] state that solutions in ether, toluene and trichloromethane are more stable than free HNCO. The Stauffer Chemical Co. patent[22] ascribes the stability of HNCO in ether solutions, particularly in 1,2-dimethoxy ethane, to complex formation. (See Chapter 2.4). This supposition is supported by the work of Hoover and Rothrock[30], who found that HNCO and ether form a maximum-boiling point azeotrope. Such negative deviations from Raoult's law can often be explained by compound formation.

In order to store HNCO for longer periods of time, it is necessary to lower the temperature so that the rate of polymerisation becomes insignificant. Groving and Holm[10] found that, at room temperature, the infra-red spectrum of a solution of HNCO in dichloromethane decreased in intensity slowly only one hour after the solution had been prepared. This decrease in intensity was accompanied by formation of a white precipitate. However, at -80°C, the spectra of concentrated solutions did not show any change "in the course of some hours". Winnewisser and Winnewisser[31] recommended that, to prevent polymerisation of HNCO in the vapour phase, the temperature should not be greater than -23°C. At this temperature, the saturated vapour pressure is about 75mm Hg. (See Ref.4 and Chapter 3). It was found that HNCO, diluted with argon, could be kept at -30 to -40°C for up to 30 hours with no noticeable polymerisation or decomposition. At dry ice or liquid nitrogen temperature, HNCO is solid. (See Chapter 3) and the saturated vapour pressure is negligible[4]. Substantial amounts can be stored thus indefinitely without change[32].

CHAPTER 3

Physical properties and structure of isocyanic acid.

3.1 Melting point. Both the standard handbooks[33,34] give -80°C as the melting point of HNCO but the original source is obscure. Von Dohlen and Carpenter[35] quote a figure of -80°C, but give no details. However, Linhard[36] obtained a value of -86°C using Beckmann's method (depression of freezing-point of a solvent).

3.2 Boiling point. This is given as 23.5°C at 760mm Hg[33] and -64°C at "0mm Hg"[34]. Again, the original sources are obscure. By extrapolation from vapour pressure data, Linhard[4] obtained a value of 23.5°C at 760mm Hg.

3.3 Density. This is given[33,34] as 1.140g/cm^3 for the liquid. The original source is Troost and Hautefeuille[37].

Van Dohlen and Carpenter[35] obtained an approximate figure for the solid of 1.40g/cm^3 at liquid nitrogen temperature.

3.4 Vapour pressure. Linhard[4] made several series of vapour pressure measurements in the temperature range -76 to -6°C. The data all showed good agreement with Nernst's theoretical equation. Selected data are given in Table 1.

Table 1 Some saturated vapour pressures of HNCO

Temperature/deg C	P_{HNCO}/mm of Hg
-76.27	1.28
-64.36	3.97
-54.93	8.80
-45.43	18.02
-35.93	35.11
-23.97	74.72
-14.97	125.19
- 5.94	201.99

3.5 Crystal Structure. Von Dohlen and Carpenter[35] found two forms of solid isocyanic acid. The super-cooled liquid gave a low temperature form. This gave the high-temperature form on warming, with a transition temperature of about -100°C, but the high-temperature form did not give the low-temperature form on cooling. The high-temperature form was found to be orthorhombic, with the most probable space-group being Pnma.

3.6 Thermodynamic properties. The 1974 supplement to the JANAF Thermochemical Tables[38] gives a comprehensive tabulation of values of C_p^o, S^o, $-(G^o - H_{298}^o)/T$, $H^o - H_{298}^o$, ΔH_f^o, ΔG_f^o and log Kp for HNCO at temperatures in the range 0-6000K. ΔH_f^o (i.e. at zero K) is given as -23.6 k cal mol^{-1} and $\Delta H_{f(298.15)}^o$ as -24.3 K cal mol^{-1}. The values are derived from the results of Okabe[113] on the onset of photodissociation of HNCO. Values of heat capacity and entropy are calculated from the vibrational frequency determinations of Herzberg and Reid[5].

Compernolle[43] has recently obtained a value of ΔH_f^o of $- 25 \pm 3$ k cal mol^{-1}, from mass spectrometric measurements.

Thermodynamic data for the dissociation of HNCO in aqueous solution are discussed in Chapter 7.

3.7 Spectra. The spectra of isocyanic acid have been extensively studied, particularly the microwave spectrum (for cosmological detection) and the ultra-violet spectrum (for elucidation of molecular properties). Only those features having a laboratory analytical application will be dealt with here.

3.7.1 Ultra-violet. The absorption spectrum in this region was first investigated by Woo and Liu[39]. They discussed the products and energies of dissociation of HNCO. The absorption spectrum has since been photographed with high resolution in the range 200-280nm by Dixon and Kirby[40], who list band wavelengths in four progressions, and by Rabalais, McDonald and McGlynn[41].

3.7.2 Infra-red. The wavenumbers of the absorptions due to the six fundamental vibration frequencies, as determined by Herzberg and Reid[5], are given in Table 3.

Table 3. Wavenumbers of the fundamental vibrations of isocyanic acid.

Wavenumber, cm^{-1}	572	670	797	1327	2274	3531

Combinations and overtones of the fundamental frequencies also give rise to bands. The main features of the I.R. spectrum have subsequently been confirmed by other workers[28,31,42].

3.7.3 Proton nuclear magnetic resonance. Nelson, Spratt and Nelson[42] found a broad triplet at $\tau = 6.65$ (at infinite dilution in $C\,Cl_4$). For the ^{14}N-H spin coupling, $J=64\pm1$ Hz. There were 200 Hz side-bands.

3.7.4 Mass spectrum. The mass spectrum of isocyanic acid has been obtained by several workers[8,43,44,45]. The main peaks are listed and identified in Table 4.

Table 4. Main peaks in the mass spectrum of isocyanic acid.

m/e:	15	29	42	43
Identity:	NH^+	HCO^+	NCO^+	$HNCO^+$

3.8 Structure. The wave numbers of the six fundamental vibrations giving absorption in the infra-red are given in 3.7.2 above. The vibrational assignments and the three moments of inertia have been unequivocably established[5,28,30] and indicate the isocyanic acid structure, H-N=C=0. One of the moments of inertia is very small (considerably less than that of free NH) indicating that the three heavy atoms N-C-O are in a nearly straight line, with the N-H bond forming an angle to that line which is much less than 90°.

Other evidence for the presence of an N-H bond is given by diffuse absorption bands observed in the UV spectrum by Woo and Liu[39]. According to Goubeau[46], the Raman spectrum of the liquid shows isocyanic acid to have the keto-form because the strongest frequency is at 1307 cm^{-1}, similar to the isosteric CO_2. The force constants calculated from the two vibrational frequencies appearing in the Raman spectrum are in almost exact agreement with those calculated theoretically for pure HNCO[46]. Alkyl, silver and mercury "cyanates" have similar spectra, while K, Me_4N and Pb cyanates have different spectra, showing the presence of OCN^- in the latter three.

3.9 Tautomerism.

The spectral evidence, especially Raman, sets a very low limit on the concentration of HOCN which could be in tautomeric equilibrium with HNCO (equation (2) Chapter 1). The existence of such a tautomerism was first postulated by E.A. Werner[47] who supposed that, on hydrolysis[16], cyanic acid gave ammonium cyanate and isocyanic acid gave urea while on polymerisation[16,48], cyanic acid gave cyamelide and isocyanic acid gave cyanuric acid. In each case, the ratio of amounts of products was assumed to indicate a ratio of 60% HOCN to 40% HNCO at 0°C. This has since been found to be wildly wrong.

Huckel[49] contended that, although tautomerism would be expected for cyanic acid, all its reactions could be explained by the structure H-N=C=O. Hantzsch[50] disagreed because his alkylation experiments produced, inter alia, some of the oxy-ester of cyanuric acid. This, he suggested, can only be formed by polymerisation of the genuine oxy-ester of cyanic acid, $CH_3 - O - C \equiv N$, proving the tautomerism of cyanic acid.

3.9.1 Evidence from vapour pressure measurements.

Linhard[4] used his vapour pressure data (see chapter 3.4) to calculate a value of Trouton's constant. The value obtained was higher than that expected from Nernst's revised form of

Trouton's rule and it was inferred that isocyanic acid is not a normal liquid. This is usually explained by assuming association of molecules in the liquid phase, either physical or chemical, or tautomeric transformation.

In a later paper[51], Linhard dismissed the work of Hantzsch and considered that all the reactions of "cyanic acid" could be explained by the formula H-N=C=O. A lengthy discussion was given of the electron system of HNCO and changes in it likely to occur.

3.9.2 Evidence from the reaction with diazobutane.

Recently, Groving and Holm[10] set out to prove the existence of HOCN. Reaction with diazo-isobutane gave a complex reaction mixture of about fourteen components. When separated by gas-liquid chromatography, the main component was isobutyl isocyanate, but there was also a "negligible" peak ascribed to isobutyl cyanate. This was confirmed by infra-red spectroscopy. This happened whether the reactants were in dichloromethane solution or in the gas phase. The relative proportions of isocyanate and cyanate were in the ratio 100:3. However, the relative yields of isocyanate and cyanate are not simply related to the tautomeric proportions of HNCO and HOCN. Those yields depend both on the rates which each component is formed from the other and on the rates at which each component reacts with diazo-isobutane. This is an elementary point forgotten by Werner.

3.9.3 Evidence from pKa values

Values of pKa for HNCO have recently been calculated from a theoretical formula by Finkel'shtein and Moncharzh[52]. From this, a value of 3.3 was obtained for the logarithm of the equilibrium constant for "the tautomerization of HNCO to CNOH".

This can be interpreted[52] as predicting an equilibrium ratio for HNCO to HOCN of 2,000:1.

3.10 Association

Evidence for the existence of intermolecular hydrogen bonding in liquid isocyanic acid, via the N-H group, is given by the large shift in the Raman N-H stretching frequency on the transformation from vapour to liquid and the additional shift on the transformation from liquid to solid [5,46]. X-ray diffraction analysis[35] of the high temperature solid indicates zig-zag chains of HNCO molecules, joined by N-H----N hydrogen bonds. (The stronger N-H----O bonds could be present in the low temperature solid).

CHAPTER 4

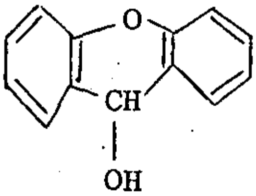
METHODS OF ANALYSIS FOR ISOCYANIC ACID

4.1 Classical quantitative methods.

Two general methods are described in the literature. One involves conversion of HNCO to urea which is then determined by the xanthydrol method; the other involves precipitation of silver isocyanate.

4.1.1 The xanthydrol method.

Xanthydrol is 9-hydroxy xanthene, $C_{13}H_{10}O_2$ (13).



(13)

Two molecules condense with one of urea to form dixanthylurea, $CO(NH.C_{13}H_9O)_2$. The gravimetric xanthydrol method was first used by Fossé[53] for the determination of small quantities (0.002-0.0025g) of urea. It was adapted for the determination of HNCO by his co-workers, e.g. Laude[24].

An approximation is made in Fossé's method, giving rise to low results[53] e.g. an error of -1% for a 0.5% solution of urea. At lower concentrations, the precipitate contains sufficient xanthydrol as impurity to give high results[53], e.g. +1 to 2% for a 0.2% solution of urea. For HNCO determination, conversion to urea must first be effected (see Chapter 7). This will cause further error.

A titrimetric finish was employed by Luck[60]. The dixanthylurea precipitate is dissolved in dilute sulphuric acid and the solution is titrated at 70-75°C with standard potassium manganate (VII) solution. The method is said to determine 0.1mg of urea with an error of ±5%. A colorimetric method, as modified by Engel and Engel[54] was used to monitor HNCO levels by Dirnhuber and Schütz[55]. The dixanthylurea urea precipitate is dissolved in 50% sulphuric acid and the absorbance measured at 420nm. Engel and Engel were able to measure very low levels of urea with an accuracy of about ±1%, but at very low levels the precipitate took up to 24 hours to form.

4.1.2 The silver isocyanate method.

Laude[24] used a gravimetric finish to determine HNCO in liquor from the ammoniacal manganate (VII) oxidation of carbon. Silver isocyanate is precipitated from a solution acidified with nitric acid. After double recrystallization from hot water, the AgNCO is treated with excess ammonium chloride and dilute ammonia. The solution is neutralized and the silver chloride formed filtered off and weighed. Figures given by Laude[24] evince the purity of the silver isocyanate and its quantitative conversion to silver chloride, but no attempt was made to confirm recoveries of standard additions of HNCO to the oxidation liquor to estimate accuracy at the initial precipitation stage.

Werner and Fearon[16] used a volumetric finish. The precipitated AgNCO is dissolved in excess dilute nitric acid and the cyanate ion titrated with standard silver ion solution by Volhard's method. No estimate of accuracy or precision was given.

4.2 American Chemical Society standard method (1948) for isocyanates[61].

A weighed sample of an organic isocyanate is treated with a solution of 1-aminobutane in dioxane. A substituted urea is formed, according to (14). (See Chapter 9).

$$R.NCO \quad + \quad C_4H_9NH_2 \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}C_4H_9 \qquad (14)$$

After reaction is complete, excess amine is extracted into water and determined by titration with standard acid to a methyl red end-point. Oertel, Holtschmidt and Zenner[11] have applied the method to the determination of isocyanic acid itself in solution in inert, organic solvents like acetone. The results were satisfactory when compared to those obtained by non-specific methods, viz gasometric determination of the CO_2 produced by reaction of HNCO with dilute nitric acid; and Kjehldahl nitrogen determination. The 1-aminobutane method is probably more accurate, rapid and easy to perform than either the xanthydrol or silver isocyanate methods because a non-aqueous solvent is used and low temperature conditions are possible, precluding side-reactions of HNCO. Comparative data between the different methods are not, however, available.

4.3 Classical qualitative methods

Conversion to urea and subsequent formation of a precipitate with xanthydrol (see 4.1.1 above) has been used[16,27] as a sensitive test to detect HNCO. One part of urea in 10,000 in aqueous solution produces a precipitate within 15 seconds and one part in 800,000 within about ten minutes, but the method is tedious for smaller traces.

Two very sensitive colour tests have been devised. Werner[56] used a solution of a copper salt containing a little pyridine. HNCO (not cyanate; alkaline solutions must be neutralised) gives a lilac-blue precipitate. If chloroform be added, a sapphire-blue colour is obtained in the organic layer. One part of HNCO in 20,000 in aqueous solution can be detected. Fossé et al[24,27] treated sample solutions with potassium and ethanol and then triturated a few drops with cobalt acetate. The presence of cyanate was shown by a strong blue colour, due to the formation of $Co(OCN)_2.KOCN$.

Such methods, requiring as they do an aqueous solution, are rendered unnecessary by the availability of spectral methods, which are more rapid and convenient and are non-destructive.

4.4 Spectral methods.

The features of the ultra-violet, infra-red, proton - N.M.R. and mass spectra of HNCO have been described in Chapter 3.7. All, except U.V., have been used to check on the purity and stability of HNCO samples. The I.R. technique is particularly convenient, especially for gaseous samples, because the I.R. spectrum of gaseous HNCO is simple and distinctive. The use of this technique for semi-quantitative study of isocyanic acid consumption in reactions has been demonstrated[10,32].

CHAPTER 5

THE POLYMERISATION OF ISOCYANIC ACID

Even at temperatures below 0°C, isocyanic acid is unstable with respect to polymerisation. In the gas phase at high temperatures, polymerisation leads to cyanuric acid as the sole product[16], as in (15).

$$3HNCO_{(g)} \rightleftharpoons C_3N_3(OH)_{3(s)} \qquad (15)$$

At lower temperatures, cyamelide is also formed and becomes the predominant product of liquid phase polymerisation. (See 5.3 below). Cyamelide is thought[57] to be a linear polymer of alternating -CO- and -NH- groups, with carbonamide, $-CONH_2$, end groups. Davis and Blanchard[20] proposed the formation of a dimer, as in (16), as an explanation of certain of the properties of isocyanic acid in aqueous solution.

$$2HNCO_{(aq)} \longrightarrow HN_2.COO.CN_{(aq)} \qquad (16)$$

Formation of such a dimer, although it may only have the briefest of existences, is an obvious first step in any mechanism of polymerisation of pure isocyanic acid.

5.1 Equilibrium constant

Using a modified Victor Meyer apparatus, Schmidt[6] measured the densities of vapours produced from cyanuric acid samples at temperatures in the range 638-707K (365-434°C). Molecular weights were calculated from the vapour densities. The vapours were equilibrium mixtures of isocyanic acid, cyanuric acid and cyamelide but, because the heats of vapourisation of cyamelide and cyanuric acid were found to be the same (see below), the molecular weight values could be used to calculate equilibrium constant values for the depolymerisation of cyanuric acid (the reverse of reaction (15)).

Schmidt's data are given in Table 5.

Table 5. Equilibrium constants for the reaction

$$C_3N_3(OH)_{3(g)} \rightleftharpoons 3HNCO_{(g)}$$

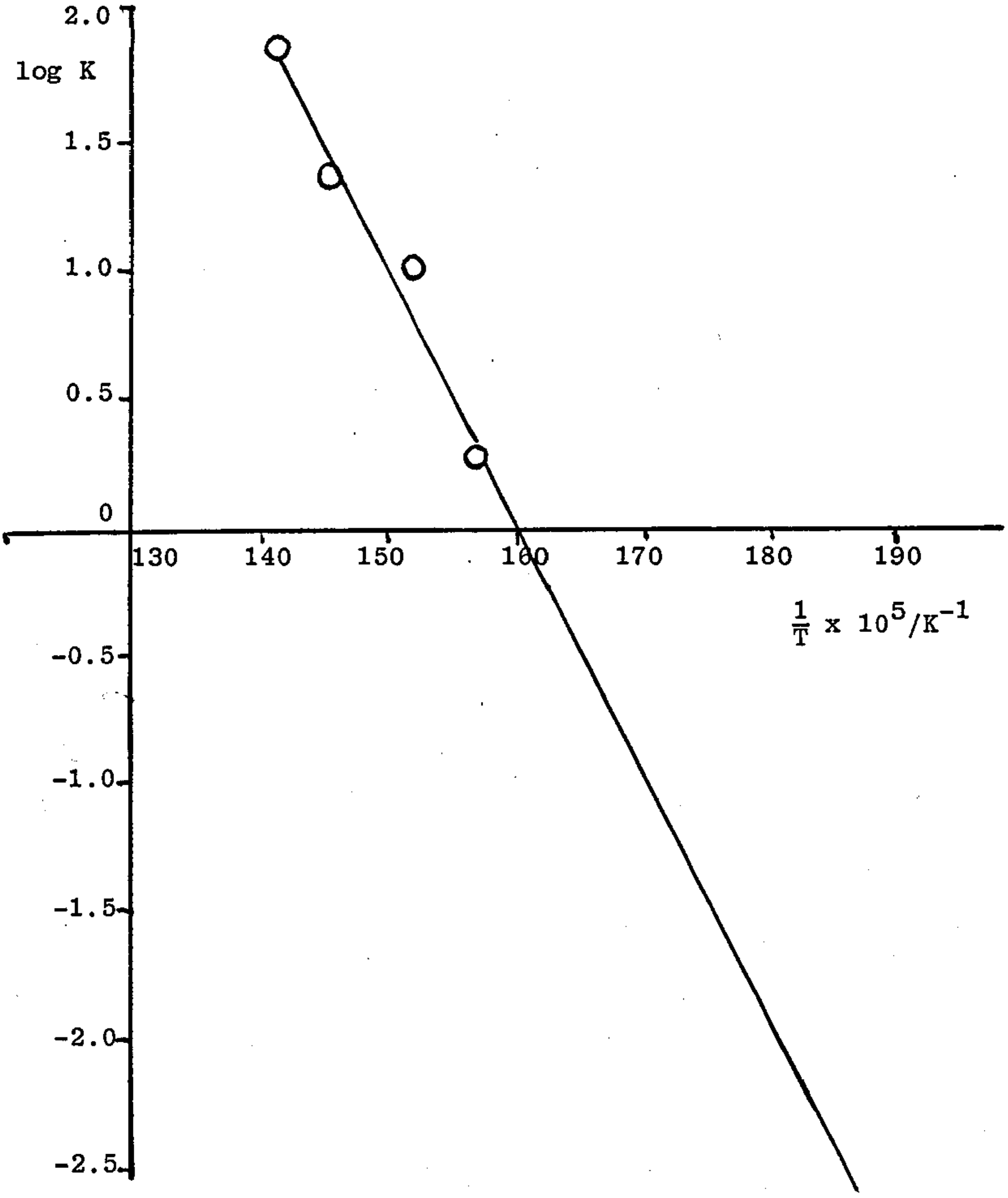
$t/^{o}C$	Molecular Weight	K/atm^2
365	63.2	1.915
389	50.0	9.63
413	45.9	27.45
434	44.25	74.3

It has already been shown (Chapter 2.1) that, at 434^{o}C, the point of equilibrium is so much in favour of HNCO that it forms 98.7% of the vapour at that temperature. It is difficult to extrapolate these limited data at high temperatures to obtain a value of the equilibrium constant at room temperature, but it seems that $K \simeq 10^{-18}$ atm^2 at 298K. At the same time, the vapour pressure of cyanuric acid is extremely low. Schmidt[6] measured vapour pressures of cyanuric acid at different temperatures. It was found that these conformed to expression (17).

$$\log p = -\frac{6740}{T} + 12.5 \qquad (17)$$

Expression (17) shows the vapour pressure of cyanuric acid at 298K (25^{o}C) to be $\sim 10^{-10}$ atm ($\sim 10^{-7}$mm Hg). It must be emphasised that these figures only relate to vapour phase polymerisation of isocyanic acid, but give an indication of how thermodyamically unstable isocyanic acid is with respect to solid cyanuric acid. Substitution in expression (17) shows that the "sublimation point" of cyanuric acid (i.e. temperature at which vapour pressure is 1 atm) is 539K (266^{o}C). Extrapolation of a plot of the Van t'Hoff equation

FIG.1: Van't Hoff equation plot for the gas phase depolymerisation of cyanuric acid.



(log K vs$\frac{1}{T}$) for Schmidt's data, here shown in Table 5, (see fig. 1), gives the value of K at 539K as $\sim 4 \times 10^{-3}$atm^2. These data show how important it is to raise the temperature of cyanuric acid vapour in order to get a good yield of isocyanic acid from it. (See Chapter 2.1). The reaction becomes thermodynamically reversible ($\Delta G = 0$; $K = 1$) at 623K (350°C) (interpolated from Fig. 1) and at higher temperatures, cyanuric acid vapour becomes rapidly more and more unstable with respect to isocyanic acid. At 450°C, the vapour phase is nearly 100% isocyanic acid, as previously shown (See Chapter 2.1). When the gas is frozen at liquid nitrogen temperature, the isocyanic acid (now solid) is thermodynamically unstable with respect to polymerisation, but the rate of attainment of equilibrium will be extremely slow.

For the process (18), the equilibrium constant is equal

$$\text{cyanuric acid (solid)} \rightleftharpoons \text{cyanuric acid (vapour)} \qquad (18)$$

to the vapour pressure of cyanuric acid, p, the activity of the solid being unity. The Van t'Hoff equation has the form (19).

$$\log p = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{R} \qquad (19)$$

From Schmidt's empirical expression (ref. 6 and see (17) above), (20) is evident.

$$\frac{\Delta H^o}{2.303R} = 6740 \qquad (20)$$

Hence a value of enthalpy change of vapourisation for cyanuric acid of 30.8 kcal mol^{-1} was obtained by Schmidt. By the same method, the enthalpy change of vaporisation of cyamelide was found to be 29 ± 1 kcal mol^{-1}.

Schmidt[6] also obtained a value of ΔH^o from a graph of Van t'Hoff's equation (log K versus $\frac{1}{T}$) for the gas phase depolymerisation of cyanuric acid. Schmidt quotes a value of 55 kcal mol^{-1} but replotting of his data (fig. 1) gives a value of 42.10 kcal mol^{-1}, much nearer to that obtained[6] from standard enthalpy change of formation data, viz 45.95 kcal mol^{-1} at 298K.

5.2 Proportions of cyanuric acid and cyamelide in the polymerisate.

E.A. Werner and Fearon[16] investigated the proportions of the products in the polymerisate from liquid isocyanic acid in the temperature range 0-20°C. Their results are shown in Table 6. In several experiments where the acid polymerised when the containing vessel was plunged into water at 20°C, the temperature rose suddenly to about 70°C. The proportion of cyanuric acid was found to be 70-80%, much higher than that quoted in the table, for experiments where this sudden rise in temperature did not occur. The temperature of 20°C is very close to the boiling point and the anomalous observations were probably caused by reaction initiating in the gas phase. This earlier work was extended to lower temperatures (0 to 20°C) by A.E.A. Werner and Gray[48]. Their results are also shown in Table 6. They confirm that the proportion of cyamelide increases with decreasing temperature.

Table 6. Proportions of cyanuric acid and cyamelide in polymerisates from liquid isocyanic acid.

Ref.	Temp. of polym. /°C	Wt. of polymeride /g	Cyanuric acid found/g	% comp. of polymeride	
				Cyamelide	Cyanuric Acid
16	20	0.24	0.136	42.92	57.08
16	10	0.105	0.045	57.27	42.73
16	5	0.42	0.174	58.58	41.42
16	0	0.53	0.216	59.25	40.75
48	0	0.541	0.218	59.6	40.4
48	0	0.532	0.219	58.8	41.2
48	-10	0.562	0.213	62.1	37.9
48	-10	0.550	0.202	63.2	36.8
48	-15	0.609	0.206	66.1	33.9
48	-15	0.652	0.223	65.8	34.2
48	-20	0.448	0.135	69.8	30.2

Kern, Paul and Mehren[57] measured the proportions of cyamelide in polymerisates obtained at 15°C from isocyanic acid solutions of different concentrations in benzene. They showed a graph of percentage cyamelide against percentage of the total change completed during the course of polymerisation. The proportion of cyamelide increased as the polymerisation proceeded. Large fluctuations occurred in the results, which were ascribed to insufficient purification of the isocyanic acid. It was found that the course of reaction was very dependent on small amounts of impurities. (See 5.3 below).

5.3 Kinetics of polymerisation

Kern, Paul and Mehren[57] also obtained graphs of weight of polymerisate against time for solutions of isocyanic acid in benzene. Three different concentrations were investigated, all at 15°C. Many substances were found to have inhibiting effects and many were positive catalysts.

5.3.1 Inhibitors

Two groups of inhibitors could be distinguished by different types of effect shown:

i) Hydroxy-compounds, e.g. dodecanol, isoborneol, benzyl alcohol and cyclohexanol. There was first an induction period, then the polymerisation suddenly started and proceeded faster than without the inhibitor.

ii) Compounds with easily removed halogen atoms, e.g. p-toluene sulphonyl chloride, triphenylchloromethane. The inhibiting effect was noticeable over the whole course of the reaction and the polymerisation time was longer than that without the inhibitor.

Known inhibitors of free radical polymerisation, such as quinone, hydroquinone, copper powder, pyrogallol, phenyl β-naphthylamine and trinitrotoluol, had <u>no</u> effect.

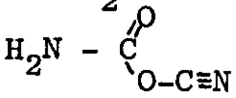
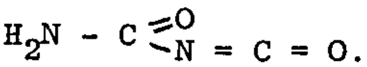
5.3.2 Positive catalysts

Polymerisation of isocyanic acid was accelerated by amines, particularly tertiary amines. The most effective were found to be pyridine and dimethyl aminobenzene; also tin (IV) chloride. Ineffective were $AlCl_3$, $FeCl_3$, benzoyl peroxide, tetralin hydroperoxide and the redox couple benzoyl peroxide /benzene sulphonic acid. With small amounts of catalyst at 15°C, the polymerisation could be very violent, even explosive. This last observation is similar to those of Werner and Fearon described in 5.2 above and might be explained in the same way. Kern, Paul and Mehren discounted a free radical mechanism for the polymerisation and concluded that the mechanism was ionic.

First order kinetics, with a half-life of 18.0hr at 30°C, were found for the gas-phase polymerisation by Smith and Jonassen[8].

5.4 Isocyanic acid dimer

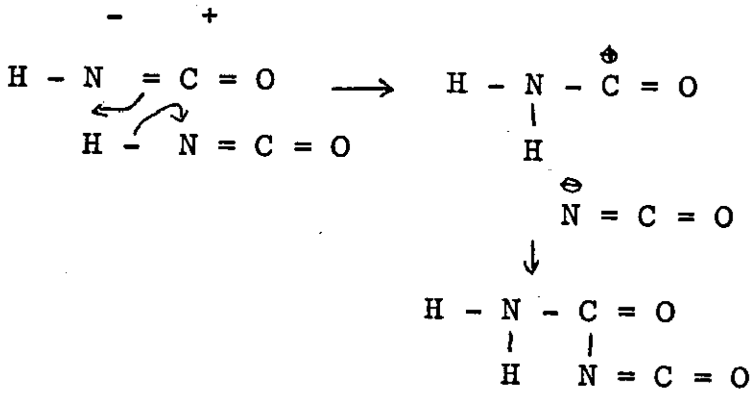
The dimerisation of HNCO was first postulated by Davis and Blanchard[23] and was used by them[58] to explain allophanate formation with alcohols (see Chapter 7.3), but their evidence was refuted by A.E.A. Werner and Gray[48]. Amell[59] included dimerisation as a step in his mechanism for the hydrolysis of HNCO, but mechanisms proposed subsequently do not include it (see Chapter 7). Close and Spielman[9] modified the mechanism of allophanate formation due to Davis and Blanchard using the modern concept of concerted attack of two molecules of HNCO on one of alcohol. (See Chapter 7.3). This process would occur simultaneously with that involving one molecule of HNCO and one of alcohol.

In both references 23 and 58, a condensed formula is given for the dimer, viz $NH_2.COO.CN$, which implies the carbamoyl cyanate structure.  $H_2N-C(=O)-O-C{\equiv}N$ It is more likely that such a dimer would have the carbamoyl isocyanate structure,  $H_2N-C(=O)-N=C=O$. This is suggested for two reasons:-

i) The analogous addition compound formed by isocyanic acid with isothiocyanic acid has been shown to have the carbamoyl isothiocyanate structure (see Chapter 10.5).

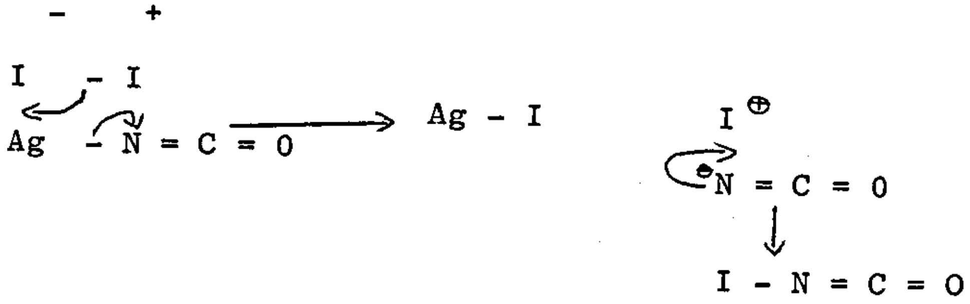
ii) The highly polar N and C atoms of one HNCO molecule can approach and react with the H-N bond of a second

HNCO molecule, rather than the C=N bond of the latter, as in (17).



(17)

An analogous type of interaction has been given by Linhard and Betz[51] to explain the reaction between silver isocyanate and iodine (18).



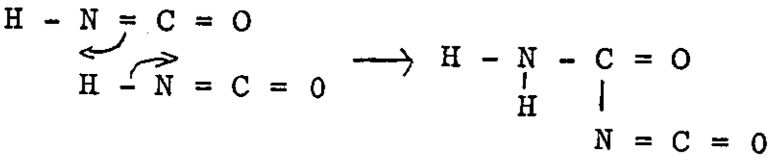
(18)

Hydrogen and silver have similar electronegativity values (2.1 and 1.93 respectively) so the H-N and Ag-N bonds in these circumstances will be similar.

The process described is ionic and so conforms to the findings of Kern, Paul and Mehren[57] (see 5.3.2 above). The isocyanate ion is expected to exhibit a mesomeric polarisability as in (19).

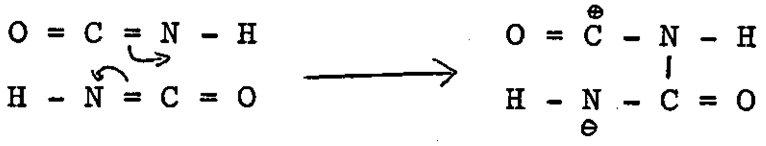
$$^{\ominus}N = C = O \longleftrightarrow N \equiv C - O^{\ominus} \qquad (19)$$

but the facts that $I - N = C = O$ and $H_2N.CO.N = C = S$ are formed, but not their respective cyano-isomers, indicates that the two steps shown in (18) occur simultaneously. This may be summarised for two HNCO molecules by (20).



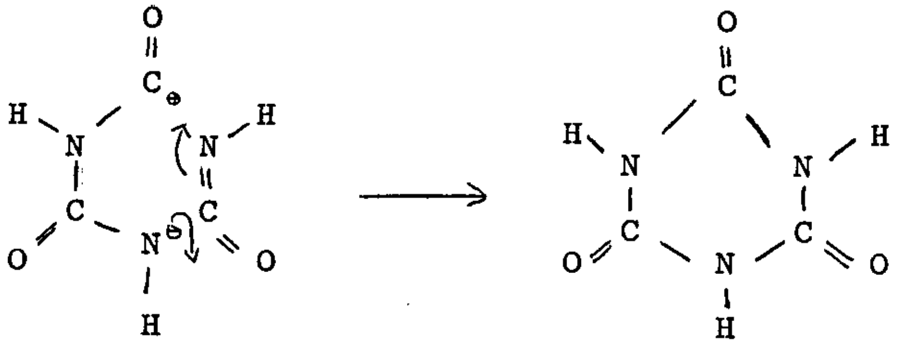
(20)

If the highly polar N atom of one HNCO molecule does approach the C atom of a second, rather than the H atom, (21) ensues.



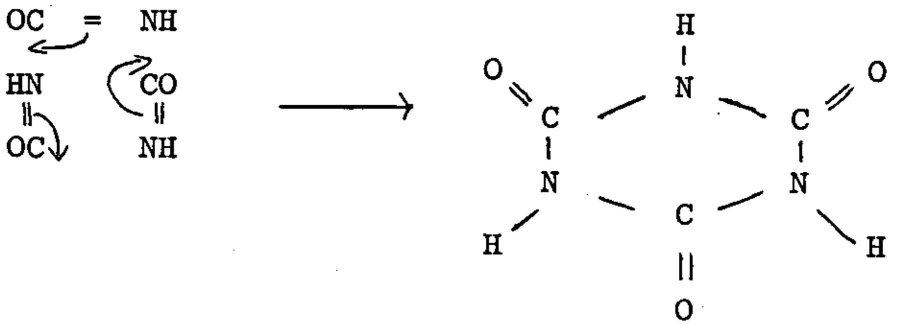
(21)

Interaction with a third HNCO molecule gives cyanuric acid as in (22).



(22)

Again, the two steps would occur simultaneously, giving rise to the trimolecular concerted attack mechanism in (23).



(23)

These two types of general reaction, attack on the H-N bond and attack on the N=C bond, can be used to explain all the properties of isocyanic acid. In the case of reaction between HNCO molecules, either could happen with similar results, as shown by (20) and (24) on the one hand and (23) on the other.

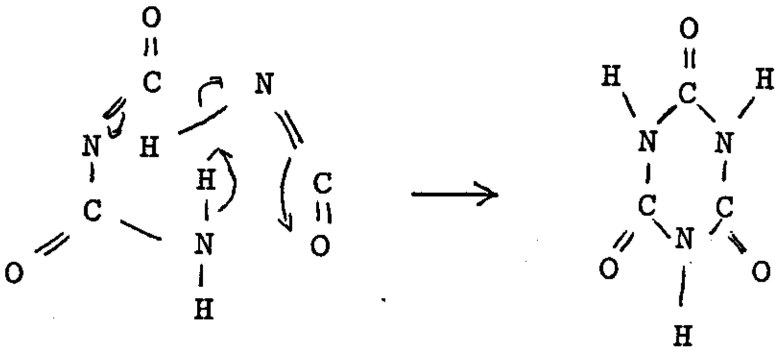
5.5 Mechanism of polymerisation

5.5.1 Formation of cyanuric acid and cyamelide

Cyanuric acid can be formed by:

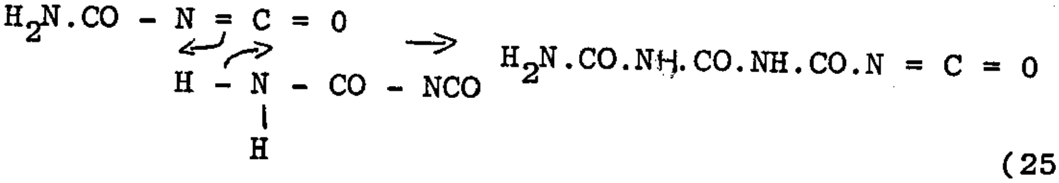
i) the concerted reaction of three molecules of HNCO, as in (23) above.

ii) Stepwise addition of HNCO molecules to form, in the first instance, the dimer. (Equation (20) above). The joining of a dimer molecule with a monomer (HNCO) molecule could result in cyclic trimer (cyanuric acid) formation, as in (24).



(24)

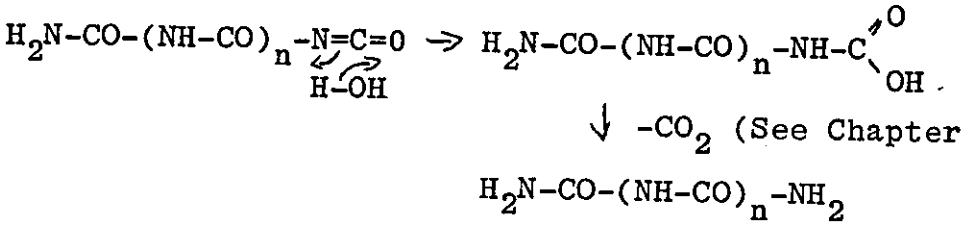
But when two dimer molecules join together, as in (25), the possibility of forming cyanuric acid is lost.



$$\begin{array}{l} H_2N.CO-N=C=O \\ \quad\quad\quad\; H-N-CO-NCO \\ \quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\;\; H \end{array} \longrightarrow H_2N.CO.NH.CO.NH.CO.N=C=O$$

(25)

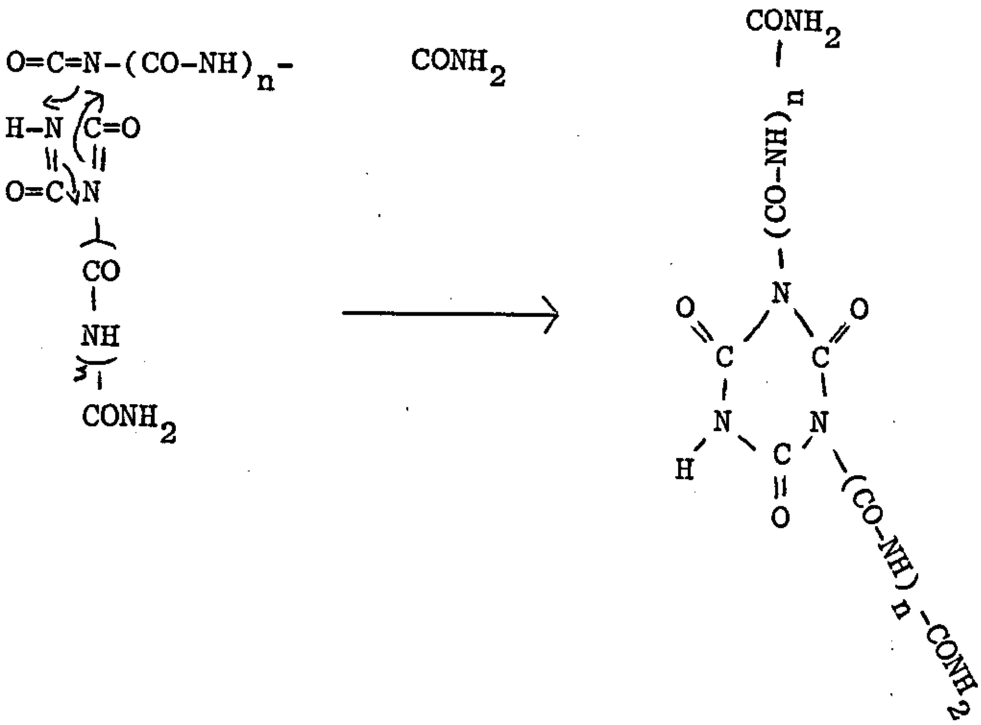
Similar, further addition of either monomer, dimer or tetramer molecules would propagate chain molecules of the type proposed[57] for cyamelide. Chain termination could be achieved by a trace of water, as in (26).



$$\begin{array}{l} H_2N\text{-}CO\text{-}(NH\text{-}CO)_n\text{-}\underset{H-OH}{N=C=O} \rightarrow H_2N\text{-}CO\text{-}(NH\text{-}CO)_n\text{-}NH\text{-}C\begin{smallmatrix}\nearrow O \\ \searrow OH\end{smallmatrix} \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \downarrow -CO_2 \text{ (See Chapter 7)} \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad H_2N\text{-}CO\text{-}(NH\text{-}CO)_n\text{-}NH_2 \end{array}$$

(26)

Chain termination is more likely to involve HNCO molecules and/or the -N=C=O groups of polymer chains in a concerted reaction as, for example, in (27).



(27)

Thus, a sample of "cyamelide" could consist of many different molecular types. Chain termination reactions like (27) could also involve one molecule of polymer and two of HNCO or three of polymer; a wide range of chain lengths is also likely.

5.5.2 First order kinetics

Three possible reaction pathways are proposed, (28)A, (28)B and (28)C.

(28)A $3HNCO \longrightarrow (HNCO)_3$

B i) $2HNCO \rightleftharpoons NH_2.CO.NCO$

ii) $NH_2.CO.NCO + HNCO \longrightarrow (HNCO)_3$

C i) $2HNCO \rightleftharpoons NH_2.CO.NCO$

ii) $2NH_2.CO.NCO \longrightarrow$ tetramer

iii) tetramer and subsequent polymers + HNCO ⟶ chain propagation

iv) chain termination ((27) above).

In a reaction involving gaseous isocyanic acid, in which only cyanuric acid is formed, (28)C is not significant. For such a reaction, first-order kinetics have been found[8] (see 5.3 above). This is not explicable by either mechanism

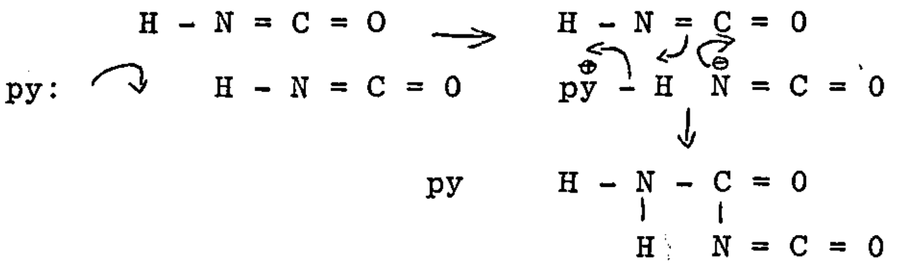
(28)A or (28)B, considered to occur wholly in the gas phase. The pyrolysis of HNCO has been shown to be a surface reaction[7] (see Chapter 6.1). This is probably the case also for polymerisation in the gas phase; the rate seems to depend on the nature of the surface with which the HNCO vapour is in contact[32]. In this event, the obedience to first-order kinetics is explained if the rate-determining step is migration of HNCO to the walls of the vessel (29),

$$HNCO_{(g)} \longrightarrow HNCO_{(ads)} \qquad (29)$$

and the polymerisation of HNCO adsorbed on the surface, by some mechanism like (28)A or (28)B, is fast.

5.5.3 Catalysis

The effects observed by Kern, Paul and Mehren[57] (see 5.3 above) were on reactions carried out in benzene solution. Thus, they must be explained by some homogeneous process. The fact that basic substances like pyridine and dimethylaminobenzene were effective positive catalysts for HNCO polymerization, while Lewis acids like $AlCl_3$ and $FeCl_3$ were not, suggests an anionic polymerisation mechanism rather than a cationic one. Both reactions (17) and (21) involve anion formation. The action of a catalyst like pyridine (py) is best illustrated by assistance in breaking the N-H bond in reaction (17). This is shown in (30).



(30)

The inhibitive effect of certain halide compounds may be explained by irreversible removal of $^{\ominus}NCO$ at this stage (31);

$$R - Cl + {}^{\ominus}N = C = 0 \rightarrow R - N = C = 0 + Cl^{-} \qquad (31)$$

or by termination of chains of the type suggested in (25). Hydroxy-compounds, which comprise the other type of inhibitors, react with HNCO (see Chapter 8). This may occur during the induction period, giving rise to a carbamate ester, $H_2N.COOR$, which then behaves as a positive catalyst, like other amines.

The whole theory of ionic polymerisation is very complicated and much more data is required before the effects of these catalysts can be fully explained.

CHAPTER 6

PYROLYSIS AND PHOTOLYSIS OF ISOCYANIC ACID

When the temperature of HNCO vapour is raised above 500°C, decomposition begins to compete with polymerisation for the removal of HNCO molecules. The chief products are CO, N_2 and H_2. Pyrolysis of HNCO vapour at high temperatures has been little studied, but photolysis at low temperatures has been more thoroughly investigated.

6.1 Pyrolysis of HNCO vapour

Pyrolysis in the temperature range 550-700°C, at pressures between 5 and 20 mm Hg, has been studied by Back and Childs[7]. The reaction was found to be very slow at 500°C, but almost too fast to study at 700°C. The products observed were CO, N_2, H_2, HCN and CO_2. Curves of amount of each product against time were given in Ref. 7. There was evidence that some NH_3 and NH_2CN were also formed, but experiments were complicated by polymerisation and secondary reactions. The decomposition of HNCO was shown to be a zero-order, surface reaction at pressures above 10 mm Hg. Poor reproducibility, due to irreproducible surface conditions, polymerisation and secondary reactions, did not allow quantitative treatment of pyrolysis kinetics.

6.2 Photolysis of HNCO vapour

This has been studied by Back and co-workers[62]. Low temperatures were used, typically 310K (37°C), and UV light between 200 and 240 nm was effective. In all cases, the only products observed were CO, N_2 and H_2. As in the case of the pyrolysis reaction, the elemental balance implied the production of some ammonia, but this would rapidly react with HNCO to give non-volatile urea. Quantum yields of CO, N_2 and H_2 were measured for direct photolysis of HNCO alone, mixed with each of CH_3N_2, NO and O_2 and for the decomposition of HNCO caused by mercury atoms excited by radiation of the appropriate wavelength. It was shown that the H-N bond in HNCO was rather strong, the dissociation energy probably being greater than 400 kJ mol^{-1}.

Bradley, Gilbert and Svejda[63] report similar work and results on the direct photolysis of HNCO. The ratio of amounts of gaseous products, $CO:N_2:H_2$, was about 3:1:1. At 303K, from a starting partial pressure of HNCO of 41.5mm of Hg, typical product partial pressures were 13.3mm for CO, 4.4mm for N_2 and 3.9mm for H_2. A significant fraction of the HNCO polymerised.

The observations of pyrolysis and photolysis suggest that decomposition of HNCO starts with (32).

$$HN = CO \longrightarrow HN: + :CO \qquad (32)$$

Carbon monoxide is a stable molecule and is always a product. Other products depend on the reactions of the NH radical. Mostly, N_2 and H_2 are produced, as in (33).

$$2NH \longrightarrow N_2 + H_2 \qquad (33)$$

Other products are formed by reaction of NH with CO.

6.3 Reaction with noble gas metastables

Stedman[65] reacted HNCO with metastable Ar*, Kr* and Xe* atoms produced in streams of noble gases by a hollow electric discharge. The emission spectra of NH, CO and N_2 were observed as a result, which also suggests that the weak part of the HNCO molecule with respect to decomposition is the nitrogen-carbon double bond.

CHAPTER 7

REACTIONS IN WATER

Isocyanic acid is weakly dissociated in water, as in equation (34).

$$HNCO \rightleftharpoons H^+ + {}^{\ominus}N = C = O \leftrightarrow N \equiv C - O^{\ominus} \qquad (34)$$

However, the undissociated molecule is also unstable to hydrolysis. Basically, ammonia and carbon dioxide are produced, as in equation (35).

$$HNCO + H_2O \rightleftharpoons NH_3 + CO_2 \qquad (35)$$

The final products of hydrolysis depend on the reaction conditions. The reaction has only been investigated in aqueous solution. No gas phase experiments have been reported. However, Gisbier[64] has calculated equilibrium constants for reaction (35) in the gas phase. These are shown in Table 7.

Table 7. Theoretical equilibrium constants for $HNCO + H_2O \rightleftharpoons NH_3 + CO_2$

T/Kelvin	298.15	500	800	1000	1500
$\log_{10} K$	12.0123	6.7072	3.7625	2.8360	1.6803

The instability of HNCO with respect to hydrolysis decreases with increasing temperature, but ΔG is still negative at 1500K.

7.1 Weak acidity. Several workers have measured the acid dissociation constant of HNCO. Caramazzo[66] and Boughton[67] used the pH-titration method, which would be open to errors caused by hydrolysis of HNCO. Lister[68] and Amell[59] obtained their values from treatment of reaction rata data obtained by methods obviating errors due to hydrolysis. The values are all shown in Table 8, converted to pK where necessary, to allow comparison.

FIG. 2 Values of pK for isocyanic acid dissociation, plotted against temperature.

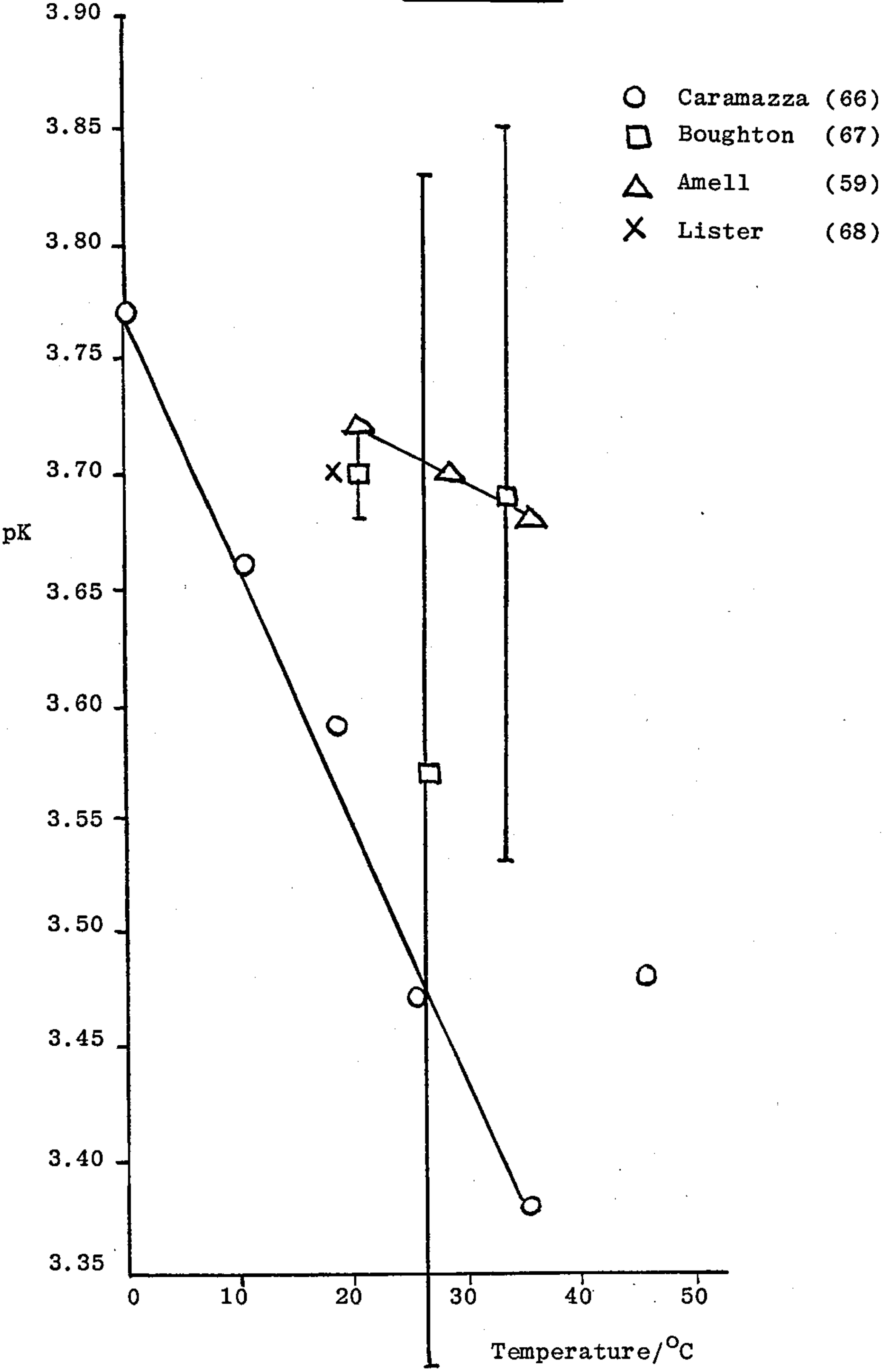


Table 8. Values of pK for isocyanic acid and derived thermodynamic functions

Temp. /$^{\circ}$C	pK	Ref.	ΔC_p^{o} cal. mol^{-1} K^{-1}	ΔS^{o} cal. mol^{-1} K^{-1}	ΔH^{o} kcal mol^{-1}	ΔG^{o} kcal mol^{-1}
0	3.77	66	-134.6	+6.16	+6.390	+4.720
10	3.66	66				
18	3.59 3.7	66 68	-165.9	-3.18	+3.690	+4.700
20	3.70 ± 0.02 3.72	67 59				
25	3.47	66	-178.1	-7.37	+2.480	+4.740
26	3.57 ± 0.26	67				
28	3.70	59				
33	3.69 ± 0.16	67				
35	3.38 3.68	66 59				
45	3.48	66	-212.9	-20.20	+1.430	+5.010

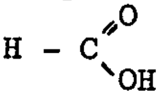
The pK data seem to fall into two groups, depending on whether error due to hydrolysis was eliminated or not, as is shown in Fig. 2. The values of Lister[58] and Amell[59], obtained by reaction rate methods, are in close agreement and little variation in pK with increasing temperature is apparent. On the other hand, the values of Caramazza[66], obtained by a method where hydrolysis was likely to have an effect, are generally lower and a comparatively large variation in pK with increasing temperature seems to be shown. Boughton[67], who used a method similar to that of Caramazza, estimated limits of error for his values. These agree with the values of Lister and Amell when the errors are taken into account. It will be noticed that all the pK values obtained by Caramazza in the temperature range 0-45°C lie within the limits of error considered possible by Boughton! The variation of dissociation constants with temperature of acids of similar structure, particularly  $H-C{\overset{O}{\diagup\!\!\!\!\!\diagup}}\diagdown OH$ have been measured by many workers with great precision. The values[33] in Table 9 have been converted from K to pK to allow comparison with those in Table 8.

Table 9. The variation of pK with temperature for methanoic acid, H.COOH.

Temp. /°C	0	5	10	15	20	25	30	35	40	45
pK	3.786	3.772	3.763	3.757	3.753	3.752	3.753	3.758	3.766	3.773

The values of pK for H.COOH in Table 9 all lie within a total range of 0.04 pH units, as do the values of Lister[68] and Amell[59] for HNCO in Table 8. It is evident that the variations of pK with temperature for HNCO found by Caramazza[66] are spurious, because the errors caused by hydrolysis were excessive.

The thermodynamic data in Table 8 were calculated by Caramazza[66] from his pK data by using an empirical relationship like (36).

$$\log K = \frac{A}{T} + B + CT + D \log T \qquad (36)$$

Expression (36) is obtained by combining an empirical relationship for the variation of change of molar heat capacity with temperature, viz. (37), with

$$\Delta Cp = a + bT \qquad (37)$$

Kirchhoff's equation and van't Hoff's "reaction isochore" equation. Substituting Caramazza's data into expression (36) generates six simultaneous equations, which can be solved in many permutations to give values of A, B, C and D. Presumably the average values obtained were used to calculate the thermodynamic data in Table 8, via expressions like (38) - (41).

$$\Delta G^o = -RT \ln K \qquad (38)$$

$$\Delta H^o = -T^2 . \frac{d(\Delta G^o)/T}{dT} \qquad (39)$$

$$\Delta S^o = \frac{-d(\Delta G^o)}{dT} \qquad (40)$$

$$\Delta Cp^o = \frac{d(\Delta H^o)}{dT} \qquad (41)$$

Caramazza's data are really not accurate or consistent enough to warrant such treatment.

It is best to assume that, in the range 0-50^{o}C, pK of isocyanic acid is 3.7 ± 0.1 and variations with temperature are small, of the same order as those found for methanoic acid, but for HNCO these await accurate determination. Amell[59] quotes values of 1.3 kcal mol^{-1} for ΔH^o and 5.0 kcal mol^{-1} for ΔG^o, but does not refer them to any temperature. It is best to assume that ΔH^o and ΔG^o are constant at these values, to two significant figures, within the temperature range considered. In comparison, the respective values for methanoic acid at 298K (calculated from data from Table 9, using equations (36), (38), (39) and (40)) are ΔG^o = +5.1 kcal mol^{-1}, ΔH^o = +0.624 kcal mol^{-1} and ΔS^o = -15.0 cal mol^{-1} K^{-1}.

7.2 <u>Hydrolysis (kinetics and mechanism)</u>.

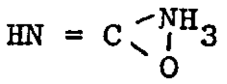
Normand and Cumming[69] found that, in water, isocyanic acid could react in three different ways, according to the conditions employed. In neutral, concentrated solutions, the main product was cyanuric acid, i.e. HNCO reacted faster by polymerisation rather than by hydrolysis, but if acid were present, ammonium cyanate and carbon dioxide were formed. In dilute solution, urea and carbon dioxide were obtained.

Experiments of Werner and Fearon[16] confirmed the formation of urea. They suggested three primary changes in dilute solution, (42), A, B and C, based on the hypothetical tautomerism of isocyanic and cyanic acids (discussed in Chapter 3.8).

(42)

$$HOCN \rightleftharpoons HNCO \xrightarrow{H_2O} CO_2 + NH_3 \qquad A$$

$$HOCN + NH_3 \longrightarrow NH_4OCN \qquad B$$



$$HNCO + NH_3 \longrightarrow HN = C\begin{smallmatrix} NH_3 \\ | \\ O \end{smallmatrix} \text{ (urea)} \qquad C$$

After completion of the primary changes, secondary changes were considered possible, (43) A, B and C.

(43)

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3 \qquad A$$

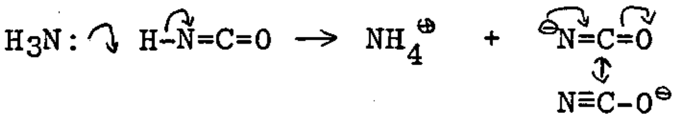
$$\text{urea} + HNCO \longrightarrow \text{biuret} \qquad B$$

production of cyamelide C

It was supposed that the proportions of ammonium cyanate and urea obtained by hydrolysis of isocyanic acid depended on the tautomeric proportions of HNCO and HOCN.

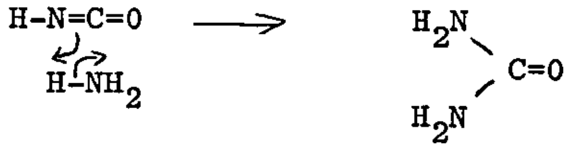
However, the possibility of forming both ammonium cyanate and urea is explained by the possibility of a nucleophile, like NH_3, interacting with either the N-H bond or the N=C bond, as previously discussed for isocyanic acid polymerisation (see Chapter 5.4). Here, the former case leads to ammonium cyanate, by a simple acid-base reaction (44), and the latter case leads to urea formation (45).

(44)



$$H_3N: \; H\text{-}N{=}C{=}O \longrightarrow NH_4^{\oplus} + {}^{\ominus}N{=}C{=}O \updownarrow N{\equiv}C\text{-}O^{\ominus}$$

(45)



$$\begin{array}{c}\mathrm{H{-}N{=}C{=}O}\\ \mathrm{H{-}NH_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{H_2N}\\ \quad\;\;\mathrm{C{=}O}\\ \mathrm{H_2N}\end{array}$$

This will be discussed more fully in Chapter 9.

Furthermore, ammonium cyanate and urea are tautomeric themselves and when equilibrium is attained, conversion to urea is nearly complete ($K \triangleq 10^4$ dm^3 mol^{-1} at ambient temperatures)[75]. The proportions of cyanate and urea will be a function of the time elapsed between reaction and analysis.

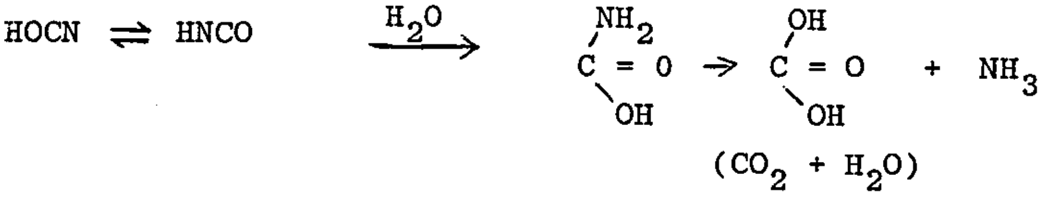
What is important in the context of the isocyanic acid -water reaction is whether the ammonium cyanate/urea is formed by the route discussed above or by some other route, such as the formation of carbamic acid.

7.2.1 Carbamic acid

The addition reactions of HNCO with alcohols and amines yield derivatives of carbamic acid, $NH_2.COOH$ (See Chapters 8 and 9). Fearon and Dockeray[70] tested the suggestion that carbamic acid might be formed as an intermediate in the hydrolysis of HNCO. Carbamic acid itself is more unstable than isocyanic acid and is only known in the form of salts. It would decompose very quickly, as in (46).

$$NH_2.COOH \longrightarrow NH_3 + CO_2 \qquad (46)$$

Fearon and Dockeray claimed to prove the formation of carbamic acid and proposed the mechanism in (47).



$$\mathrm{HOCN} \rightleftharpoons \mathrm{HNCO} \xrightarrow{H_2O} \begin{array}{l}\;\mathrm{NH_2}\\ \mathrm{C = O}\\ \;\mathrm{OH}\end{array} \rightarrow \begin{array}{c}\begin{array}{l}\;\mathrm{OH}\\ \mathrm{C = O}\\ \;\mathrm{OH}\end{array}\\ (CO_2 + H_2O)\end{array} + NH_3 \qquad (47)$$

Their experiments were carried out at 5°C.

Linhard[36] attempted to find evidence for the formation of carbamic acid in aqueous solutions of HNCO at very low temperatures (between -23°C and -102.5°C), by measuring crystallisation temperatures of solutions of different HNCO concentrations. The phase diagram showed two smooth lines of separation, one for ice and the other for solid HNCO. They crossed at -102.5°C, when a eutectic mixture containing 67% HNCO was produced.

No evidence was found for the formation of carbamic acid or of hydrates under these conditions. However, the reaction is likely to be immeasurably slow at these low temperatures. Amell[59], in his proposed mechanism (see 7.2.2 below), suggests that carbamic acid be formed in the only two slow steps.

7.2.2 Kinetics. The first detailed investigation of the kinetics of hydrolysis was carried out by Lister[68]. In the presence of HCl or HNO_3, HNCO reacted quantitatively according to (48).

$$HNCO + H^+ + H_2O \longrightarrow CO_2 + NH_4^+ \qquad (48)$$

The reaction was found to be first order with respect to HNCO and values of rate constant and activation energy were given for a range of temperatures and ionic strengths. The effect of ionic strength on rate constant was closely parallel to that of the activity coefficients of HCl. Without acid, HNCO again reacted by a first-order reaction, (49), but slower than (48).

$$HNCO + 2H_2O \longrightarrow NH_4HCO_3 \qquad (49)$$

This was followed by a rapid second stage. (50).

$$NH_4HCO_3 + HNCO \longrightarrow NH_4NCO + CO_2 + H_2O \qquad (50)$$

Values of rate constant and activation energy for (50) were given. The reaction in the presence of excess NaOH (i.e. reaction of OCN^- with H_2O or OH^-) was also investigated.

Using a different analytical technique, Amell[59] found that the rate of hydrolysis did not depend on the ionic strength, but only on the concentration of isocyanic acid.

Curve fitting to the kinetic results showed that the rate equation was not simply first order with respect to isocyanic acid. It could be expressed as (51).

$$\text{Initial rate, } R_o = k_1[\mathrm{HOCN}] + k_2 \frac{[\mathrm{HOCN}]^2}{[\mathrm{H^+}]} \qquad (51)$$

Values of k_1 and k_2 at different temperatures were given. When plotted against temperature, a curve was obtained. This was explained as being due to tautomerism between isocyanic and cyanic acids. Amell proposed the mechanism (52).

(52) i) $H^+ + OCN^- \rightleftharpoons HOCN \rightleftharpoons HNCO$ fast

ii) $HNCO + H_2O \longrightarrow NH_2.COOH$ slow

iii) $NH_2COOH \longrightarrow NH_3 + CO_2$ fast

iv) $NH_3 + H^+ \longrightarrow NH_4^+$ fast

v) $2HNCO \longrightarrow NH_2.COO.CN$ fast

vi) $NH_2.COO.CN + OH^- \longrightarrow NH_2.COOH + OCN^-$ slow

No salt effect was found, but the conditions of experiment may have minimised this.

From his kinetic work, Jensen[71,72,73] concluded that the uncatalysed hydrolysis in dilute aqueous solutions proceeds by three <u>simultaneous</u> reactions, (53) A, B and C.

$HNCO + H^+ + H_2O \longrightarrow NH_4^+ + CO_2$ (53) A

$HNCO + H_2O \longrightarrow NH_3 + CO_2$ B

$OCN^- + 2H_2O \longrightarrow NH_3 + HCO_3^-$ C

(53) A and (53) B would be too slow to take an appreciable part in strongly basic media, while 53 (C) would be negligible in more acidic solutions. Values of rate constants of all three reactions at different temperatures were given. More recently, Vogels, Uffink and Van der Drift[74] have supported Jensen's view. They determined the initial velocity, V_i, at different pH values, from which standard velocities, Vst. (54) were calculated.

$$\text{Vst.} = \frac{Vi}{[\mathrm{HNCO}]} \qquad (54)$$

The results, all obtained at 30°C, fitted equation (55).

$$Vst = k_H[H^+] + \frac{k_1[H^+]}{K+[H^+]} + k_2 \qquad (55)$$

where k_H = 2nd order rate constant of process (53) A

k_1 = 1st order rate constant of process (53) B

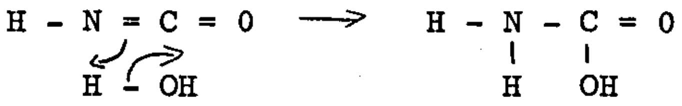
k_2 = 1st order rate constant of process (53) C

K = dissociation constant of HNCO.

At pH 2, K was negligible compared with $[H^+]$ and (53) A took place. At pH values between 3 and 8, spontaneous hydrolysis, i.e. (53) B took place. At pH 9, spontaneous hydrolysis of OCN^- predominated, (53) C. Values of k_H, k_1, k_2 and K were obtained at 30°C. It was considered[74] that reaction (53) B probably occurs via nucleophilic addition of H_2O to HNCO to give carbamic acid.

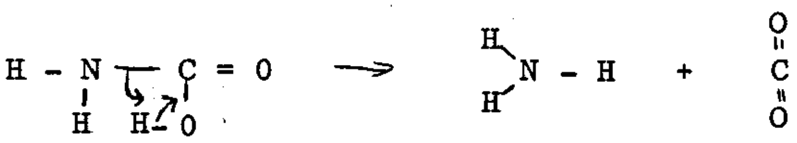
7.2.3 Mechanism

The theory of nucleophilic addition to HNCO, used in Chapter 5 to describe isocyanic acid polymerisation, leads to carbamic acid formation in the case of addition of H_2O, as in (56).



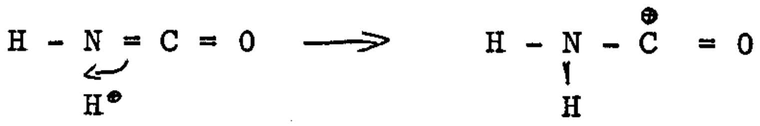
$$H-N=C=O + H-OH \longrightarrow H-N(H)-C(OH)=O \qquad (56)$$

This would immediately decompose according to (57).



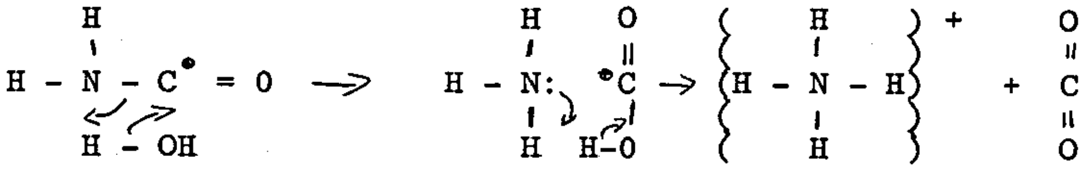
$$H-N(H)-C(OH)=O \longrightarrow H_2N-H + O=C=O \qquad (57)$$

In describing the mechanism of hydrolysis in acidic solution, equation (53) A of Jensen (the same as equation (48) of Lister) does not specify whether H^+ attacks first, or H_2O, or both simultaneously. In the first and third cases, the rate will depend on $[H^+]$; in the second case, it will not because H^+ is only involved in a secondary reaction (protonation of NH_3 formed in (57)), assumed to be fast. Amell[59] found no dependence of rate on ionic strength and therefore no dependence on $[H^+]$, but all the other workers cited[68,71-74] found such a dependence. If hydrolysis is faster in more acidic solutions, this suggests H^+ is involved in a rate determining step leading to consumption of HNCO, as in (58).



(58)

H_2O then attacks the protonated molecule, as in (59).

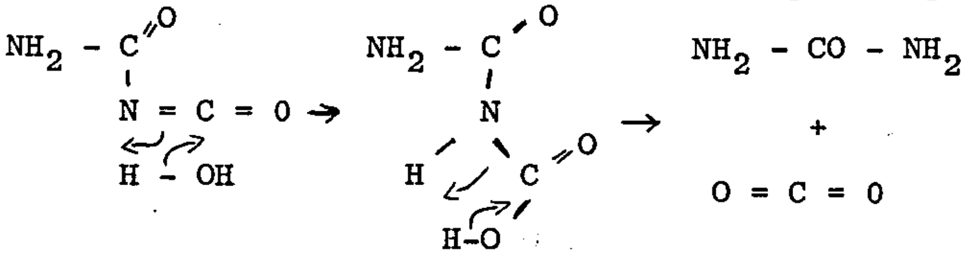


(59)

The formation of urea/ammonium cyanate can be explained in three ways:

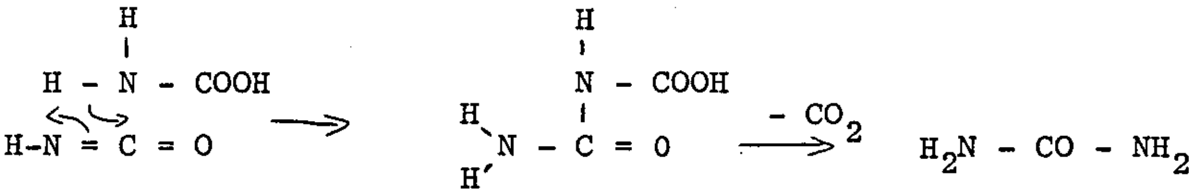
i) Secondary reaction of ammonia produced by (57) with unreacted HNCO, as in (44) and (45).

ii) Hydrolysis of isocyanic acid dimer. Use of the isocyanate structure suggested in Chapter 5 gives (60).



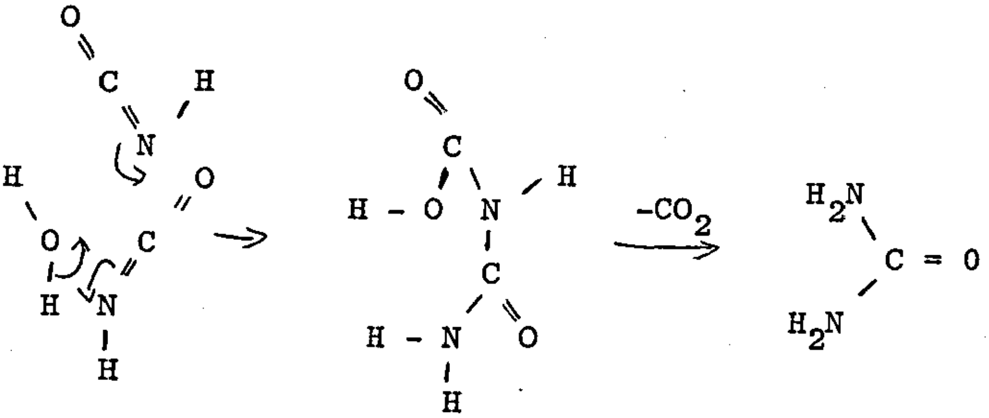
(60)

iii) Reaction of carbamic acid produced by (56) with unreacted isocyanic acid, which produces the same intermediate (allophanic acid) as in (60), followed by loss of CO_2. (61)



(61)

Urea formation in hydrolysis is analogous to allophanate formation in reaction with alcohols, as production of ammonia and carbon dioxide is to carbamate formation (see Chapter 8). If, as seems evident, allophanates are not formed by further reaction of carbamates with alcohols[9,58], route iii) above is unlikely for hydrolysis. Route ii) may be modified to a concerted attack of two HNCO molecules on one of water (62), a reaction taking place simultaneously with (56) and (57).



(62)

7.2.4 Catalysts for hydrolysis

Jensen[71,72] found that the spontaneous hydrolysis of HNCO was catalysed by HCO_3^- and the spontaneous hydrolysis of CNO^- by CO_3^{2-}. Values of rate constants were obtained for 18, 25 and 50°C.

Vogels, Uffink and Van der Drift[74] investigated the effects of a number of bivalent anions. Some acted as catalysts, others did not. Carbonate, phosphate, succinate. maleate, citrate and phthalate were all active, but oxalate, fumarate and isophthalate (the last two isomeric with maleate and phthalate respectively) were not. The amount of increase in standard velocity, Vst (Vst defined by equation (47)), depended on the pH and the concentration of the anion in obedience to (63).

$$Vst = k_a \cdot \frac{K_2[H^+]}{K(K_2 + [H^+])} \cdot A \qquad (63)$$

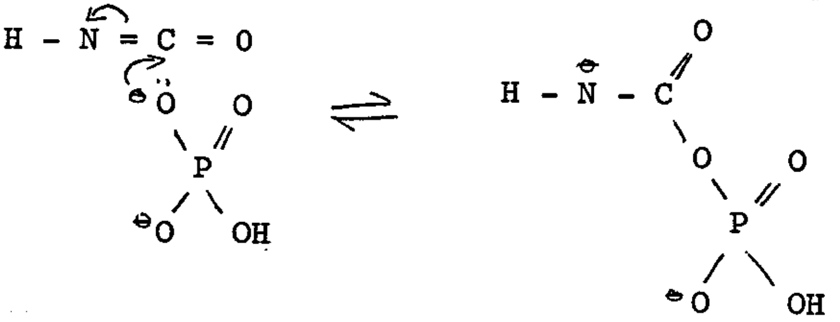
where K_2 = secondary dissociation constant of the anion

A = concentration of all forms of the anion

k_a = rate constant of the reaction catalysed by the anion.

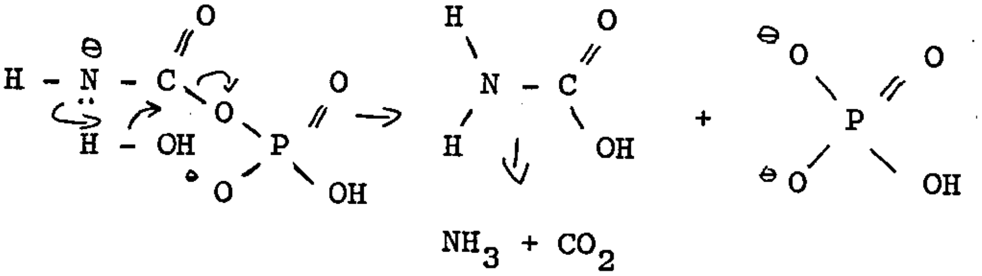
K = dissociation constant of HNCO.

It has been found that phosphate[76] and other dianions[77] can react with HNCO in preference to water, to give carbomoyl monoanions. Reaction (64) is a possible example.



(64)

In the case of some anions, hydrolysis may be made easier, as in (65), but for others not.



(65)

CHAPTER 8

Reaction with alcohols

The reactions of HNCO with alcohols are better understood than that with water. Addition of one molecule of HNCO to a molecule of an alcohol would give the alkyl carbamate, according to (66).

$$ROH + HNCO \rightarrow NH_2.COOR \qquad (66)$$

Addition of a second molecule would then give the alkyl allophanate, as in (67).

$$NH_2.COOR + HNCO \rightarrow NH_2.CO.NH.COOR \qquad (67)$$

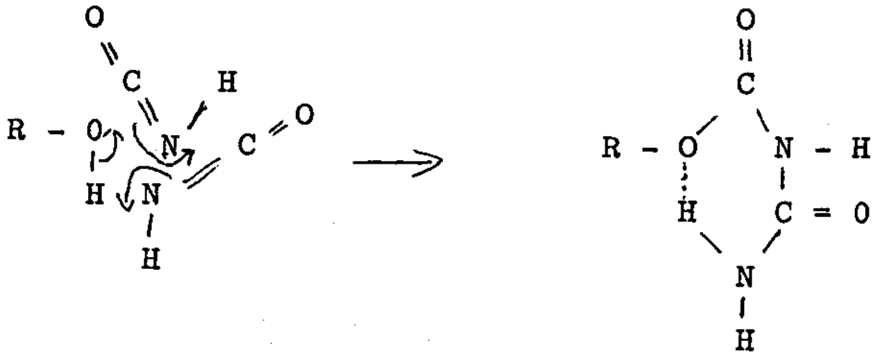
Hofmann[82] first proposed the theory that allophanate is formed by (66) and (67) occurring consecutively. The theory was supported, in their review of the reaction, by Blohm and Becker[83], who held that the first step was fast and the second was slow and rate-determining. Hofmann claimed to have made ethyl allophanate from ethyl carbamate and HNCO, but this could not be reproduced by Běhal[84]. Davis and Blanchard[58] explained carbamate formation as being due to reaction between alcohol and isocyanic acid monomer, while allophanate is formed by simultaneous reaction of "dicyanic acid dimer" (see Chapter 5.4) with alcohol, as in (61).

$$2HNCO \rightarrow NH_2COOCN + ROH \rightarrow NH_2.CO.NH.COOR \qquad (68)$$

They were able to make allophanate from carbamate and alcohol, in a sealed tube. To explain this, it was suggested that the carbamate first breaks down to give alcohol and HNCO (reverse of (66)). The HNCO then dimerises and reacts as in (68).

Close and Spielman[9] found that, when the reaction between alcohol and HNCO was carried out in ether solution, allophanate was always the major product, even when alcohol was in excess. This would suggest that carbamate is an intermediate in the reaction and that Hofmann's first step (66) is the slow one.

However, Close and Spielman confirmed the discovery of Birckenbach, Kolb and Goubeau[85] that carbamates do not yield allophanates in the absence of mineral acid. This means that carbamate cannot be an important intermediate in the direct formation of allophanate, which does occur in the absence of acid. Close and Spielman modified the mechanism of Davis and Blanchard[58] (68) using the modern concept of concerted attack of two molecules of isocyanic acid on one of alcohol (69).



(69)

Reaction (69) would proceed simultaneously with attack by one molecule of HNCO to give carbamate. It does, however, seem unlikely that a trimolecular reaction involving two reagents should predominate over a bimolecular reaction involving the same reagents. The older dimer theory[58] (68) would require the presence of a large concentration of dimer in the ether solution of HNCO, or reaction with dimer to be easier than with monomer. It seems strange that no kinetic work has been done on this reaction. Determination of the order of the reaction with respect to HNCO and alcohol would provide valuable additional evidence regarding the mechanism.

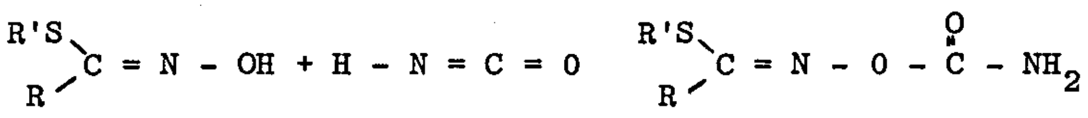
8.1 Recent patents.

Nagayama et al[15] have described the preparation of carbamates by treating aromatic alcohols (e.g. $C_6H_5.CH_2OH$) with HNCO, in the presence of an acid catalyst (e.g. $CCl_3.COOH$).

Amagasa et al[86] obtained from butan-1,3-diol a mixture of 3-carbamate and 1,3-dicarbamate at room temperature. Reaction at 120°C in dioxan gave an allophanate as well. When polyvinyl alcohol was used, two products were obtained - one soluble in boiling water and the other insoluble. Takahashi and Ozaki have prepared biuret and triuret derivatives[87] from phenols and HNCO; and sulphur-containing allophanates[88], $RS.NH.CO.NH.CO_2R'$, from RSCl, R'OH and HNCO.

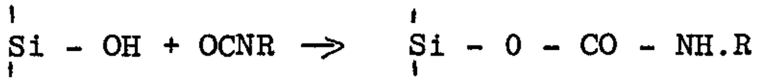
8.2 Analogous reactions.

Kofod[89] reacted cyanate with hydroxyammonia and obtained the isomers of hydroxyurea. Cummins[13] has patented the use of a similar reaction, the formation of "thiohydroxamate carbamates" from mercapto-substituted oximes (70).



$$\begin{matrix}R'S\diagdown \\ R\diagup\end{matrix} C = N - OH + H - N = C = O \quad \begin{matrix}R'S\diagdown \\ R\diagup\end{matrix} C = N - O - \overset{O}{\overset{\|}{C}} - NH_2 \qquad (70)$$

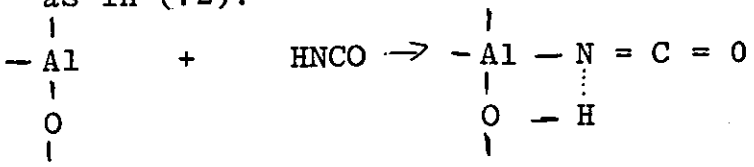
Isocyanates can be adsorbed onto the surfaces of hydrated oxides. Lange[78] and Weldes[79] showed that isocyanates in general are susceptible to reaction with surface -OH groups of silica and alumina, with formation of carbamate groups as in (71).



$$\underset{|}{\overset{|}{Si}} - OH + OCNR \rightarrow \underset{|}{\overset{|}{Si}} - O - CO - NH.R \qquad (71)$$

HNCO is different from alkyl isocyanates because of the presence of the acidic hydrogen atom. Guillet, Coudurier and Donnet[80] used infra-red spectroscopic and thermo-gravimetric methods to study the adsorption of HNCO on alumina. It was suggested that three processes occur:

1) carbamate formation, as in (71).
2) splitting of the H-N bond and addition of the moieties, as in (72).



$$\begin{matrix} | \\ -Al \\ | \\ O \\ | \end{matrix} \quad + \quad HNCO \rightarrow \begin{matrix} | & & \\ -Al & - & N = C = O \\ | & & \vdots \\ O & - & H \\ | & & \end{matrix} \qquad (72)$$

3) trimerisation to cyanuric acid.

More extensive infra-red spectroscopic studies have been carried out by Solymosi and Bansagi[81]. The adsorption of HNCO on silica, alumina, magnesia and titania surfaces was investigated. Bands due to surface isocyanate groups appeared in the 2212-2313 cm^{-1} region of the spectrum.

CHAPTER 9

Reactions with ammonia and amines

Isocyanic acid reacts with ammonia to form a mixture of ammonium cyanate and urea. As has been previously suggested (see Chapter 7.2), interaction of NH_3 with the N-H bond of HNCO leads to ammonium cyanate formation, while interaction with the N = C bond leads to urea formation (equations (44) and (45)). The reaction is inextricably related to the reversible ammonium cyanate - urea interconversion, a possible mechanism for which is (73).

$$NH_4^+ + CNO^- \rightleftharpoons NH_3 + HNCO \rightleftharpoons H_2N.CO.NH_2 \qquad (73)$$

This is discussed in 9.2 below.

Amines in general should give alkylammonium cyanates, but Michael and Hibbert[90] found that these were much less stable than ammonium cyanate and a substituted urea is invariable formed. Some amines did not react and only cyamelide was obtained, from polymerisation of HNCO. Most amines gave some cyamelide as a by-product, but the amount was decreased if the reaction was carried out in ether, toluene or chloroform solution. The increased stability of HNCO with regard to polymerisation in these solvents has already been mentioned (chapter 2.6). The lack of reactivity of some amines may be accounted for by two possible factors.

i) steric effects;
ii) nucleophilic power of the amine.

Factor ii) would correlate with base strength and this has a bearing on the mechanism of reaction of ammonia and reactive amines. This is discussed in 9.2 below.

9.1 Kinetics

Jensen[73] assumed that, in the mechanism indicated by (73), the reaction between ammonia and isocyanic acid molecules is the rate determining step. Velocity constants, k_u, were measured for the gross reactions between a number of aminium ions (including NH_4^+) and cyanate ion in aqueous solution. The presence of aminium ion was considered to give rise to acid-base catalysis of the rate-determining step and k_u was taken as a measure of the catalytic coefficient of the amine, k_B. Thus, k_u should depend on the strength of the aminium ion according to the Bronsted equation for acid-base catalysis. For an amine, the logarithmic form of this is expression (74).

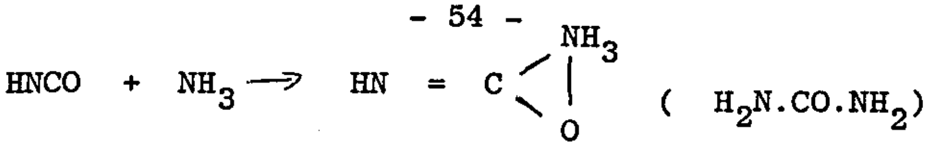
$$\log k_B = \log k_u = \log b - \beta \log K \qquad (74)$$

where b and β are constants and K is the acid dissociation constant of the conjugate aminium ion. Jensen found some correlation between log k_u and log K for the amines used, but there was a large deviation from linearity when the values were plotted. More recently, Williams and Jencks[91] have made similar measurements for a wider selection of amines and plotted a Bronsted-type graph. Two intersecting straight lines were evident, one of slope $\beta = 0.3$, on which lay most primary and secondary amines, and the other of slope $\beta = 0.8$, on which lay weakly basic amines, mainly substituted ones. The break in the graph gives an explanation for the results obtained by Jensen.

9.2 Mechanism.

Werner and Fearon[16] tested the suggestion that the formation of ammonium cyanate and urea was not due to an equilibrium set up between the two, but that each resulted from reaction of a different tautomer of cyanic acid present in the reactants. This is shown by equations (75) and (76).

$$HOCN + NH_3 \longrightarrow NH_4OCN \qquad (75)$$



$$HNCO + NH_3 \longrightarrow HN = C\begin{matrix} \diagup NH_3 \\ \big| \\ \diagdown O \end{matrix} \quad (H_2N.CO.NH_2) \qquad (76)$$

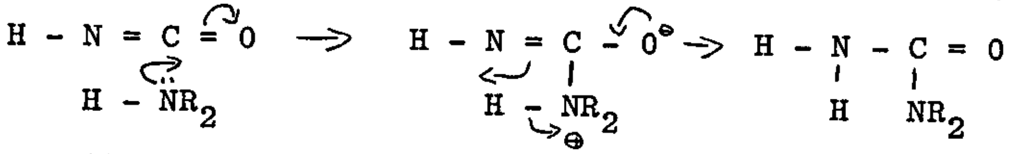
The amount of urea formed was determined by the xanthydrol method (see Chapter 4.1.1.). The amount of ammonium cyanate was obtained by subtraction of this from the amount of both expected by stoichiometry. Correlation was claimed between the proportions of urea and ammonium cyanate on the one hand and of HNCO and HOCN on the other. No account seems to have been made of the ammonia produced by hydrolysis of HNCO and its subsequent reaction with HNCO, nor of biuret production from urea and HNCO. Furthermore, as was shown in Chapter 3.8, the weight of evidence now indicated that the proportion of HOCN present in isocyanic acid is vanishingly small.

Shorter[75] has reviewed knowledge of the urea-ammonium cyanate interconversion. Two mechanisms have found favour, reversible reaction of ammonium and cyanate ions and the molecular mechanism represented by equation (73). Virtually none of the experimental kinetic data can be interpreted unambiguously in favour of either mechanism, but the molecular mechanism is theoretically more plausible. As has previously been indicated, ammonia can interact with either the H-N or C=N bond of H-N=C=0, leading to formation of ammonium cyanate or urea, respectively (see equations (44) and (45), Chapter 7.2). An earlier suggestion of Chattaway[92] was that groups such as amines and alcohols will add across the C=0 bond, giving rise to (77).

$$HNCO + NHR_2 \longrightarrow HN = C(OH)NR_2 \longrightarrow H_2N.CO.NR_2 \qquad (77)$$

This is refuted by the contention of Linhard and Betz[51] that, in the case of HNCO, the electrophilic part of an added molecule goes onto the nitrogen atom, not the oxygen atom, because of the smaller nuclear charge of the former. (See Chapter 10).

It is generally supposed[75] that, in the molecular mechanism, a zwitterionic intermediate is formed, which undergoes intramolecular proton exchange to give a urea, as in (78).



$$\begin{matrix}H-N=C=O\\ H-NR_2\end{matrix} \rightarrow \begin{matrix}H-N=C-O^{\ominus}\\ |\\ H-\overset{}{N}R_2^{\oplus}\end{matrix} \rightarrow \begin{matrix}H-N-C=O\\ |\qquad|\\ H\qquad NR_2\end{matrix}$$

(78)

The nett result of the two stages in (78) is summarised by (79), which may be compared with (45) (Chapter 7.2).

$$\begin{matrix}H-N=C=O\\ H-NR_2\end{matrix} \longrightarrow \begin{matrix}H_2N-C=O\\ |\\ NR_2\end{matrix}$$

(79)

Williams and Jencks[91] interpret their kinetic results (see Chapter 9.1, above) as showing that for the more strongly basic amines (Bronsted equation factor β = 0.3), amine attack (first stage in (78)) is rate-determining. For more weakly basic amines (β = 0.8), proton transfer (second stage in (78)) is rate determining. In a subsequent paper[93], Williams and Jencks discussed the mechanism of the proton-transfer stage in considerable detail.

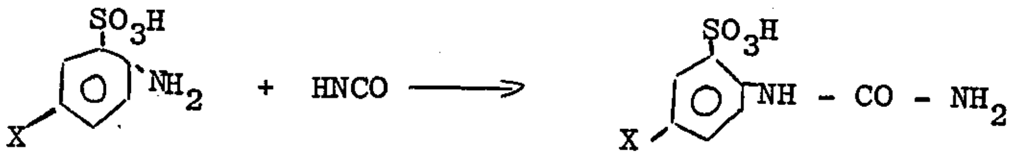
9.3 Reaction with urea

Urea behaves as an ordinary amine with isocyanic acid and gives biuret. as in (80).

$$NH_2.CO.NH_2 \quad + \quad OCNH \rightarrow H_2N.CO.NH.CO.NH_2 \qquad (80)$$

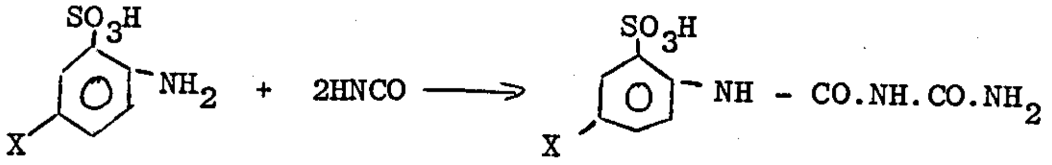
This reaction was investigated by Werner[94], who added potassium cyanate to a hydrochloric acid solution of urea. A very low yield of biuret was obtained, as most of the HNCO was lost by hydrolysis, polymerization and volatilization. Davis and Blanchard[58] found no biuret after an aqueous solution of the reactants was allowed to stand in a warm room, probably for the same reasons. However, as recognised by Werner and Fearon[16], biuret is a likely by-product whenever isocyanic acid is hydrolysed or comes together with ammonia in any other circumstances.

Scott and Cohen[95] prepared "ortho-carbamido sulphonic acids", i.e. phenyl ureas with substituents in the benzene ring, by reaction of 2-amino, 5-X benzene-1-sulphonic acid with an acidified solution of potassium cyanate. When X = H, CH_3 or SO_3H, one mole of HNCO reacted, giving the ortho-carbamido sulphonic acid, as in (81).



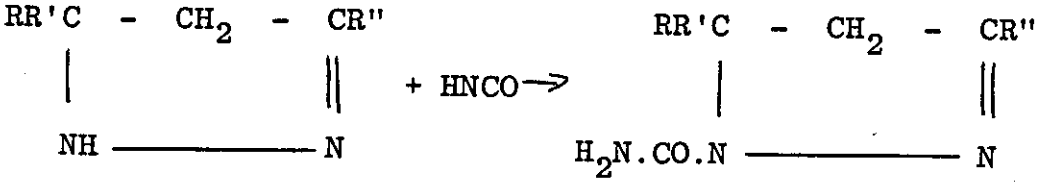
(81)

When X = Cl, Br or I, two moles of HNCO reacted, giving a derivative of asymmetric phenyl biuret, as in (82).



(82)

Locquin and Heilmann[96] prepared urea derivatives from pyrazolines by a similar technique, as shown by (83).

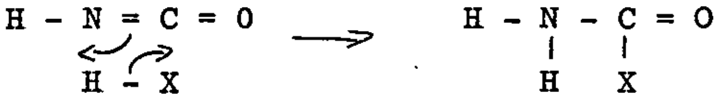


(83)

CHAPTER 10

Other addition reactions across the N=C double bond

Linhard and Betz[51], in 1940, drew together most of the then-known reactions of isocyanic acid and explained them by the addition of polar or readily-polarisable molecules to the N=C double bond, to give derivatives of carbamic acid. Thus, the reaction between HNCO and water, shown in equation (49), is the type reaction for a large number of other reactions. In this work, the importance of the principle in the reactions of HNCO by polymerisation and with water, alcohols, ammonia and amines has already been discussed. The more positive part of the added molecule is always attached to the N, rather than the O, because of the smaller nuclear charge of N[51]. The more negative part is always attached to the C, which has a positive polarity due to the high electronegativities of O and N. Thus, hydrogen halides would be expected to give carbamoyl halides, according to (84).



$$\mathrm{H-N=C=O} + \mathrm{H-X} \longrightarrow \begin{array}{c}\mathrm{H-N-C=O}\\ \quad\;\; | \quad\; | \\ \quad\;\; \mathrm{H} \quad \mathrm{X}\end{array} \qquad (84)$$

Linhard and Betz[51] effected direct addition of HF, HCl, and HBr to HNCO. Equilibrium mixtures containing carbamoyl halides were obtained.

Many other reactions of HNCO can be explained in the same way.

10.1 Oxidation by hypochlorite and chlorine

Lister[68] reported brief investigation of the reaction between cyanate solutions and sodium hypochlorite and chlorine solutions.

With hypochlorite, quantitative experiments showed that the reaction with cyanate had stoichiometry approximating to equation (85).

$$2KOCN + 3NaOCl + H_2O \rightarrow 2KHCO_3 + 3NaCl + N_2 \qquad (85)$$

Kinetic experiments showed an induction period which was shorter the lower the concentration of sodium hydroxide was. Lister assumed that oxidation of cyanate by hypochlorite ion was slow, but that by the hypochlorous acid molecule was rapid. The results were not very accurate and it is likely that more than one reaction took place.

Addition of HOCl to HNCO would give N-chloro carbamic acid, as in (86).

$$\underset{\mathrm{Cl-OH}}{\mathrm{H-N=C=O}} \longrightarrow \mathrm{H-\underset{Cl}{\underset{|}{N}}-\underset{OH}{\underset{|}{C}}=O} \qquad (86)$$

Speculation as to the subsequent reactions, as for all cases where the -COOH group of the carbamic acid molecule is left intact, best assumes that carbon dioxide is lost, as with the parent compound. (See Chapter 7.2.1.). A possible scheme is given in (87).

$$\begin{array}{lcl}
2HNCO + 2HOCl & \longrightarrow & 2NHCl.COOH \qquad (87) \\
2NHCl.COOH & \longrightarrow & 2NH_2Cl + 2CO_2 \\
2NH_2Cl + HOCl & \longrightarrow & N_2 + 3HCl + H_2O \\
\hline
2HNCO + 3HOCl & \longrightarrow & 2CO_2 + N_2 + 3HCl + H_2O
\end{array}$$

This gives stoichiometry exactly the same as that found experimentally by Lister (85).

With chlorine (in small amounts) quantitative experiments showed that the main reaction was probably represented by (88).

$$4KOCN + 3Cl_2 + 4H_2O \rightarrow 4KCl + 4CO_2 + N_2 + 2NH_4Cl \qquad (88)$$

Probably, more than one reaction can occur. Normand and Cumming[69] reported exactly the same stoichiometry for reaction with bromine. It is expected that the first step of the reaction would be addition, as in (89).

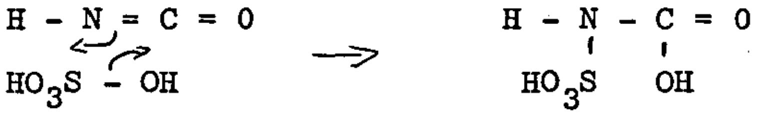
$$\underset{\mathrm{Cl-Cl}}{\mathrm{H-N=C=O}} \longrightarrow \mathrm{H-\underset{Cl}{\underset{|}{N}}-\underset{Cl}{\underset{|}{C}}=O} \qquad (89)$$

The stoichiometry of (88) can thence be achieved, as shown in (90), but the mechanism of this reaction must be extremely complicated.

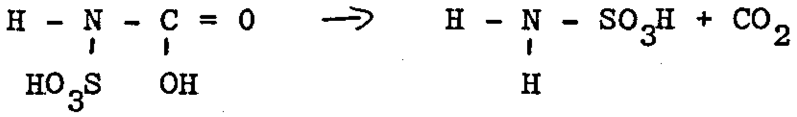
$$\begin{array}{lll} 4HNCO + 4Cl_2 & \longrightarrow & 4NHCl.COCl \qquad (90) \\ 4NHCl.COCl + 4H_2O & \longrightarrow & 2NH_4Cl + 4CO_2 + N_2 + 4HCl + Cl_2 \\ \hline 4HNCO + 3Cl_2 + 4H_2O & \longrightarrow & 2NH_4Cl + 4CO_2 + N_2 + 4HCl \end{array}$$

10.2 Addition of sulphuric acid

This reaction was investigated by Linhard[97]. Although an equimolar mixture of HNCO and H_2SO_4 in pure ether at -80°C remained clear for days, at -60 to -50°C, mixtures resulted of, typically, 61% of aminosulphonic acid, $NH_2.SO_3H$, and 32% of carbamidosulphonic acid, $NH_2.CO.NH.SO_3H$. Linhard interpreted these results as indicating addition, to the C=N bond of HNCO, of H_2SO_4 as an OH-bearing molecule rather than as an H-bearing molecule (cf. alcohols, Chapter 8). The first step is thus as in (91).


(91)

Loss of CO_2 then occurs, as in (92), in the same way as for carbamic acid.


(92)

$$H-N(SO_3H)-C(OH)=O \longrightarrow H-N(H)-SO_3H + CO_2 \qquad (92)$$

In a 2:1 mixture of HNCO and H_2SO_4, two molecules of HNCO reacted with one of H_2SO_4. In a 1:1 mixture, some H_2SO_4 molecules reacted each with one molecule of HNCO, some with two and, as a consequence, some remained unchanged. Two possible reaction paths to carbamidosulphonic acid were suggested by Linhard.

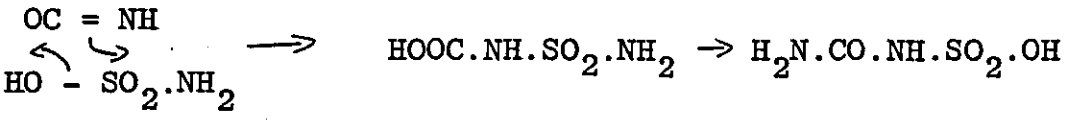
i) Concerted attack, shown by (93).


(93)

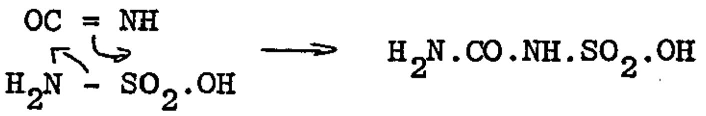
The molecule formed loses only one molecule of CO_2 and rearranges according to (94).

$$\mathrm{HOOC.NH.SO_2.NH.COOH} \xrightarrow{-CO_2} \mathrm{H_2N.SO_2.NH.COOH} \rightarrow \mathrm{HO.SO_2.NH.CO.NH_2} \qquad (94)$$

ii) Stepwise attack. Aminosulphonic acid is first formed, as in (91) and (92). This may be followed by either (95) or (96).



$$\begin{matrix} \mathrm{OC = NH} \\ \mathrm{HO - SO_2.NH_2} \end{matrix} \longrightarrow \mathrm{HOOC.NH.SO_2.NH_2} \rightarrow \mathrm{H_2N.CO.NH.SO_2.OH} \qquad (95)$$

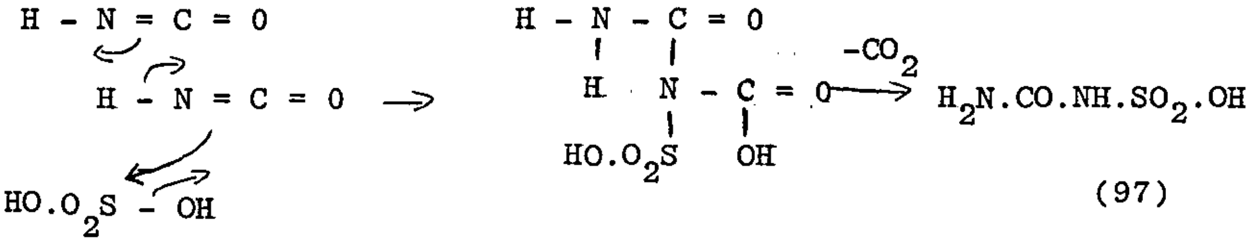


$$\begin{matrix} \mathrm{OC = NH} \\ \mathrm{H_2N - SO_2.OH} \end{matrix} \longrightarrow \mathrm{H_2N.CO.NH.SO_2.OH} \qquad (96)$$

Linhard was not able to make a direct decision as to the reaction course. An experiment showed that finely-powdered aminosulphonic acid suspended in an ethereal solution of isocyanic acid gave no noticeable reaction over several days. However, the lack of reactivity of the aminosulphonic acid may have been due to its insolubility in ether.

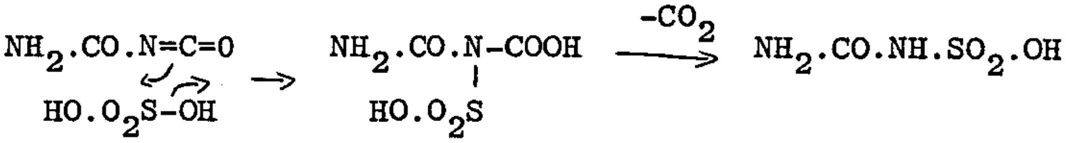
The intermediate in (95) is the same as that in the concerted attack mechanism (93) and (94). Its rearrangement seems unlikely, reducing the plausibility of these mechanisms. The need for rearrangement in both mechanisms is obviated if the ideas first suggested in Chapter 5, and applied in various situations subsequently, are applied here.

In a concerted attack mechanism, if two molecules of HNCO interact with each other, while one adds on H_2SO_4, as in (97), an intermediate derivative of carbamic acid is formed, which only has to lose CO_2 to give carbamidosulphonic acid.



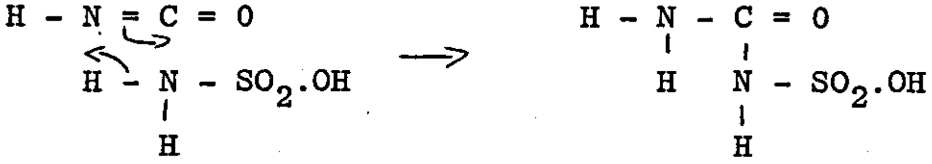
$$\begin{matrix} \mathrm{H - N = C = 0} \\ \mathrm{H - N = C = 0} \\ \mathrm{HO.O_2S - OH} \end{matrix} \longrightarrow \begin{matrix} \mathrm{H - N - C = 0} \\ \mathrm{H \quad\; N - C = 0} \\ \mathrm{HO.O_2S \quad OH} \end{matrix} \xrightarrow{-CO_2} \mathrm{H_2N.CO.NH.SO_2.OH} \qquad (97)$$

This is equivalent to addition of H_2SO_4 to isocyanic acid dimer (carbamoyl isocyanate), equation (98).



(98)

In the stepwise mechanism, carbamidosulphonic acid is obtained directly from aminosulphonic acid if the latter adds as an amine to HNCO, as in (99).

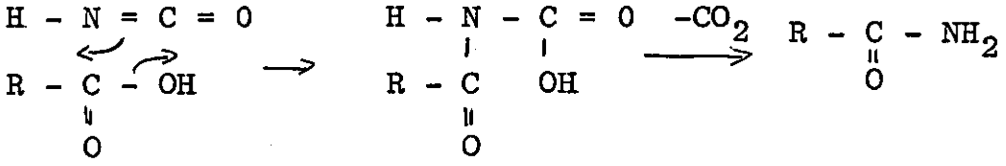


(99)

The types of concerted mechanism discussed here involve the simultaneous collision of three discrete molecules, a type of event generally having extremely low probability. For this reason, mechanisms involving (93) and (97) are unlikely. Thus, the simplest and most plausible mechanism is the step-wise one represented by (91), (92) and (99). The only plausible alternative is that represented by (91), (92) and (98), simultaneous reactions between H_2SO_4 and HNCO and H_2SO_4 and "carbamoyl isocyanate" dimer. The presence of the dimer in the requisite significant quantities in isocyanic acid has yet to be proved.

10.3 Reaction with carboxylic acids

Takahashi et al[98] have patented a process for production of N-unsubstituted carboxylic amides from carboxylic acids and HNCO. This reaction can be most easily explained by addition of the acid across the C=N bond of HNCO, as in (100).



(100)

10.4 Reaction with triphenylgermanium and triphenylsilicon hydroperoxides.

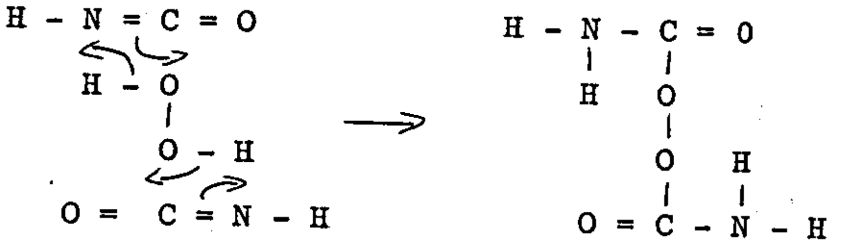
Surova et al[99] reacted $(C_6H_5)_3.GeO_2H$

with HNCO and obtained $(C_6H_5)_3.Ge.NCO$ and $H_2N.CO.O_2.CO.NH_2$. Triphenylsilicon hydroperoxide reacted in similar fashion.

If an acid-base reaction (101) is considered to take place

$$(C_6H_5)_3Ge.O.OH + HNCO \longrightarrow (C_6H_5)_3Ge.NCO + H.O.O.H \quad (101)$$

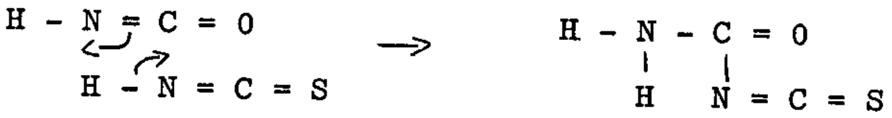
first, then the second product would be formed by the addition of hydrogen peroxide to two molecules of HNCO, either stepwise or together (102).



(102)

10.5 Addition of isothiocyanic acid

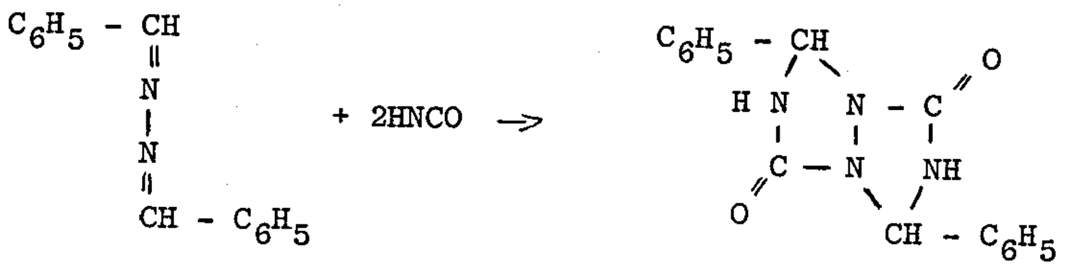
Although no reaction took place at -80°C and -15°C, Birckenbach and Kraus[100] found that, at 0°C, HNCO and HNCS did react. The properties of the product showed it to be the isothiocyanate of carbamic acid. This reaction, (103), has already been mentioned (Chapter 5.4 et seq.) as being of vital importance to theories of polymerisation of isocyanic acid, particularly those involving dimer formation.



(103)

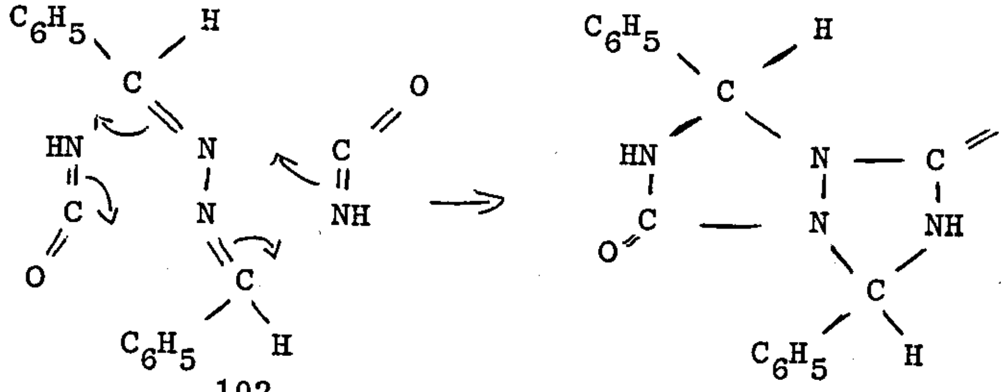
10.6 Addition to C = N - containing molecules with ring formation.

Bailey and co-workers[14,101] showed that, when HNCO and azines react, one molecule of azine and two of HNCO add together to give so-called bitrazoles, e.g. as in (104).



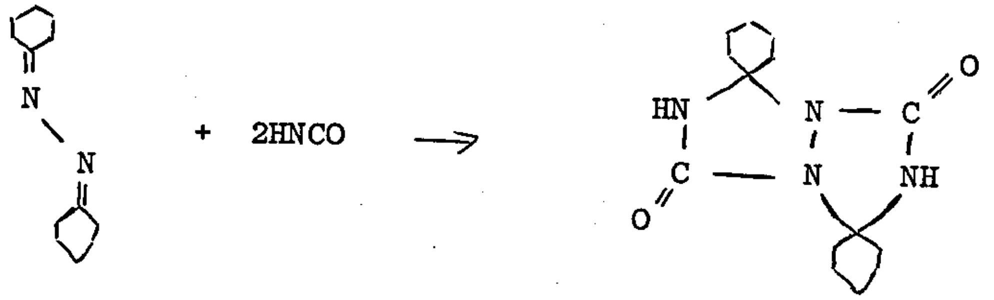
(104)

Instead of the expected 1-2, 3-4 addition, 1-3, 2-4 coupled addition had occurred (105), for which process Bailey and co-workers proposed the name, "criss-cross addition".



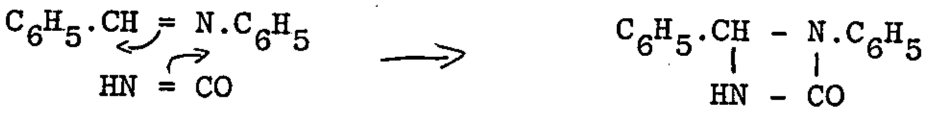
(105)

Dutt and Guha[102] later made bitriazoles from azines of cycloalkanones e.g. (106).



(106)

The similar reaction with compounds having one C = N double bond was investigated by Hale and Lange[103], using compounds of the aldehyde-imine type ("Schiff's bases"). For example, with the imine of benzaldehyde and aniline, one molecule of HNCO reacted to give a four-membered cyclic urea, as in (107).



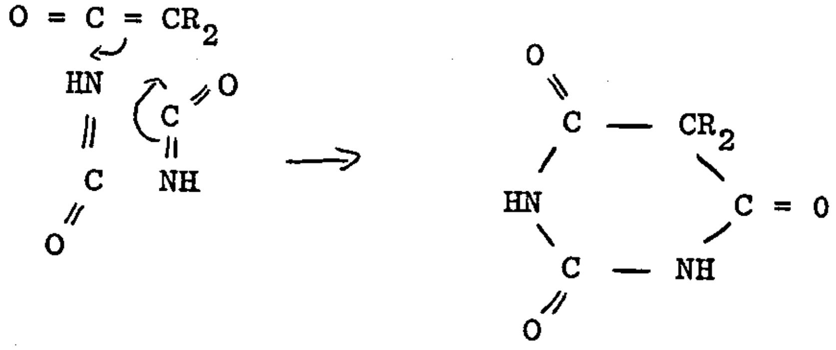
$$\begin{array}{l} C_6H_5.CH = N.C_6H_5 \\ \quad HN = CO \end{array} \longrightarrow \begin{array}{l} C_6H_5.CH - N.C_6H_5 \\ \qquad | \qquad\quad | \\ \quad HN - CO \end{array}$$

(107)

With the imine of benzaldehyde and ethylamine, however, two molecules of HNCO reacted to give a derivative of sym.-triazine, as in (108).

(108)

Staudinger[104] had earlier shown that two molecules of HNCO react with one of a ketene in a similar fashion (109).


(109)

Both reactions are analogous to the trimerisation of isocyanic acid to cyanuric acid. (Chapter 5). As was pointed out for the latter reaction, (108) and (109) represent overall changes which are likely to take place by stepwise reactions rather than by a trimolecular, concerted process.

CHAPTER 11

Addition of isocyanic acid to unsaturated molecules.

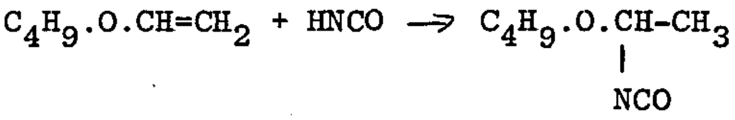
As a hydrogen pseudo-halide, isocyanic acid might be expected to undergo addition reactions with unsaturated compounds in a manner analogous to that of hydrogen halides, as in (110).

$$X = Y + H - NCO \longrightarrow XH - YNCO \qquad (110)$$

The HNCO molecule is, in fact, only a weak nucleophile[105], but some reactions with compounds having C=C, C=O and C=N bonds have been reported since 1963. The possibility of the last type of interaction being involved in the polymerisation of isocyanic acid has previously been suggested (see Chapter 5).

11.1 Addition to alkenyl compounds.

This was first achieved by Hoover and Rothrock[30], who prepared α-alkoxy isocyanates from α,β-unsaturated ethers, for example (111).



$$C_4H_9.O.CH{=}CH_2 + HNCO \longrightarrow C_4H_9.O.\underset{\displaystyle NCO}{\underset{|}{CH}}-CH_3 \qquad (111)$$

The reaction was strongly exothermic and was rapid, especially in the presence of p-toluene sulphonic acid or of other strong acids. This latter fact and the obedience of the reaction to Markownikov's rule indicate an ionic mechanism.

Subsequently, patents have been issued for the preparations of isocyanates from HNCO and various alkenes, viz. long-chain aliphatic alkenes[106], using activated silica or alumina catalysts; $(CH_3 - C = CH_2)_2\ C_6H_4$[107], either with $Na_2S_2O_5$ as catalyst or with anhydrous conditions; and 2,5-norbornadiene[108].

11.2 Addition to alkynyl compounds.

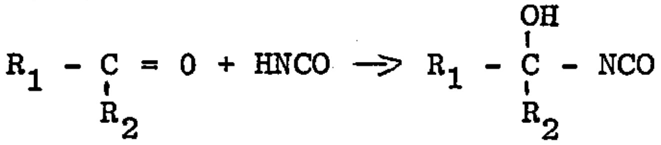
Shell Internationale Research[109] have patented the preparation of alkenyl isocyanates from alkynes as, for example, in (112).

$$CH \equiv CH + HNCO \longrightarrow CH_2 = CH.NCO \qquad (112)$$

Reaction (112) is carried out over a $Zn(NCO)_2$ catalyst at 493K.

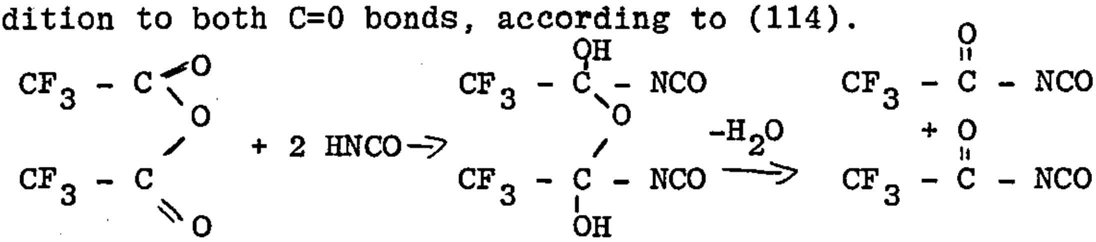
11.3 Addition to carbonyl compounds

Hoover, Stevenson and Rothrock[110] have prepared α-hydroxy isocyanates, according to (114), from methanal, s-dichlorotetrafluoropropanone, trifluoroethanal, 5H-perfluoropentanal, perfluorocyclobutanone, trichloroethanal, dichloroethanal and perfluoropropanone. They suggested that most carbonyl compounds which form hydrates (those having electronegative substituents in the α-position) will undergo this reaction. The products were highly reactive and some polymerised explosively.



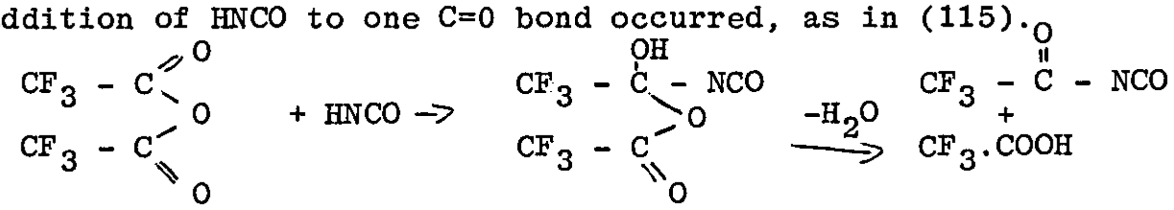
$$R_1 - \underset{R_2}{C} = 0 + HNCO \longrightarrow R_1 - \overset{OH}{\underset{R_2}{C}} - NCO \qquad (113)$$

Firth[111] has reported reactions of HNCO with trifluoroethanoic anhydride. With two moles of HNCO to one of anhydride, trifluoroethanoyl isocyanate was obtained. This reaction involves addition to both C=0 bonds, according to (114).



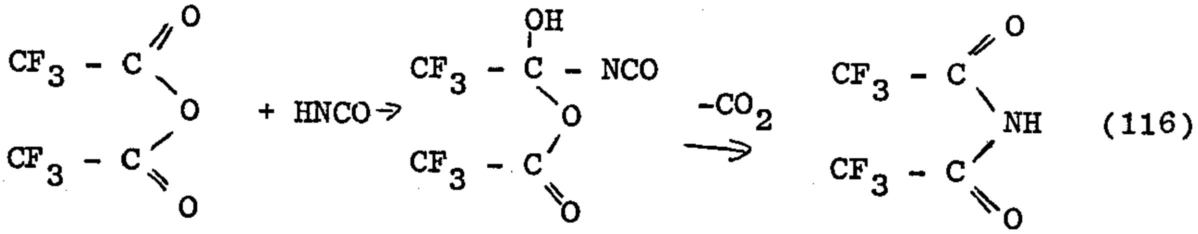
(114)

When a 1:1 mole ratio of HNCO and anhydride was used, infra-red spectroscopy showed trifluoroethanoyl isocyanate to be again present, together with trifluoroethanoic acid and unchanged $(CF_3.CO)_2O$, a mixture which could not be separated. This time, addition of HNCO to one C=0 bond occurred, as in (115).

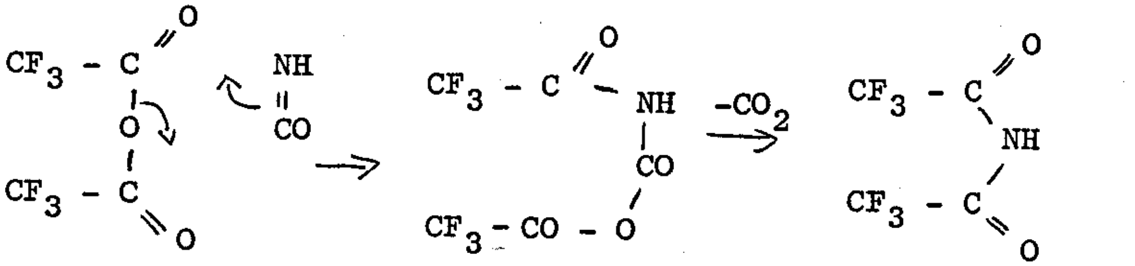


(115)

When excess $(CF_3.CO)_2O$ was used, perfluorodiethanamide was obtained. If addition of HNCO to one C=O group is again expected, considerable rearrangement, with loss of CO_2, is necessary to give perfluorodiethanamide, as shown by (116).


(116)

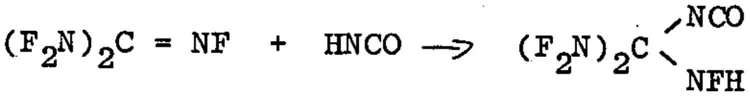
The reaction with excess $(CF_3.CO)_2O$ is explained more simply by addition of the anhydride across the N=C bond of HNCO, as described in Chapter 10.3, according to (117).


(117)

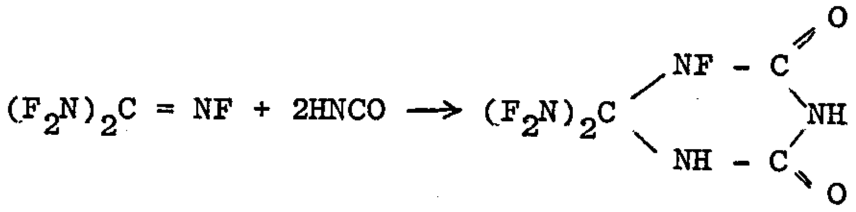
Attempts to make diethanamide from ethanoic anhydride and HNCO did not succeed, though indirect methods of preparing diamides from potassium cyanate and acid anhydrides have long been known[112].

11.4 Addition to imide compounds.

Firth, Frank and Schriffert[105] obtained a 1:1 adduct and a 2:1 adduct when $(F_2N)_2C = NF$ was reacted with HNCO in the presence of urea as a basic catalyst. Formation of the 1:1 adduct is shown by (118).


$$(F_2N)_2C = NF + HNCO \longrightarrow (F_2N)_2C\begin{matrix} NCO \\ NFH \end{matrix} \qquad (118)$$

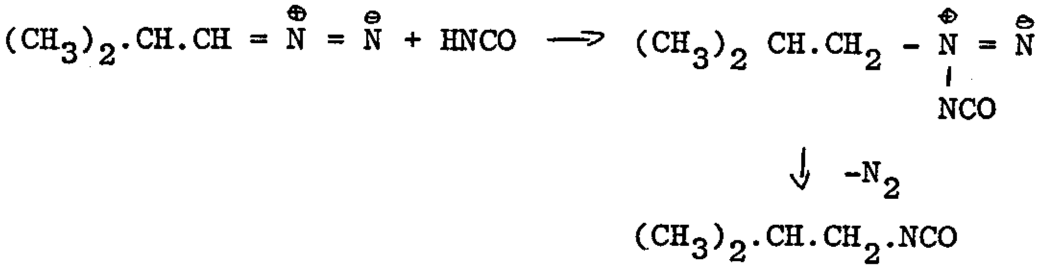
The 2:1 adduct, which could be made from the 1:1 adduct and HNCO, is similar to the sym.-triazine derivatives described in Chapter 10.6. Like them, it will be formed by addition involving two HNCO and one imino C=N double bonds, as in (119).



(119)

All the compounds involved were strong oxidising agents and very explosive.

The formation of isobutyl isocyanate from HNCO and diazoisobutane, reported by Groving and Holm[10] may be explained by initial addition of HNCO to the C=N double bond, as in (120).



$$(CH_3)_2.CH.CH = \overset{\oplus}{N} = \overset{\ominus}{N} + HNCO \longrightarrow (CH_3)_2\,CH.CH_2 - \underset{NCO}{\overset{\oplus}{N}} = \overset{\ominus}{N} \xrightarrow{-N_2} (CH_3)_2.CH.CH_2.NCO$$

(120)

CHAPTER 12

SUMMARY AND CONCLUSIONS

12.1 Preparation and storage of isocyanic acid

12.1.1 Methods of preparation. The most popular method has been the thermal depolymerisation of cyanuric acid. A silica tube and two bunsen burners can be used with efficacy but the method developed by Linhard[4] is probably the best. In any case, it is necessary to heat the vapour, once formed, to effect depolymerisation but the high temperature favoured by Herzberg and Reid[5] is not necessary. The cyanuric acid should be recrystallized before use as recommended by Linhard[4] (see Chapter 2.1).

The thermal decomposition of urea with in situ removal of ammonia has potential advantages compared to the use of cyanuric acid, viz the starting material is more easily available, a lower temperature can be used and it is probably not necessary to heat the vapour. This method is deserving of further investigation.

Other methods, particularly the decomposition of nitrourea solution and reaction of an alkali metal cyanate with a suitable acid, can be particularly useful for individual applications where in situ generation of HNCO in a solution is required.

12.1.2 Storage. The most efficient and convenient way to store isocyanic acid is as a solid in a liquid nitrogen bath. Solid carbon dioxide and acetone is a more widely available and only slightly less reliable substitute cooling medium.

12.2 Physical properties and structure of isocyanic acid.

12.2.1 Physical properties. The exact freezing point of isocyanic acid is uncertain but, from a practical point of view, it is certain that HNCO is solid at dry ice temperature and below.

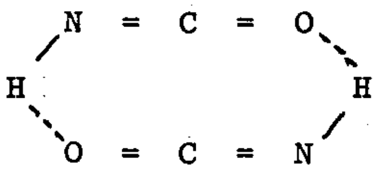
The normal boiling point of 23.5°C and liquid density of 1.140g cm^{-3} seem reliable. The range of vapour pressure measurements made by Linhard[4] could be usefully extended above -6°C.

Thermodynamic functions for HNCO are well established (see Chapter 3.6) and its spectra are well documented (see Chapter 3.7).

The existence of the low temperature form of isocyanic acid reported by Von Dohlen and Carpenter[35] should be confirmed and its crystal structure determined.

12.2.2 Structure of the molecule. The spectroscopic evidence available all points to H-N=C=O being the sole molecular structure in the gas phase. The high value[4] of Trouton's constant for the liquid is almost certainly due to association of molecules caused by the hydrogen-bonding known to be present (see Chapter 3.10). The proportion of HOCN would seem to be very small indeed. The presence of HOCN in the very small maximum proportion suggested by theory[52] (see Chapter 3.9.3) would be very difficult to detect. However, the presence or absence of HOCN might be finally established by detailed analysis of high resolution spectra.

12.2.3 Association. The opinion of Von Dohlen and Carpenter[35] that the stronger N-H---O hydrogen bonds are present in a solid form stable at lower temperatures while weaker N-H---N bonds are present at higher temperatures seems to be a contradiction in terms (see Chapter 3.10). If their opinion is correct, it is likely that the crystalline structure of the low temperature solid as a whole is weaker than the high-temperature form for steric reasons. It may be that it is easier to form a dimer, as in (120), rather than chains when N-H---O bonds are formed. As in the case of ethanoic acid, this dimer


(120)

may be present in the liquid state and could be detected by methods such as molecular weight determination from colligative properties in a suitable solvent and x-ray diffraction analysis.

12.3 Methods of analysis. Because the emphasis in the past has been on reactions in aqueous solution, earlier quantitative and qualitative methods used this medium. They cannot be highly accurate because of hydrolysis. The best available non-aqueous quantitative method seems to be the modification[11] of the American Chemical Society standard method for isocyanates[61] (see Chapter 4.2). The method of choice nowadays for qualitative analysis would be infra-red spectroscopy, in solution or gas phase. Where pure isocyanic acid is used as a reagent, it is an indication of its purity that is required. It has been demonstrated that spectroscopic methods (e.g. I.R. spectroscopy[5,10,31], mass-spectroscopy[8]) can be used.

12.4 Polymerisation of isocyanic acid.

12.4.1 Isocyanic acid dimer. It seems unlikely that a large equilibrium concentration of dimer present in isocyanic acid should go undetected. However, if the dimer had the carbamoyl isocyanate structure suggested in Chapter 5.4, it would be extremely difficult to distinguish chemically from the monomer. Also, absorption spectra, such as that in the infra-red region, would not be likely to show much difference between dimer and monomer, nor would proton-Nuclear Magnetic Resonance spectroscopy, but ^{14}N-N.M.R. would distinguish between the two. The molecule NH_2.CO.NCO has two ^{14}N atoms, with different chemical environments, the molecule HNCO has only one ^{14}N atom. It should also be possible to distinguish between the structure $NH_2.CO.NCO$ and $NH_2.CO.OCN$. The detection of relative masses up to 86 in the Mass Spectrometric fragmentation pattern would give useful information, but the situation would be complicated by the unavoidable presence of cyanuric acid and cyamelide. Any proportion of dimer, as suggested below, would be greater the lower the temperature.

Confirmation of the existence or absence of a dimer would assist in deciding between the two possible general types of mechanism in the reactions of HNCO leading to the formation of urea derivatives, viz:-

1) Stepwise reaction of HNCO, first with another HNCO molecule and then with a reagent molecule.
2) Stepwise reaction of HNCO, first with a reagent molecule and then with a second HNCO molecule.

The concerted attack of two molecules of HNCO on one of a reagent is highly unlikely.

The other possible dimer structure is that held together by hydrogen-bonding, discussed in Chapter 12.2.3 above. This obviates the need for a covalently-bound dimer, but serves to bring two HNCO molecules together prior to reaction with a reagent molecule. A covalently-bound dimer would, of course. be detected by the methods suggested in 12.2.3, but a hydrogen-bonded dimer would not be detected by the methods suggested above for a covalently-bound dimer.

12.4.2 The isocyanic acid - cyanuric acid equilibrium

The vapour density and vapour pressure data of Schmidt[6] show that

1) HNCO is extremely unstable with respect to solid cyanuric acid at ordinary temperature (but the reaction is very slow below the boiling point).

2) The sublimation point temperature of cyanuric acid is 266°C, but the reaction does not become thermodynamically reversible until 350°C and complete dissociation to HNCO does not occur until about 450°C.

3) The standard enthalpy change for dissociation of cyanuric acid is about 42 k cal mol^{-1}, in fairly good agreement with theory.

Schmidt's data cover the range in which the point of equilibrium swings from one extreme to the other and so cannot be usefully extended.

12.4.3 Proportions of products of polymerisation. It is well established that the proportion of cyanuric acid in the end-product increases with increasing applied temperature[16,48]. Data for gas-phase polymerisation (i.e. above 20°C) would be useful. The temperature ,above which cyanuric acid is the sole product, is not known.

Dimerisation of HNCO would be exothermic and so any concentration of dimer would be greater at lower temperatures. If the stepwise mechanism represented by (28) B and C (Chapter 5.5.2) is considered, reaction of dimer with dimer, leading to cyamelide formation, will be more likely at lower temperatures, while reaction of dimer with monomer, leading to cyanuric acid formation, will be more likely at higher temperatures.

It is also established that, at least in benzene solution, the proportion of cyanuric acid present at any time diminishes as the reaction progresses[57]. Again, it is not known how composition of the polymerisate varies with time during reaction in the gas phase.

In terms of the stepwise mechanism, reaction (28) Bii) must be faster than reaction (28) cii), but once the latter is in progress, the subsequent reactions of chain propagation and termination become increasingly faster. Thus, although cyanuric acid is formed faster at first, cyamelide is being formed much more quickly by the end of the reaction.

12.4.4 Mechanism of polymerisation. It is evident that any useful theory of the polymerisation (and other reactions) of HNCO must involve the formation of a dimer of some sort.

In gaseous isocyanic acid, polymerisation seems to be a surface reaction[8,32]. For this reason, kinetic experiments are not likely to give much information with regard to mechanism. The evidence of Kern, Paul and Mehren[57] indicates an ionic polymerisation mechanism in benzene solution. Confirmation of this, and further evidence for elucidation of the mechanism, would be obtained by kinetic experiments performed on solutions of HNCO in solvents of different polarities (bearing in mind that, in some solvents, HNCO is stabilised with respect to polymerisation by complex formation [22,29,30]). It could be confirmed that other substances which should catalyse or inhibit anionic polymerisation do so. This should include carbamate esters (see Chapter 5.5.3).

12.4.5 Structure of cyamelide. It has been suggested (Chapter 5.5.1) that cyamelide could consist of several molecular types, based on polyamide chains (with carbonamide end groups) which are attached to cyclic cyanuric acid residues. Cyamelide is amorphous, as might be expected for this type of structure, so x-ray diffraction methods of investigating the molecular structure are of little help. The substance is insoluble in most solvents and sublimes on heating, so spectroscopy is only possible in the vapour and solid phases.

To summarise, it should be evident from this section that the state of our knowledge concerning the polymerisation of isocyanic acid is unsatisfactory in many respects. Little useful evidence with regard to kinetics and mechanism, both in the gas phase and in solution, has been obtained. The processes which determine the proportions of cyanuric acid and cyamelide formed are not well understood and the structure of cyamelide remains largely a mystery. A lot more work needs to be done on this most ubiquitous reaction of isocyanic acid.

12.5 Pyrolysis and photolysis of isocyanic acid. Nitrogen, hydrogen and carbon monoxide are the main products of both reactions [7,62,63,65]. The results suggest that the N-H bond is particularly strong[62], but it is still not likely to be as strong as the C=N bond. It is the N-H bond which is broken by the less energetic quanta available in mercury photo-sensitized decomposition at 253.7nm, but the more energetic quanta giving direct photolysis at around 200nm are required to break the C=N bond[62]. Individual bond energies in polyatomic molecules are difficult to estimate, as witness the different values for N-H and C=N average bond energies in different sources. The value for N-H is variously quoted at 84[114,115] and 94[116,117] and for C=N as 94[115] and 147[116] (all values in k cal mol^{-1}). A strengthening of the N-H bond may also occur in the similar hydrogen pseudohalide, hydrazoic acid (HN_3), for which one value given is 97[114], though in another source[33] it it given as 85. On the other hand, the presence of the electron-withdrawing carbonyl oxygen atom can weaken a C-N bond. In the molecule $(CH_3)_2$ N-CHO, the bond energy is about

59 k cal mol^{-1}, compared to 80 k cal mol^{-1} for C-N in CH_3NH_2 [114]. No values of bond energies for HNCO have yet been obtained. These would be interesting.

More sophisticated pyrolysis and photolysis experiments than those reported, particularly with regard to the control of surface conditions, should allow kinetic experiments to be performed. The use of pressures below 10mm Hg may eliminate the effect of the container surface and reduce side-reactions. Emission spectra, as employed by Stedman[65], could be used to monitor the formation of products (CO and N_2) and intermediate (NH) as the reaction proceeds.

12.6 Reactions of isocyanic acid with nucleophiles

Nucleophilic molecules can interact either with the H-N bond or with the N=C bond of HNCO. The former type of interaction gives a substituted isocyanate, the latter a derivative of carbamic acid. The known reactions, as discussed in this thesis, are summarised in Table 10. Where two molecules of HNCO react with one of reagent, a derivative of urea is obtained and the chief problem, assuming a stepwise mechanism, is the sequence of interaction of molecules. The ability of HNCO to form a dimer is of vital importance deciding in the type of mechanism.

Table 10. Reactions of isocyanic acid with nucleophiles.

Reagent	Bond Attacked	Products	Ref.
H_2O	i) H-N ii) N=C	$H_3O^{\oplus} + {}^{\ominus}N{=}C{=}O \leftrightarrow N \equiv C{-}O^{\ominus}$ $NH_2.COOH \rightarrow NH_3 + CO_2$; $NH_2.CO.NH_2$	See Ch. 7
R.OH	N=C	$NH_2.COOR$; $NH_2.CO.NH.COOR$	82
NH_3	i) H-N ii) N=C	$NH_4^{\oplus} + {}^{\ominus}N{=}C{=}O \leftrightarrow N \equiv C{-}O^{\ominus}$ $NH_2.CO.NH_2$	See Ch. 9
$R.NH_2$	N=C	$NH_2.CO.NHR$	90
HX (X=Halogen)	N=C	$NH_2.COX$	51
HOCl	N=C	NHCl.COOH → secondary reactions	68
Cl_2	N=C	NHCl.COCl → secondary reactions	68
H_2SO_4	N=C	$NH.SO_3H.COOH \rightarrow NH_2.SO_3H$; $NH_2.CO.NH.SO_3H$	97
R.COOH	N=C	$R.CO.NH.COOH \rightarrow R.CONH_2$	98
Ph_3YO_2H (Y=Ge,Si)	H-N	$Ph_3Y.NCO$	99
H_2O_2	N=C	$NH_2.CO.O_2.CO.NH_2$	99
HNCS	N=C	$NH_2.CO.NCS$	100
$(RR'C{=}N)_2$	N=C	RR'C.NH.CO.N.N.CO.NH.CRR'	14,101, 102
RCH=NR'	N=C	RCH.NH.CO.NR'; R CH.NH.CO.NH.CO.NR'	103
$R_2C{=}C{=}O$	N=C	$NH.CO.NH.CO.CR_2.CO$	104
HNCO	i) H-N ii) N=C	$NH_2.CO.NCO \rightarrow$ NH.CO.NH.CO.NH.CO, cyamelide NH.CO.NH.CO.NH.CO	See Ch.5

12.6.1 Weak acidity in water. The pK value of HNCO is 3.7 ± 0.1[59,68]. More accurate values are required, without errors caused by hydrolysis, at at least four different temperatures so that reliable values of the thermodynamic functions for the reaction can be calculated. The variation of pK with temperature in the range 0-50°C is probably small, giving values of ΔG^o, ΔH^o, and ΔS^o similar to those for methanoic acid.

12.6.2 Hydrolysis and reaction with alcohols. Work on the hydrolysis of HNCO is incomplete and gives no really clear information with respect to the mechanism of the reaction. There are two main reasons; firstly, reactions have always been performed in dilute aqueous solution. Water being in large excess, the part played by the H_2O molecule in the mechanism has been obscured. The second reason is the instability of the expected product, carbamic acid.
A product of its decomposition, ammonia, is likely to react with isocyanic acid to produce urea, a product which can also be formed directly by reaction of HNCO with water.
An alcohol-HNCO system is much simpler. Here, the choice of mechanism is clear-cut, between:

1) the consecutive reactions type, in which reaction with one molecule of HNCO produces carbamate and this reacts with a second HNCO molecule to produce allophanate.

2) the simultaneous reactions type, in which carbamate and allophanate are produced simultaneously, the former from reaction with isocyanac acid monomer and the latter from reaction with dimer.

The evidence so far seems to support 2). Determination of the relative proportions of carbamate and allophanate at the completion of reactions at different temperatures and at different stages during a reaction would give support to a simultaneous reactions mechanism if effects are observed similar to those obtained with polymerisation of HNCO (see Chapter 12.4.3). Kinetic data are required. The order of reaction with respect to HNCO may be obtained using dilute solutions of HNCO in alcohol, the order with respect to alcohol from solutions in a mutual, inert solvent.

The reaction between HNCO and alcohols and also that between HNCO and sulphuric acid, are useful model systems for providing information which can be referred to the water-HNCO system.

With regard to the water-HNCO system itself, one problem is to isolate the effects of the H_2O molecule and the hydrated H^+ ion. It is not established conclusively that H^+ is or is not involved in the mechanism. Kinetic experiments should be performed in the vapour phase and in dilute solutions of HNCO and water in a mutual, inert solvent to elucidate the effect of H_2O. With this base-line, experiments in dilute aqueous solutions of HNCO of different pH values will show up any effect due to H^+.

The extent of the role played by ammonia in urea-formation might be assessed by measuring amounts of CO_2 and urea during the progress of a reaction.

12.6.3 Reaction with ammonia and amines. It is not the intention of this thesis to pronounce on the mechanism of the ammonium cyanate - urea interconversion, especially in view of the recent, comprehensive review of the subject[75]. The apparently excellent kinetic work of Jensen[73] and of Williams and Jencks[91,93] was coloured by interest in this topic to the extent that solutions containing ammonium and cyanate ions were used to investigate the reaction between ammonia and isocyanic acid molecules. Similar kinetic work should be performed with the molecular starting materials in the vapour phase, or in solution in a suitable, inert solvent. This would confirm that the assumption[73] regarding the rate-determining step in (73) (see Chapter 9.1) is justified and that the conclusions of Jensen and Williams and Jencks (see Chapter 9.2) are valid.

12.7 Addition of isocyanic acid to unsaturated molecules.

The HNCO molecule can itself add as a nucleophile across multiple bonds, but its power to do so is low[105]. The known reactions, as discussed in this thesis, are summarised in Table 11. It is the H-N bond in HNCO that is broken, -H being attached to the more electronegative atom and -NCO to the less.

Table 11 Addition reactions of isocyanic acid.

Type of bond	Examples	Ref.
C=C	$RO.CH{=}CH_2 + HNCO \rightarrow RO.CH(NCO) - CH_3$ $R_1R_2C{=}CH_2 + HNCO \rightarrow R_1R_2C(NCO) - CH_3$	30 106,107,108
C≡C	$CH{\equiv}CH + HNCO \rightarrow CH_2{=}CH.NCO$	112
C=O	$R_1R_2C{=}O + HNCO \rightarrow R_1R_2C(NCO) - OH$ (R_1 or R_2, high e.n.) $(CF_3.CO)_2O + 2HNCO \rightarrow 2CF_3.CO.NCO$	110 111
C=N	$(F_2N)_2C{=}NF + HNCO \rightarrow (F_2N)_2C(NCO) - NFH$ $(CH_3)_2.CH.CH = \overset{\oplus}{N}{=}\overset{\ominus}{N} + HNCO$ $\downarrow$ $(CH_3)_2.CH.CH_2-\overset{\oplus}{N}(NCO){=}\overset{\ominus}{N} \rightarrow (CH_3)_2.CH.CH_2.NCO$	105 10

12.8 Applications

12.8.1 Synthesis. Many important polymers used in the plastics industry have the isocyanate group in their molecules. This is why a number of patents for the preparation of HNCO and its use in making isocyanates have been issued, as quoted throughout this thesis. Numerous other types of compounds can also be made using HNCO (see Table 10).

12.8.2 Prevention of isocyanic acid polymerisation. As was mentioned in Chapter 1, isocyanic acid is a by-product of certain industrial processes involving thermal decomposition. Under the conditions employed, the HNCO polymerises and the cyanuric acid/cyamelide tends to "plate-out" on solid surfaces, which causes nuisance. Any additive intended to react with HNCO, forestalling polymerisation, should, preferably, form gaseous products. The reactions of HNCO so far studied, as listed in Tables 10 and 11, do not offer much promise in this respect, but may give clues for the discovery of some reaction which will.

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