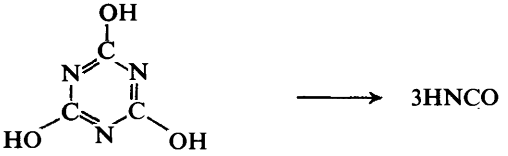
Preparation and Properties of Isocyanic Acid

By D. J. Belson and A. N. Strachan,
DEPARTMENT OF CHEMISTRY, LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY, LOUGHBOROUGH LE11 3TU

1 Introduction

As long ago as 1846, Liebig and Wöhler[1] showed that cyanuric acid depolymerizes on being heated to yield isocyanic acid according to equation (1):



(1)

However, because the HNCO formed is difficult to keep, the investigation of its properties in the intervening years has been fragmentary. Yet HNCO is often formed when compounds containing the amide group (*e.g.* NH_2CONH_2[2] and $NH_2CON{:}NCONH_2$ [3]) are heated, as they often are in industrial processes. An understanding of the nature and properties of isocyanic acid is therefore of considerable importance. The purpose of this review is to bring together what is known and not known about this simple and interesting compound.

2 Preparation

A. Depolymerization of Cyanuric Acid.—Liebig and Wöhler's method,[1] shown in equation (1) was further developed, to give a purer product and better yield, by Linhard[4] and by Herzberg and Reid.[5] Cyanuric acid, on being heated, tends to sublime without reaction. In order to achieve depolymerization, heat must first be applied to the solid to vaporize it and then the resulting vapour must be heated still further.

Herzberg and Reid[5] gave the cyanuric acid a preliminary heating *in vacuo* to 200 °C in order to remove water. The solid was then volatilized slowly *in vacuo* at 450 °C and the gas stream was passed through a tube furnace at 700 °C. The bulk of the HNCO was collected in a trap at −80 °C. After oxidation by

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[1] J. Liebig and F. Wöhler, *Annalen*, 1846, **39**, 29.
[2] F. J. Schiltknecht, Thesis, Zürich, 1963.
[3] A. S. Prakash, W. A. Swann, and A. N. Strachan, *J. Chem. Soc., Perkin Trans. 2*, 1975, 46.
[4] M. Linhard, *Z. anorg. Chem.*, 1938, **236**, 200.
[5] G. Herzberg and C. Reid, *Discuss. Faraday Soc.*, 1950, **9**, 92.

Ag_2O of any HCN present, drying with P_2O_5, and distillation at $-30\,°C$, a product considered to be better than 99.5% pure was obtained. Other workers[6] have used a similar method to produce HNCO but have collected it as a solution in ether, which is then filtered to remove suspended cyanuric acid and cyamelide.

B. Acidification of Alkali Isocyanates.—A variety of ways of acidifying alkali isocyanates to produce isocyanic acid has been employed. Smith and Jonassen[7] heated a mixture of $KHSO_4$ and KNCO but found that, in addition to HNCO, large amounts of CO_2 were produced. Groving and Holm[8] passed gaseous HCl over finely powdered NaNCO and considered this method gave a product with fewer impurities than that obtained from the depolymerization of cyanuric acid. Oertel and co-workers[9] also used HCl and their patent claims 85% and 95% yields of HNCO when HCl gas is passed into suspensions of alkali isocyanates in inert organic liquids. In another patent[10] a solution of trichloroacetic acid in hexane is added to a warm solution of NaNCO in hexane. The HNCO gas is then bubbled through a hexane solution containing the compound with which reaction is desired.

Instead of producing HNCO first and then using it in the reaction later, many workers have preferred to generate it *in situ*, which this method allows. For example, dry HCl gas can be passed into a suspension of KNCO in the molten reactant[11] or KNCO can be added to a solution of the reactant in an anhydrous solvent saturated with HCl.[11] Alternatively, KNCO can be added to a solution of the reactant in glacial acetic acid.[12] Although HNCO is hydrolysed by water (see Section 4C) even aqueous solutions of reactants can sometimes be used with NaNCO added first and then the mixture acidified.[13]

C. Other Methods.—Isocyanic acid is formed whenever urea is heated[2] in accordance with equation (2):

$$NH_2CONH_2 \rightarrow HNCO + NH_3 \qquad (2)$$

Although this method has not been used for preparative purposes in the laboratory, it is the basis of several patents[14] for producing HNCO industrially. In the case of nitrourea it is only necessary to heat a solution of the compound in water for decomposition to occur in accordance with equation (3):[15]

$$NH_2CONHNO_2 \rightarrow HNCO + NH_2NO_2 \qquad (3)$$

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[6] F. Zobrist and H. Schinz, *Helv. Chim. Acta*, 1952, **35**, 2380; T. C. Waddington, *J. Chem. Soc.* 1959, 2499.

[7] S. R. Smith and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, 1967, **29**, 860.

[8] N. Groving and A. Holm, *Acta Chem. Scand.*, 1965, **19**, 1768.

[9] G. Oertel, H. Holtschmidt, and K. F. Zenner, U.S.P. 3 374 060/1968.

[10] I. Nagayama, A. Maruyama, S. Yamada, S. Nakai, and T. Kutsuma, Jap. P. 16 433/1972.

[11] A. E. A. Werner and J. Gray, *Sci. Proc. R. Dublin Soc.*, 1946, **24**, 77.

[12] J. R. Bailey and H. N. Moore, *J. Amer. Chem. Soc.*, 1917, **39**, 279.

[13] E. W. Cummins, Fr. P. 2 065 597/1971.

[14] A. Schmidt, F. Weinrotter, and W. Mueller, Ger. P. 1 467 205/1972; I. Takahashi and S. Ozako, Jap. P. 45 078/1974; J. D. M. Verstegen, Ger. P. 2 461 676/1975.

[15] T. L. Davis and K. C. Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

The decomposition is accelerated by the presence of bases and the nitramide formed decomposes further in accordance with equation (4):

$$NH_2NO_2 \rightarrow N_2O + H_2O \qquad (4)$$

and thus is easily removed. The method is clearly useful for *in situ* generation of HNCO in aqueous solutions.

The removal of hydrogen halide from a carbamoyl halide as in equation (5):

$$H_2NCOX \rightarrow HNCO + HX \qquad (5)$$

can be brought about by reagents such as ethers with basic properties sufficient to remove HX but insufficient to promote polymerization of HNCO.[16] Other methods by which HNCO may be prepared include the pyrolysis of alkyl carbamates (*e.g.* NH_2CO_2Me)[17] and the reaction of molten alkali cyanate with urea, biuret, or cyanuric acid.[18]

D. Storage and Safety.—At ambient temperature isocyanic acid cannot be stored either in the gas phase[5,7] or as a concentrated solution in an organic solvent[8,19] since in both cases it polymerizes at an appreciable rate. It keeps for some time at room temperature without serious loss, however, as a dilute solution in such solvents as CCl_4[19] and ethers.[16,20] To store it for longer periods of time it is necessary to slow the polymerization down to an insignificant rate by keeping the temperature at $-30\,^\circ C$ or below.[21] Stored at dry ice or liquid nitrogen temperatures, isocyanic acid can be kept without change indefinitely.[22]

Liquid isocyanic acid is reported to be strongly acidic and to raise painful blisters on the skin.[23] This apart there is no evidence in the literature to suggest that HNCO is particularly hazardous to handle, nor are there any reports of its being toxic. If the liquid is allowed to evaporate, an explosion as a result of pressure build-up of gas is improbable since polymerization in the gas phase is rapid, the rate increasing with increasing pressure (see Section 4A). Likewise, inhalation or ingestion of isocyanic acid is unlikely to cause serious or permanent damage because of the ease with which the compound is hydrolysed to harmless products on contact with water (see Section 4C). This hydrolysis will be particularly rapid under the acid conditions which prevail in the stomach. Thus, as regards safety, HNCO is almost certainly less hazardous to use in the laboratory than say HCl.

[16] Stauffer Chemical Co., Neth. P. Appl. 6 600 575/1966.

[17] J. J. Godfrey, U.S. P. 3 314 754/1967.

[18] E. S. Roberts and L. J. Christmann, Ger. P. 1 159 411/1963.

[19] J. Nelson, *Spectrochim. Acta*, 1970, **26**, 109.

[20] A. Michael and H. Hibbert, *Annalen*, 1909, **364**, 129.

[21] B. P. Winnewisser and M. Winnewisser, *J. Mol. Spectrosc.* 1969, **29**, 505.

[22] D. J. Belson and A. N. Strachan, unpublished data.

[23] T. W. J. Taylor and W. Baker, 'Sidgwick's Organic Chemistry of Nitrogen', Clarendon Press, Oxford, 2nd Edn., 1937, p. 322.

3 Physical Properties and Structure

A. Spectra.—The microwave[24] and infra-red[5,19,21] spectra of isocyanic acid vapour have been investigated by several workers and the values and assignments of the six fundamental frequencies and three moments of inertia have been unequivocably established. One of the moments of inertia is very small and considerably less than that of free NH, indicating that the three heavy atoms N—C—O are near linear with the H atom off that line at an angle much different from 90 °. Two of the vibrational frequencies appear in the Raman spectrum of the liquid.[5,25] One of these is the N—H stretching frequency which undergoes a large shift between the vapour phase and the liquid phase as a result of hydrogen bonding. An additional large shift in this frequency occurs in going from the liquid to the low temperature form of the solid,[5] indicating even stronger hydrogen bonding. This apart, the infra-red spectrum of the solid is similar to that of the vapour.[5]

In the ultra-violet, isocyanic acid starts to absorb weakly around 280 nm. The absorption continues, increasing in intensity all the while, to beyond 200 nm.[26,27] High resolution reveals four progressions of diffuse bands, which at longer wavelengths have well resolved coarse rotational structure.[28]

The proton nuclear magnetic resonance spectrum[29] is a broad triplet as a result of ^{14}NH spin coupling, with a coupling constant of 60 Hz.

Several groups of workers[7,30,31] have investigated the mass spectrum, which is of interest in having a major m/e peak at 29 corresponding to HCO^+. How this is formed from HNCO has been the subject of considerable speculation, but hard evidence in favour of any particular mechanism is lacking.

B. Structure.—Werner[32] in 1913 postulated that cyanic acid HOCN and isocyanic acid HNCO exist together in tautomeric equilibrium. It was supposed[33] that on hydrolysis cyanic acid gave ammonium cyanate and isocyanic acid gave urea, and that on polymerization cyanic acid formed cyamelide whereas isocyanic acid formed cyanuric acid. Although some later workers[34,8] supported Werner's postulate, others[35] contended that all the chemical reactions could be explained by the structure HNCO.

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[24] R. Kewley, K. V. L. Sastry, and M. Winnewisser, *J. Mol. Spectrosc.*, 1963, **10**, 418.

[25] J. Goubeau, *Ber.*, 1935, **68**, 912.

[26] Sho-Chow Woo and Ta-Kong Liu, *J. Chem. Phys.*, 1935, **3**, 544.

[27] J. W. Rabalais, J. R. McDonald, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **51**, 5103.

[28] R. N. Dixon and G. H. Kirby, *Trans. Faraday Soc.*, 1968, **64**, 2002.

[29] J. Nelson, R. Spratt, and S. M. Nelson, *J. Chem. Soc. (A)*, 1970, 583.

[30] J. M. Ruth and R. J. Philippe, *Anal. Chem.*, 1966, **38**, 720; C. W. Hand and D. J. Bogan, *J. Phys. Chem.*, 1971, **75**, 1532.

[31] F. Compernolle, *Org. Mass Spectrom.*, 1975, **10**, 289.

[32] E. A. Werner, *J. Chem. Soc.*, 1913, **103**, 1010.

[33] E. A. Werner and W. R. Fearon, *J. Chem. Soc.*, 1920, **117**, 1356; A. E. A. Werner and J. Gray, *Sci. Proc. R. Dublin Soc.*, 1947, **24**, 209.

[34] A. Hantzsch, *Z. Anorg Chem.*, 1932, **209**, 213.

[35] W. Hückel, 'Theoretischen Grundlagen der organischen Chemie', Academische Verlagsgesellschaft, Leipzig, 1931, vol. 1, p. 193; M. Linhard and K. Betz, *Ber.*, 1940, **73**, 177.

Russian[36] workers, on the basis of predictions of the pK_as of the two acids, have recently estimated that in aqueous solution the ratio of isocyanic acid to cyanic acid will be 2000:1. A ratio of this order of magnitude is certainly in much better accord with the spectral information outlined above and the *X*-ray data on the solid[37] than earlier estimates of 40:60[33] and 100:3.[8] Thus, if in the pure state the two acids do exist together in tautomeric equilibrium, the evidence all points to the proportion of cyanic acid being negligibly small. Hence for all practical purposes the compound, whether in the gaseous, liquid, or solid state, can be taken to have the isocyanic acid structure HNCO.

C. Liquid and Solid.—There is some uncertainty over the melting point of HNCO. Most sources[37,38] give it as −80 °C but Linhard[39] found it to be −86 °C. Measurements of the vapour pressure have been made over the temperature range −76 to −6 °C.[4] The vapour pressure is approximately 1 mmHg at −80 °C, 10 mmHg at −53 °C, 100 mmHg at −19 °C and the normal boiling point by extrapolation is 23.5 °C.[4] The Trouton's constant calculated from the vapour pressures is higher than that expected for a 'normal' liquid.[4] This indicates considerable association of molecules in the liquid state, which on the basis of the infra-red spectrum discussed above, can be ascribed to intermolecular hydrogen bonding. The density of the liquid at 20 °C is 1.140 g cm^{-3}.[38]

Van Dohlen and Carpenter[37] found two forms of solid isocyanic acid. A low temperature form is observed when super-cooled liquid crystallizes. Its structure has not been determined. On warming, this changes to the high temperature form, the transition temperature being about −100 °C. The high temperature form is orthorhombic. It can be cooled below −100 °C without the transition back to the low temperature form occurring, and has a density at the temperature of liquid nitrogen of 1.40 g cm^{-3}.

D. Thermodynamic Properties.—The 1974 supplement to the JANAF Thermochemical Tables[40] gives a comprehensive tabulation of thermodynamic properties of HNCO in the range 0—6000 K. The standard enthalpy of formation at 25 °C is given as −24.3 kcal mol^{-1} (−101.6 kJ mol^{-1}). This is derived from a study of the onset of photodissociation.[41] The validity of this value is confirmed by an independent estimate of -25 ± 3 kcal mol^{-1} from mass spectrometric data.[31]

4 Chemical Properties

A. Polymerization.—Liquid isocyanic acid polymerizes to form a mixture of

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[36] A. I. Finkel'shtein and E. M. Moncharzh, *Russ. J. Phys. Chem.*, 1972, **46**, 1685.

[37] W. C. Von Dohlen and G. B. Carpenter, *Acta Crystallogr.*, 1955, **8**, 646.

[38] 'Lange's Handbook of Chemistry'. McCraw-Hill, New York, 11th Edn., 1973; 'Handbook of Chemistry and Physics', Chemical Rubber Co., Boca Raton, Florida, 61st Edn., 1980.

[39] M. Linhard, *Z. Anorg. Chem.*, 1938, **239**, 155.

[40] M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, 1974, **3**, 311.

[41] H. Okabe and M. Lenzi, *J. Chem. Phys.*, 1967, **47**, 5241; H. Okabe, *ibid*, 1970, **53**, 3507.

cyanuric acid and cyamelide.[33] The two can readily be separated since cyanuric acid is soluble in hot water whereas cyamelide is not. The proportion of cyanuric acid formed increases with temperature, from 30% at −20 °C to 57 % at 20 °C.[33] Although the structure of cyanuric acid is well established, that of cyamelide remains largely undetermined. Several suggestions as to its make-up have been put forward.[42,43] but the polymer has never been thoroughly investigated.

Gaseous isocyanic acid at high temperatures polymerizes to form cyanuric acid as the sole product in accordance with equation (7):[33]

$$3\ \mathrm{HNCO}\ (g) \rightleftharpoons (\mathrm{HNCO})_3\ (g) \qquad (7)$$

The reaction is reversible. At lower temperatures some cyamelide is also formed. Values of the equilibrium constant K for the reaction shown in equation (7) between 365 and 434 °C have been determined from vapour density measurements.[44] From a plot of log K *versus* T^{-1} the mean heat of reaction for equation (7) over the temperature range is $-55\,\mathrm{kcal\,mol^{-1}}$. Extrapolation of such a plot leads to the prediction that $K = 1\,\mathrm{atm^{-2}}$ at 350 °C. Hence below 350 °C isocyanic acid will always tend to polymerize, whereas above 350 °C it can be formed by the depolymerization of both cyanuric acid and cyamelide.

An investigation of the polymerization of isocyanic acid in benzene at 15 °C has shown that the proportion of cyamelide in the polymerides increases as the polymerization proceeds, and that small amounts of many additives have either an inhibiting or a catalytic effect on the rate.[43] The evidence points to an ionic rather than a free-radical mechanism. The fact that amines such as pyridine appear to be the best catalysts and Lewis acids such as $AlCl_3$ and $FeCl_3$ are ineffective, suggests that the polymerization is anionic rather than cationic.

First-order kinetics with a half life of 18h have been found for the gas phase polymerization at 30 °C.[7] Whether this is truly an homogeneous reaction, or really takes place heterogeneously on the walls of the reaction vessel, has not been investigated.

B. Decomposition.—The photochemical decomposition of HNCO has been extensively studied.[45–48] Whereas the primary process in the mercury photosensitized decomposition[46] at 253.7nm appears to be solely that shown in equation (8):

$$\mathrm{HNCO}^* \rightarrow \mathrm{H} + \mathrm{NCO} \qquad (8)$$

in the direct photolysis[47,48] at shorter wavelengths nearer 200nm a competing primary process, shown in equation (9), also occurs.

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[42] T. W. J. Taylor and W. Baker, in ref. 23, p. 323.

[43] W. Kern, H. Paul, and W. Meyren, *Makromol. Chem.*, 1954, **14**, 146.

[44] A. Schmidt, *Monatsh. Chem.*, 1970, **101**, 866.

[45] J. Y. P. Mui and R. A. Back, *Canad. J. Chem.*, 1963, **41**, 826; R. A. Back, *J. Chem. Phys.*, 1964, **40**, 3493; J. L. Brash and R. A. Back, *Canad. J. Chem.*, 1965, **43**, 1778; R. A. Back and R. Ketcheson, *ibid*, 1968, **46**, 531.

[46] N. J. Friswell and R. A. Back, *Canad. J. Chem.*, 1968, **46**, 527.

[47] J. N. Bradley, J. R. Gilbert, and P. Svejda, *Trans. Faraday Soc.*, 1968, **64**, 911.

[48] W. D. Woolley and R. A. Back, *Canad. J. Chem.*, 1968, **46**, 295.

$$HNCO^* \rightarrow NH + CO \qquad (9)$$

The gaseous products are CO, N_2, and H_2 with the N_2:CO ratio ~ 0.4. Some workers[47] find the H_2:CO ratio to be similar, but others[48] find it to be much less. Some NH_3 is probably also formed but is not detected owing to its removal by reaction with HNCO to form ammonium cyanate and/or urea. Various secondary reactions of H, NCO, and NH radicals with HNCO and with themselves are postulated to account for the products and the effect on yields of additives such as C_2H_4, H_2, NO, and O_2. However, most of the secondary reactions are speculative and definite proof of their occurrence is lacking.

Confirmation that with sufficient energy input breakage of the carbon—nitrogen bond occurs, as shown in equation (9), comes from studies of the reaction of HNCO with electric discharge-excited inert-gas atoms, where the emission spectra of both NH and CO are observed.[49]

A brief study has been made of the pyrolysis of HNCO vapour.[50] This is very slow at 500 °C but becomes almost too fast to follow at 700 °C. The products are CO, N_2, H_2, HCN, and CO_2. The decomposition appears to be a surface reaction. Poor reproducibility owing to surface effects, polymerization, and secondary reactions, has inhibited detailed investigation.

C. Reaction with Water.—In aqueous solution isocyanic acid undergoes both ionization in accordance with equation (10):

$$HNCO \rightleftharpoons H^+ + NCO^- \qquad (10)$$

and hydrolysis in accordance with equation (11):

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (11)$$

Under some conditions, polymerization to form cyanuric acid and cyamelide is also significant.[51]

Several groups of workers[52,53] have attempted to determine the pK_a value for the reaction shown in equation (10). The determination is made difficult by the competing hydrolysis reaction. Despite this, all workers find pK_a values close to 3.7 with little variation apparent between 0 and 45 °C. Thus, as an acid, HNCO is very similar to HCO_2H.[38]

Although no studies have been made of the gas-phase reaction shown in equation (12):

$$HNCO(g) + H_2O(g) \rightleftharpoons NH_3(g) + CO_2(g) \qquad (12)$$

calculated values of the equilibrium constant K for the reaction shown in equation (12) indicate that the equilibrium lies well to the right at all temperatures up to

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[49] D. H. Stedman, *J. Chem. Phys.*, 1970, **52**, 3966.

[50] R. A. Back and J. Childs, *Canad. J. Chem.*, 1968, **46**, 1023.

[51] C. W. B. Normand and A. C. Cumming, *Proc. Chem. Soc.*, 1912, **28**, 225; *J. Chem. Soc.*, 1912, **101**, 1852.

[52] R. Caramazza, *Gazz Chim. Ital.*, 1958, **88**, 308; J. H. Broughton, Ph.D. Thesis, University of Colorado, 1965.

[53] A. R. Amell, *J Am. Chem. Soc.*, 1956, **78**, 6234.

1000 K and beyond.[54] At 25 °C, K is estimated to be 10^{12}. Hence at ambient temperature the hydrolysis reaction [equation (11)] whether occurring in the gas phase or in solution is, for all practical purposes, irreversible.

The kinetics and mechanism of the hydrolysis reaction have been studied extensively.[33,51,53,55–58] Early workers[33,51] found both ammonium cyanate and urea in the products and believed that these were formed by the reactions of the ammonia from equation (11) with cyanic acid and isocyanic acid, respectively. Since it is now clear that no significant amount of cyanic acid is present in solution, the two products must both be formed from isocyanic acid. Moreover, because ammonium cyanate is steadily converted into urea in aqueous solution,[59] the proportions of the two found will depend upon the time elapsed between reaction and analysis.

Recent work[57,58] has shown that the hydrolysis is pH dependent and occurs most rapidly in acid solutions *via* the reaction shown in equation (13):

$$HNCO + H_2O + H^+ \rightarrow NH_4^+ + CO_2 \tag{13}$$

In more neutral solutions, however, the reaction follows equation (14):

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{14}$$

and in alkaline solutions hydrolysis takes place according to equation (15):

$$NCO^- + 2H_2O \rightarrow NH_3 + HCO_3^- \tag{15}$$

Rate constants and activation energies for the reactions given in equations (13), (14), and (15) have been determined.[57,58]

The reactions shown in equations (14) and (15) probably occur through the formation of carbamic acid and carbamate, respectively, as intermediates [equations (16) and (17)]:

$$HNCO \xrightarrow{H_2O} NH_2COOH \longrightarrow NH_3 + CO_2 \tag{16}$$

$$NCO^- \xrightarrow{H_2O} NH_2COO^- \xrightarrow{H_2O} NH_3 + HCO_3^- \tag{17}$$

Carbamic acid is very unstable with a half-life time at 0 °C of ~ 0.009 s,[60] which explains why efforts to detect it have been unsuccessful.[39] Carbamate is more stable,[60] but so also is cyanate, and conclusive evidence that the reaction shown in equation (15) proceeds by way of that shown in equation (17) is lacking.

The reactions shown in equations (14) and (15) are both found to be catalysed by certain bivalent anions such as carbonate and phosphate.[57,58] This presumably occurs through the formation between HNCO or NCO^- and the dianion of a

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[54] M. W. Lister, *Canad. J. Chem.*, 1955, **33**, 426.
[55] J. Gisbier, *Z. Chem.*, 1971, **11**, 394.
[56] W. R. Fearon and G. C. Dockeray, *Biochem. J.*, 1925, **20**, 13.
[57] M. B. Jensen, *Acta Chem. Scand.*, 1958, **12**, 1657; 1959, **13**, 659.
[58] G. D. Vogels, L. Uffink, and C. Van der Drift, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 500.
[59] J. Shorter, *Chem. Soc. Rev.*, 1978, **7**, 1.
[60] F. J. W. Roughton, *J. Am. Chem. Soc.*, 1941, **63**, 2930.

carbamoyl compound, which is then hydrolysed more rapidly than the HNCO or HCO^- on their own.[58,61]

D. Reaction with Polar Compounds.—Many polar compounds react with HNCO to add across the nitrogen–carbon bond. The more negative part of the adding molecule becomes attached to the carbon and the more positive part (usually, but not always, a hydrogen atom) to the nitrogen.[35] Thus hydrogen halides react according to equation (18):[35]

$$\begin{array}{c}\text{H—X}\\ +\\ \text{HN=CO}\end{array} \rightarrow NH_2COX \qquad (18)$$

alcohols according to equation (19):[10,15,62,63]

$$\begin{array}{c}\text{H—OR}\\ +\\ \text{HN=CO}\end{array} \rightarrow NH_2CO_2R \qquad (19)$$

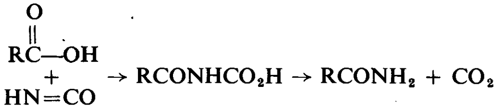
amines according to equation (20):[20,64]

$$\begin{array}{c}\text{H—NRR}'\\ +\\ \text{HN=CO}\end{array} \rightarrow NH_2CONRR' \qquad (20)$$

sulphuric acid according to equation (21):[65]

$$\begin{array}{c}HO_3S\text{—OH}\\ +\\ \text{HN=CO}\end{array} \rightarrow HO_3SNHCO_2H \rightarrow HO_3SNH_2 + CO_2 \qquad (21)$$

and carboxylic acids according to equation (22):[66]



$$\begin{array}{c}\overset{\overset{\text{O}}{\|}}{\text{RC}}\text{—OH}\\ +\\ \text{HN=CO}\end{array} \rightarrow RCONHCO_2H \rightarrow RCONH_2 + CO_2 \qquad (22)$$

These reactions are often complicated by the fact that the product formed, as can be seen from equations (18)—(22), invariably contains an $—NH_2$ group. This is often capable of reacting with a second HNCO molecule. Thus with alcohols the product is usually an alkyl allophanate rather than an alkyl carbamate as a result of the reaction shown in equation (23):

$$HOR + 2HNCO \rightarrow NH_2CONHCO_2R \qquad (23)$$

This reaction [equation (23)] probably occurs by way of equation (19) followed by equation (24):[62]

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[61] C. M. Allen and M. E. Jones, *Biochemistry*, 1964, **3**, 1238.

[62] H. W. Blohm and E. I. Becker, *Chem. Rev.*, 1952, **51**, 471; M. Amagasa, Y. Kasuga, Y. Saito, T. Yamauchi, and H. Takegawa, *Kobunshi Kagaku*, 1971, **28**, 42.

[63] W. J. Close and M. A. Spielman, *J. Am. Chem. Soc.*, 1953, **75**, 4055.

[64] M. B. Jensen, *Acta Chem. Scand.*, 1959, **13**, 289; A. Williams and W. P. Jencks. *J. Chem. Soc., Perkin Trans. 2*, 1974, 1753, and 1760.

[65] M. Linhard, *Annalen*, 1938, **535**, 267.

[66] I. Takahashi, S. Ozaki, A. Kurokawa, and Y. Koyama, Jap. P. 20 522/1973.

$$\begin{matrix}\text{H—NHCO}_2\text{R}\\ +\\ \text{HN=CO}\end{matrix} \rightarrow \text{NH}_2\text{CONHCO}_2\text{R} \qquad (24)$$

although some authors[15,63] dispute this. With amines the initial urea formed according to equation (20) can react further to give a biuret by equation (25):[67]

$$\begin{matrix}\text{H—NHCONRR}'\\ +\\ \text{HN=CO}\end{matrix} \rightarrow \text{NH}_2\text{CONHCONRR}' \qquad (25)$$

Similarly with sulphuric acid, the aminosulphonic acid produced by the reaction shown in equation (21) is capable of further reaction, as shown in equation (26), to form carbamidosulphonic acid:[65]

$$\begin{matrix}\text{H—NHSO}_3\text{H}\\ +\\ \text{HN=CO}\end{matrix} \rightarrow \text{NH}_2\text{CONHSO}_3\text{H} \qquad (26)$$

It can be seen from equations (23), (25), and (26) that the product of the reaction with two HNCO molecules also contains an $—\text{NH}_2$ group, so that further consecutive reactions with HNCO are possible, resulting in polymerization of the isocyanic acid. This would explain why, particularly in the reaction with amines, cyamelide is usually a by-product and is in some cases the sole product.[20]

Ammonia and primary and secondary amines react initially with HNCO in two ways, as shown in equation (27) to form cyanates and as in equation (28) to form ureas:

$$\text{NHRR}' + \text{HNCO} \rightleftharpoons \overset{+}{\text{NH}_2\text{RR}'}\ \overset{-}{\text{NCO}} \qquad (27)$$

$$\text{NHRR}' + \text{HNCO} \rightleftharpoons \text{NH}_2\text{CONRR}' \qquad (28)$$

Both reactions are reversible with the result that the cyanate can be transformed into the urea and *vice versa*.[59] At ambient temperature, however, the overall equilibrium lies heavily in favour of the urea, so although some cyanate may be formed initially, the ultimate product is always the urea.

The kinetics of the forward reaction of equation (28) have been studied in very great detail.[59,64] The evidence points to the forward process occurring *via* a zwitterion intermediate as in equation (29):

$$\begin{matrix}\text{H—NRR}'\\ +\\ \text{HN=CO}\end{matrix} \rightarrow \begin{matrix}\text{H—}\overset{+}{\text{N}}\text{RR}'\\ \overset{-}{}\quad |\\ \text{HN—CO}\end{matrix} \rightarrow \text{NH}_2\text{CONRR}' \qquad (29)$$

The first stage in equation (29) may be regarded as nucleophilic attack by the lone pair electrons of the amine nitrogen on the positively polarized carbon of the HNCO (or equally, as electrophilic attack by the HNCO carbon on the amine nitrogen). The second stage involves a simple proton transfer. The slow rate-determining step appears to be the first stage with strongly basic amines, and the second stage with weakly basic ones.[64]

Other compounds that have been reported as reacting with HNCO in a similar

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[67] J. R. Scott and J. B. Cohen, *J. Chem. Soc.*, 1922, **121**, 2034.

way (*i.e.* by addition across the nitrogen–carbon bond) are phenols,[68] hydroperoxides,[69] oximes,[13] hydroxylamine,[70] isothiocyanic acid,[71] and pyrazolines.[72] The oxidation of HNCO by halogens[51,54] and hypochlorite[54] probably starts in the same way.

E. Reaction with Unsaturated Compounds.—Just as polar compounds add across the unsaturated part of HNCO, so HNCO itself can add across the double and triple bonds of unsaturated molecules. The hydrogen–nitrogen bond is now involved and the molecule reacts as a pseudo hydrogen halide, in accordance with equation (30):

$$X{=}Y + HNCO \rightarrow XH{-}YNCO \qquad (30)$$

A catalyst is often required for this reaction to occur.

The first report of the addition to alkenyl compounds is that of the formation of α-alkoxy-isocyanates from α,β-unsaturated ethers[73] as in equation (31):

$$BuOCH{=}CH_2 + HNCO \rightarrow BuO\underset{\displaystyle NCO}{\underset{|}{C}}H{-}CH_3 \qquad (31)$$

Subsequently, patents have been issued for the preparation of isocyanates from HNCO and various alkenes,[74] and also from alkynes[75] in accordance with equation (32):

$$CH{\equiv}CH + HNCO \rightarrow CH_2{=}CHNCO \qquad (32)$$

Isocyanates are also formed when HNCO reacts with diazo-compounds[8] as illustrated by equation (33), the initial addition now almost certainly taking place across the carbon–nitrogen double bond.

$$Me_2CHCH{=}N_2 + HNCO \rightarrow Me_2CHCH_2NCO + N_2 \qquad (33)$$

The addition of HNCO across the carbonyl group leads to the formation of α-hydroxy-isocyanates[76] as in equation (34):

$$RR'C{=}O + HNCO \rightarrow RR'C(OH)NCO \qquad (34)$$

These are highly reactive and some polymerize explosively. With trifluoroacetic anhydride[77] and excess HNCO, trifluoroacetyl isocyanate is obtained as indicated in equation (35). However, when excess $(CF_3CO)_2O$ is used, the product is

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[68] I. Takahashi, S. Ozaki, and T. Tamaki, Jap. P. 36 706/1974.

[69] R. P. Surova, N. P. Muraeva, O. N. Druzhkov, N. M. Lapshin, and O. S. D'yachkovskaya, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1628.

[70] H. Kofod, *Acta Chem. Scand.*, 1956, **10**, 256; *ibid*, 1959, **13**, 461.

[71] L. Birckenbach and K. Kraus, *Ber.*, 1938, **71**, 1492.

[72] R. Locquin and R. Heilmann, *C.R. Hebd. Seances Acad. Sci.*, 1925, **180**, 1757.

[73] F. W. Hoover and H. S. Rothrock, *J. Org. Chem.*, 1963, **28**, 2082.

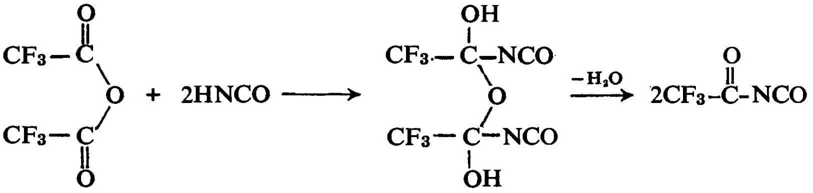
[74] J. M. Cross and S. H. Metzer, U.S. P. 3 471 542/1969; I. Takahashi, S. Ozaki, and Y. Kamiyama, Jap. P. 20 574/1974; E. Boizov, G. Balabanov, M. Iwanov, M. Pfeifer, and P. Creutzberg, E. Ger. P. 116 550 and 116 551/1975.

[75] Shell Internationale Research, Neth. Appl. P. 72 17 060/1974.

[76] F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, 1963, **28**, 1825.

[77] W. C. Firth, *J. Org. Chem.*, 1968, **33**, 441.

perfluorodiacetamide in accordance with equation (36). Whereas the reaction shown in equation (35) probably proceeds as indicated by addition of HNCO across the carbonyl groups, the initial step in equation (36) is more likely to be the addition of the anhydride across the nitrogen–carbon bond of HNCO as in equation (37):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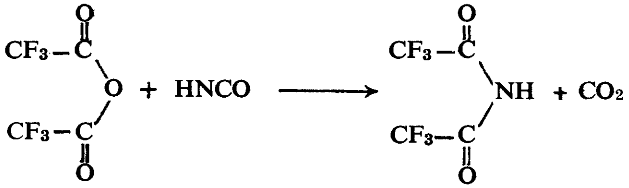

(36)


(37)

$$\begin{matrix}\overset{\displaystyle O}{\overset{\|}{CF_3C}}\text{—}OCOCF_3\\ +\\ HN{=}CO\end{matrix} \rightarrow CF_3CONHCO_2COCF_3 \rightarrow CF_3CONHCOCF_3 + CO_2 \qquad (37)$$

Finally, HNCO reacts readily with compounds containing carbon–nitrogen double bonds. This is undoubtedly the reason that HNCO polymerizes so readily, the N—H bond in one molecule adding across the C=N bond of another as shown in equation (38):

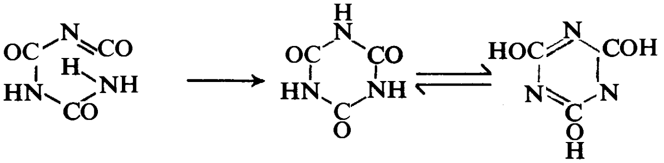
$$\begin{matrix}H\text{—}NCO\\ +\\ HN{=}CO\end{matrix} \rightarrow NH_2CONCO \qquad (38)$$

Although the initial product, NH_2CONCO, is too reactive ever to have been isolated, the corresponding thio-compound, NH_2CONCS has been shown to be formed when HNCO reacts with HNCS.[71] The addition of a further molecule leads to a trimer as in equation (39):

$$\begin{matrix}H\text{—}NCO\\ +\\ NH_2CON{=}CO\end{matrix} \rightarrow NH_2CONHCONCO \qquad (39)$$

This can then either undergo cyclization to form cyanuric acid as indicated in equation (40) or add further HNCO molecules (and possibly also cyanuric acid molecules) to form cyamelide.

In its reactions with other compounds containing carbon–nitrogen double


(40)

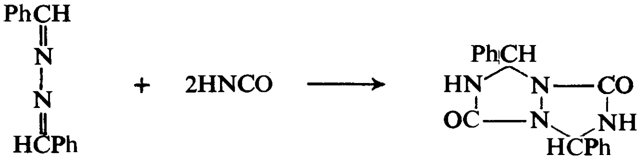
bonds, the tendency towards cyclization is also strong. Thus, with the imide $(F_2N)_2C{=}NF$,[78] in addition to the expected 1 : 1 adduct formed as in equation (41):

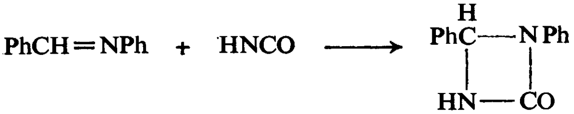
$$(F_2N)_2C{=}NF + HNCO \rightarrow (F_2N)_2C(NCO)NFH \qquad (41)$$

a 2 : 1 cyclic adduct is also produced as shown in equation (42). With azines,[11,79] instead of the expected 1,2 and 3,4 addition, 1,3 and 2,4 addition occurs to give bitriazoles with two five-membered rings as illustrated by equation (43). In the case of Schiff's bases[80] sometimes a four-membered ring is formed as in equation (44) and sometimes a six-membered ring as shown in equation (45).

This last reaction is similar to those shown in equations (40) and (42) and also to the reaction of HNCO with ketenes,[81] which proceeds according to equation (46).


(42)


(43)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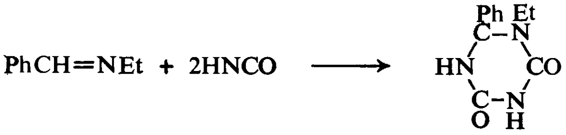
(45)

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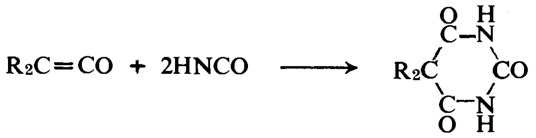
[78] W. C. Firth, S. Frank, and E. J. Schriffert, *J. Org. Chem.*, 1973, **38**, 1080.

[79] J. R. Bailey and H. N. Moore, *J. Am. Chem. Soc.*, 1917, **39**, 279; J. R. Bailey and A. T. McPherson, *ibid*, 1917, **39**, 1322.

[80] N. A. Lange, *J. Am. Chem. Soc.*, 1926, **48**, 2440.

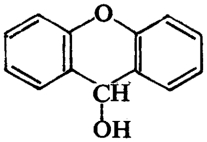
[81] H. Staudinger, *Annalen*, 1911, **374**, 11; *Ber.*, 1917, **50**, 1042.



(46)

5 Analysis

A. Classical Quantitative Methods.—Two general analytical methods have found use. One involves conversion of HNCO into urea, which is then determined by the xanthydrol [9-hydroxyxanthene (1)] method; the other involves precipitation of silver isocyanate.

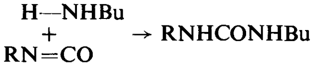


(1)

In the first method, two molecules of xanthydrol ($C_{13}H_{10}O_2$) condense with one of urea to form insoluble dixanthylurea, $CO(NH{\cdot}C_{13}H_9O)_2$. The finish may be gravimetric,[82] titrimetric[83] [the precipitate is dissolved in dilute sulphuric acid and titrated at 70—75 °C with potassium manganate(VII)], or colorimetric[84] (the precipitate is dissolved in 50% sulphuric acid and the absorbance measured at 420nm).

In the second method,[82] silver isocyanate is not weighed as such, but is treated with excess ammonium chloride and dilute ammonia. The solution formed is neutralized and the resulting silver chloride precipitate is filtered off and weighed. Alternatively, the silver isocyanate can be dissolved in excess dilute nitric acid and the cyanate ion (OCN^-) titrated with standard silver ion solution by Volhard's method.[33]

B. Standard Method for Isocyanates.[85]—An organic isocyanate is treated with a solution of 1-aminobutane in dioxane. A substituted urea is formed, according to equation (47). [*cf.* equation (20) in Section 4D].



$$\begin{matrix} \text{H—NHBu} \\ + \\ \text{RN=CO} \end{matrix} \rightarrow \text{RNHCONHBu} \qquad (47)$$

After reaction is complete, excess amine is extracted into water and determined by titration with standard acid to a Methyl Red end-point. The method has been

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[82] G. Laude, *C.R. Hebd. Seances Acad. Sci.*, 1930, **191**, 1135.

[83] J. M. Luck, *J. Biol. Chem.*, 1928, **79**, 211.

[84] P. Dirnhuber and F. Schitz, *Biochim. Biophys. Acta*, 1948, **2**, 362.

[85] 'Standard Methods of Chemical Analysis', ed. F. J. Welcher, Van Nostrand, Princeton, 6th Edn., 1963, vol. II, part A.

applied to the determination of isocyanic acid itself, in solution in inert organic solvents like acetone.[9] This method is probably more accurate, rapid, and easy to perform than either of the methods described in Section 5A because a non-aqueous solvent is used and low-temperature conditions are possible, precluding side-reactions of HNCO.

C. Classical Qualitative Methods.—Conversion into urea and subsequent formation of a precipitate with xanthydrol (see Section 5A) has been used[33,85] as a sensitive test to detect HNCO, but the precipitate takes more than ten minutes to form for traces smaller than one part in 800 000 of aqueous solution.

Two very sensitive colour tests have been devised. In the presence of a copper salt containing a little pyridine, HNCO gives a lilac-blue precipitate. If chloroform is added, a sapphire-blue is obtained in the organic layer.[86] Alternatively, HNCO solutions are treated with potassium and ethanol and then a few drops are triturated with cobalt acetate. The presence of cyanate is shown by a strong blue colour, resulting from the formation of $Co(OCN)_2.KOCN$.[82,87]

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.

D. Spectral Methods.—Infra-red, ^1H-n.m.r., and mass spectra of HNCO have all been used to check on the purity and stability of HNCO samples (see Section 3A). The infra-red technique is particularly convenient, especially for gaseous samples, because the i.r. spectrum of HNCO is simple and distinctive. The use of this technique for semi-quantitative study of isocyanic acid consumption in reactions has been demonstrated.[8,22]

6 Conclusion

Methods are now available for preparing HNCO in a high state of purity either on its own or dissolved in an inert solvent. When required for reaction purposes it is also possible to generate it *in situ*. It can be readily stored at low temperatures and is no more hazardous to handle or use than HCl. A variety of reliable analytical methods for its detection and measurement are available. With the exception of its melting point and low temperature solid form, the physical properties, spectra, and structure of HNCO are well established. The compound has the isocyanic acid and not the cyanic acid structure.

In contrast the polymerization of HNCO is much less well understood. Although the structure of one of the products, cyanuric acid, is known, that of the other, cyamelide, remains largely a mystery. Many other unanswered questions surround the polymerization such as the factors which determine the proportions of the two products, and the mechanism of the polymerization process both in solution and in the gas phase.

[86] E. A. Werner, *J. Chem. Soc.*, 1923, **123**, 2577.

[87] R. Fosse, P. de Graeve, and P. E. Thomas, *C.R. Hebd. Seances Acad. Sci.*, 1936, **202**, 1544.

Investigations of the photolysis and pyrolysis of HNCO have yielded minimal information owing to the complexity of the secondary reactions in the case of photolysis and to surface effects in the case of pyrolysis. Studies of the reaction with water have proved more rewarding. The pK_a value has been established and the kinetics of the hydrolysis in aqueous solution have been largely unravelled.

Investigations of the reactions of HNCO with other compounds have established two main types of reaction. The first involves the addition of polar compounds across the carbon–nitrogen double bond of the molecule, and the second the addition of HNCO itself across the double and triple bonds of other unsaturated species. However, many aspects of these reactions remain obscure, such as whether, in the reaction with alcohols, allophanates are formed directly or *via* carbamates. Furthermore, little or no studies have been made of reactions of HNCO in the gas phase. It would be very interesting to know, for example, how fast HNCO(g) and NH_3(g) react and in what proportions the resulting urea and ammonium cyanate are formed.

Thus, to summarize, although much is now known about isocyanic acid, many interesting features of its chemisty still remain to be explored and elucidated.