Synthesis, Properties and Dimerization Study of Isocyanic Acid

Gerd Fischer, Janna Geith, Thomas M. Klapötke, and Burkhard Krumm

Department of Chemistry, University of Munich (LMU),
Butenandtstrasse 5 - 13 (D), D-81377 Munich, Germany

Reprint requests to Prof. Dr. Th. M. Klapötke. Fax: +49 (0)89 2180 7492.
E-mail: tmk@cup.uni-muenchen.de

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Isocyanic Acid, Dimeric Isocyanic Acid

Isocyanic acid was prepared in pure form by reaction of KOCN or NaOCN with stearic or oxalic acid in good yield. Identification, characterization and investigation of the thermal stability of HNCO and evidence for a possible existence of “dicyanic acid” have been studied in gas phase, liquid and solid state by vibrational and NMR spectroscopy and mass spectrometry.

1. Introduction

In an 1830 publication J. Liebig and F. Wöhler [1] first reported on the preparation of isocyanic acid, which later was improved by A. Baeyer [2]. The preparation and properties of HNCO and some of its derivatives have been described in the literature [3, 4]. The polymerization of HNCO leads to a mixture of cyanuric acid (trimer of HNCO) and cyamelide [3, 5]. Cyanuric acid is a commercially available substance [3, 6]. However, there has been some doubt regarding the thermal stability of HNCO and possible formation of dimers or other oligomers with the formula $(HNCO)_n$ [7].

Isocyanic acid forms very strong hydrogen bonds, therefore the formation of dimers is possible. These dimers should have bands in the same region as the ν_1 fundamental of monomeric HNCO [8]. Owing to a formal analogy between isomeric cyanic acid:

$$\mathrm{HN{=}C{=}O} \;-\!\circ\!\!\rightarrow\; \mathrm{HO{-}C{\equiv}N} \qquad (1)$$

and that of cyanamide:

$$\mathrm{HN{=}C{=}NH} \;-\!\circ\!\!\rightarrow\; \mathrm{H_2NC{\equiv}N} \qquad (2)$$

attempts have been made to prepare a dimeric form of HNCO, which would bear the same relationship to dimeric cyanamide, as in the case for the trimers cyanuric acid and melamine [7].

Ponsgen [9] had reported about the existence of “dicyanic acid”, but it was later shown by Hallwachs [10], that this substance was impure cyanuric acid. Schmidt [11] also claimed to have prepared a small amount of $(HNCO)_2$ by the treatment of triuret with excess phosgene, but the presented evidence by Schmidt is questionable. Another attempt for a preparation of $(HNCO)_2$ by decomposition of both nitrourea and nitrobiuret in aqueous and alcoholic solutions was published by Davis and Blanchard [12] according to the following equation:

$$2\ \mathrm{HN{=}C{=}O} \rightarrow \mathrm{H_2NC(O)N{=}C{=}O} \qquad (3)$$

However, isolation of this material failed due to complete hydrolysis during evaporation.

On the other hand, thiodicyanic acid, $H_2NC(O)N{=}C{=}S$, was obtained in good yield by the reaction of HNCO and HNCS in ethereal solution at 0 °C [13]. This compound can be heated up to 105 °C before undergoing decomposition. The dimer of HNCS was prepared by passing HCl through an aqueous solution of KSCN [14].

In a theoretical study [15] it was found that the reaction:

$$2\ \mathrm{HN{=}C{=}O} \rightarrow \mathrm{HN{=}C{=}NH} + \mathrm{CO_2} \qquad (4)$$

is less favorable than the dimerization of HNCO to give $(HNCO)_2$ of C_{2v} symmetry.

In view of the theoretical investigation of the polymerization pathways of isocyanic acid we have performed semi-empirical (PM3/VSTO-3G(d) method) and ab initio HF and MP2 calculations employing the 6-31G(d,p) basis set [16]. It was found that the polymerization of HNCO to oxo (keto) cyanuric acid is thermodynamically the most favorable. The dimeric HNCO (keto-structure of C_{2v} symmetry) is the favored compound at all the levels of theory applied.

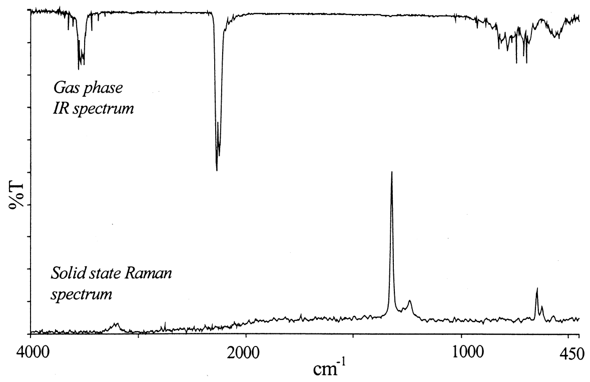

Fig. 1. Vibrational spectra of HNCO: IR spectrum of HNCO gas at 25 °C and Raman spectrum of solid HNCO at –80 °C.

2. Results and Discussion

2.1. Synthesis

The preparation of HNCO has been reported by several research groups [3, 4]. The methods reported here represent optimized literature procedures [4] (eq. (5)) using stearic acid and a new alternative procedure with oxalic acid for the preparation of HNCO in good yield (eq. (6)):

$$\mathrm{MOCN + R\text{-}COOH \rightarrow HNCO + R\text{-}COOM} \quad (5)$$

$$(\mathrm{M = Na, K; R = C_{17}H_{35}})$$

$$\mathrm{2\,MOCN + (COOH)_2 \rightarrow 2\,HNCO + (COOM)_2} \quad (6)$$

$$(\mathrm{M = Na, K})$$

Liquid isocyanic acid can be stored at –78 °C without decomposition at least for 5 days. Isocyanic acid is a gas at room temperature (b. p. 24 °C) and behaves much like ketene; its tendency to form hydrogen bonds leads to the possible formation of dimers. In this regard we have investigated the stability of HNCO in the gas, liquid and solid state by vibrational and NMR spectroscopy, as well as mass spectrometry in the temperature ranges between –80 and 160 °C (see below).

2.2. Vibrational spectra

The structure of HNCO has been established by many infrared and Raman studies [17]. The dimers should have bands in the same region as the ν_1 fundamental of the HNCO-monomer [8]. To our knowledge, prior to this study, there had been no reports on the investigation of gas phase stability (temperature dependence, with or without presence of N_2) of HNCO up to 160 °C and possible formation of dimers by (high-temperature) gas phase FT-IR spectroscopy.

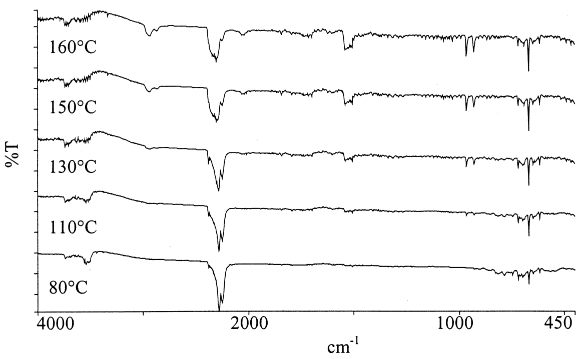

Fig. 2. Temperature dependent IR spectra of gas phase HNCO at 80, 110, 130, 150 and 160 °C.

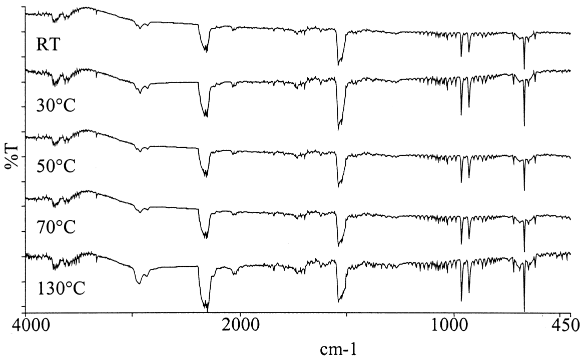

Fig. 3. IR spectra by cooling gas phase HNCO from 160 °C to 25 °C.

While the spectra of HNCO are well investigated and understood, there remain some unclear points in the spectra of its derivatives [8, 17]. The IR spectrum of HNCO in the gas phase is very complex because of its quasilinearity. HNCO belongs to C_s point group with six vibrational fundamentals, but only four of these six can be found [17].

The IR spectrum of gas phase HNCO at 25 °C and the Raman spectrum of solid isocyanic acid at –80 °C are shown in Fig. 1. Experimental wavenumbers are in good agreement with literature data [8, 17].

The most intense and characteristic absorption peak in the FT-IR spectrum of HNCO gas is the band at 2259 cm^{-1} (ν_{asNCO}), the most intense band in the Raman spectrum is the band at 1323 cm^{-1} (ν_{sNCO}). The comparison of the infrared spectrum of HNCO vapor with that at low temperature in the

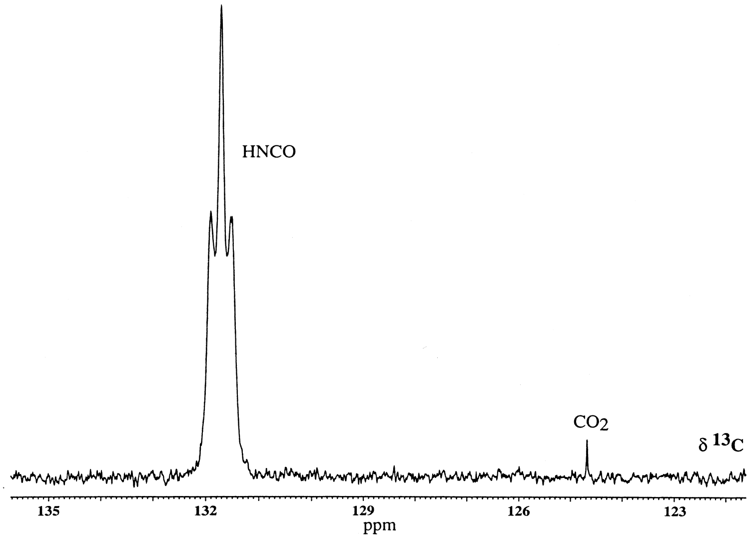

Fig. 4. ^{13}C NMR spectrum of HNCO in $CDCl_3$ at 25 °C.

condensed phase shows that free HNCO in the gas phase consists of HNCO monomers.

The thermal behavior of HNCO in the gas phase measured with a heating rate of ca. 10 $°C \cdot min^{-1}$ is shown in Fig. 2 (heating) and Fig. 3 (cooling).

By varying the time between 0 und 140 min and the temperature from 25 up to 160 °C (Fig. 2), with or without N_2, it was found, that up to 80 °C only HNCO itself was present in the gas phase. At temperatures higher than 80 °C in the FT-IR spectrum HNCO, CO_2 and NH_3 are the only products observed. The formation of CO_2 and NH_3 is probably the result of the reaction of HNCO with traces of water vapor:

$$(HN{=}C{=}O \text{-}\!\circ\!\!\longrightarrow N{=}COH) + H_2O \rightarrow NH_3 + CO_2 \quad (7)$$

NMR spectra

The NMR spectra of isocyanic acid were recorded in $CDCl_3$ solution. At 25 °C the ^1H NMR resonance, a triplet, is found at $\delta = 3.74$ with a coupling constant of $^1J_{H\text{-}^{14}N} = 67.0$ Hz, which is in good agreement with the previously reported value of 64 Hz [18b]. Upon cooling to –60 °C the triplet collapses to a broadened singlet, whereas the triplet still exists after rapid heating to 60 °C. The ^{13}C NMR spectrum of HNCO at 25 °C, shown in Fig. 6, reveals also coupling to the ^{14}N nucleus.

The resonance at $\delta = 131.7$ is nicely distinguishable from a trace of CO_2 by its (broadened) triplet fine structure with a coupling of $^1J_{C\text{-}^{14}N} = 19.2$ Hz. Again, this triplet collapses at lower temperatures. The resonance for CO_2 at $\delta = 124.7$ was confirmed by an authentic sample of CO_2 in $CDCl_3$. The nitrogen NMR spectra at –30 °C show singlets. The ^{14}N resonance in $CDCl_3$ is relatively sharp at $\delta = -357$ with a half-line width of 60 Hz. The ^{15}N NMR spectrum was recorded as neat liquid at –30 °C and a shift of $\delta = -356.6$ was observed. The recording of the ^{15}N NMR spectrum at higher temperatures (already 0 °C) caused significant decomposition. In all NMR spectra no evidence for a possible existence of a dimer of HNCO was detected.

2.4. Mass spectra

Mass spectrometry of HNCO has been performed by several groups [19], but to our knowledge only in the electron ionization (EI) mode. The thermal behaviour of HNCO and the possible existence of $(HNCO)_2$ have not successfully been studied using mass spectrometric analysis. Mass spectra of HNCO and its polymer contain a number of both fragment and molecular ions. This makes identification difficult, especially when the polymer can be a mixture of some unknown substances [3, 20]. In this study we would like to introduce the use both of EI and chemical ionization (CI) mass spectrometry for the study of the thermal behaviour of HNCO.

The EI mass spectrum of pure HNCO vapor at –40 °C is shown in Table 1 and Fig. 5 and is in agreement with [19]. The molecular peak of HNCO

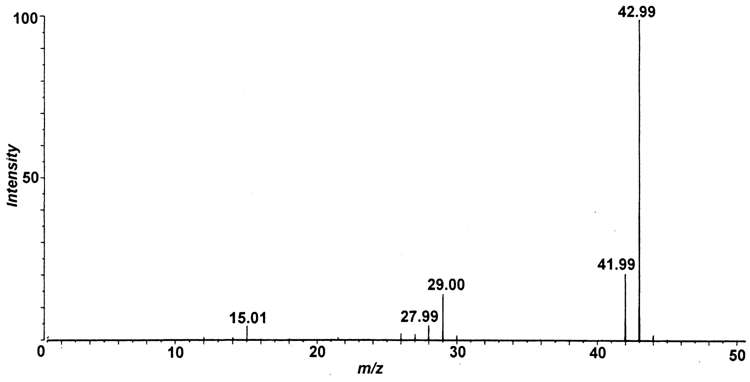

Fig. 5. EI-mass spectrum (70 eV) of HNCO vapor at –40 °C.

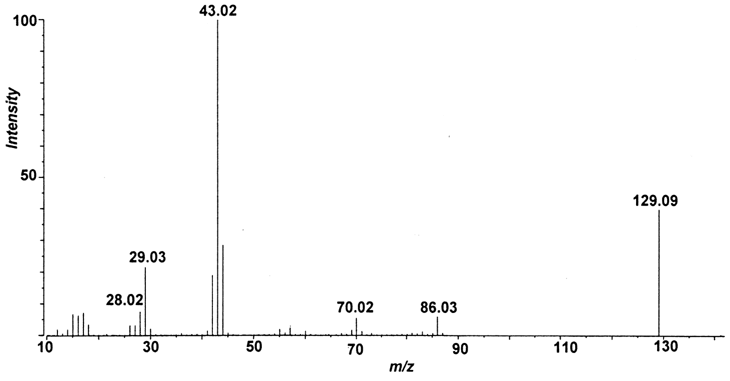

Fig. 6. The EI-mass spectrum of solid polymer after complete polymerization.

Table 1. EI-mass spectrum (70 eV) of HNCO vapor at –40 °C.

Mass	Relative intensity	Assignment	Mass	Relative intensity	Assignment
12	0.7	C^+	27	1.8	CNH^+
14	0.7	N^+	28	4.5	CO^+/N_2^+
15	4.2	NH^+	29	14.2	COH^+
16	0.2	O^+	30	1.3	NO^+
21.5	0.7	$HNCO^{2+}$	42	20.9	NCO^+
26	1.9	CN^+	43	100	$HNCO^+$

(m/z 43; correct isotopic pattern) is the base peak and also the highest observable peak.

After complete polymerization at room temperature, an EI mass spectrum was recorded. There were no non-condensable products except HNCO in the gas phase in any of these experiments. Fig. 6 shows the EI mass spectrum of the white solid polymer after complete polymerization at 25 °C.

The ion m/z 43 is considered as ionized isocyanic acid. The ions at m/z 28 and 16 were considered as residual dinitrogen and oxygen, respectively. The m/z 129 coincides with the trimerization product (M^+ of cyanuric acid, the trimer of HNCO):

$$3\,HNCO \rightarrow (HNCO)_3 \tag{8}$$

The presence of ion m/z 17 (ammonia) and ion m/z 44 (carbon dioxide) can be interpreted by reaction of HNCO with the residual water vapor [e g. (7)].

The ion m/z 60 (M^+ of urea) can be understood by the reaction of ammonia with isocyanic acid:

$$NH_3 + HNCO \rightarrow (NH_4)NCO \rightarrow (NH_2)_2CO \tag{9}$$

The peak at m/z 86 could possibly arise from the dimerization of HNCO:

$$2\,HNCO \rightarrow (HNCO)_2 \tag{10}$$

The CI-ammonia and isobutane spectra of the polymer were recorded as follows:

CI (isobutane): m/z = 130 ($(HNCO)_3 + H^+$)), 100%; m/z = 104 (biuret + H^+), 10%; m/z = 87 ($(HNCO)_2 + H^+$)), 44%; m/z = 86 ($(HNCO)_3$-$HNCO^+$)), 4%; m/z = 61 (urea + H^+), 78%.

The base peak at m/z 129 can be interpreted by trimerization of HNCO to cyanuric acid. Exact mass by HR: calcd. 129.0174, found: 129.0165 (–1.0 mmu).

The peaks at m/z 43, 44 and 60 are considered being isocyanic acid, CO_2 and urea, respectively. The detection of ion m/z 103 (probably biuret) supports in part the decomposition reaction of HNCO.

These results suggest that several polymerization reactions and the simple decomposition reaction occur simultaneously. It is remarkable that authentic cyanuric acid, measured under identical conditions, exhibits neither a peak at m/z 86, nor at 87, which is more intense than 1%.

Therefore it can be concluded that m/z 86 or m/z 87 do not represent fragment ions of cyanuric acid, but dimerization product of isocyanic acid, $(HNCO)_2$. This is strongly supported by high resolution measurements of the polymer: m/z 86.0109 (–0.7 mmu); calcd. for $H_2N_2C_2O_2$ m/z 86.0116.

3. Experimental Section

3.1. Preparation and purification

First method: The preparation of HNCO was carried out by the reaction of one equivalent of purified anhydrous potassium or sodium cyanate with two equivalents of dry stearic acid. The reagents were heated under vacuum but in contrast to [4] at 130 °C. Gaseous HNCO was passed through a tube filled with P_4O_{10} and collected in a liquid nitrogen trap. Yield: 70%.

Second method: This is a similar procedure as above, except using oxalic acid. In this method, which has not been previously described, the reagents were heated in vacuo under anhydrous conditions and the reaction products were collected in a liquid nitrogen trap. Repeated trap-to-trap distillation in vacuo reduced the impurities (most CO_2) to less than 1%. This was estimated by vibrational and NMR spectroscopy as well as mass spectrometry investigations. Yield: 65%.

3.2. Polymerization of HNCO

Samples of liquid HNCO in a tube in vacuo were immersed in baths at 0 (ca. 1 d), 24 (ca. 1 h) and 100 °C (ca. min). Upon complete polymerization, the gas phase IR and mass spectra were recorded. The polymer was extracted with hot water (80 °C), and, after removal of the insoluble cyamelide, the filtrate concentrated. The collected crystalline material was dried at 110°C. Elemental analysis for residue: Found C 27.8; N 33.6; H 2.8. Calcd (for cyanuric acid): C 27.9; N 32.6; H 2.3%.

3.3. Spectroscopy

The infrared spectra were obtained using KBr discs for the solids and a 10 cm cell equipped with KBr windows for the gases by means of a Perkin-Elmer IR Spectrum One spectrometer. Raman spectra were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer. NMR spectra were recorded both as $CDCl_3$ solutions and neat HNCO using a JEOL Eclipse 400 instrument. Chemical shifts are with respect to $(CH_3)_4Si$ (^1H and ^{13}C) and CH_3NO_2 (^{14}N, ^{15}N). Mass spectra were obtained with a Jeol MStation JMS 700 gas inlet system (100 °C). The source was operated at a temperature of 200 °C, and the probe temperature was varied from –40 °C up to room temperature. In the EI mode the electron energy was 70 eV; in the CI mode alternatively ammonia and isobutane were used as reagent gases. Elemental analysis was performed with a C,H,N-Analysator Elementar Vario El.

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