New Light on an Old Story: The Solid-State Transformation of Ammonium Cyanate into Urea

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According to a long held tradition, organic chemistry started in 1828 when Friedrich Wöhler heated ammonium cyanate to obtain urea. Even the Encyclopaedia Britannica[1] states: "Wöhler's classical experiment (1828) was the thermal conversion of ammonium cyanate into urea

$$NH_4{\cdot}NCO \xrightarrow{HEAT} H_2N{\cdot}CO{\cdot}NH_2$$

From this experiment Wöhler concluded that heat had transformed ammonium cyanate into urea."

If this account were true, the above reaction would qualify as the very first solid-state chemical reaction. In fact, however, Wöhler did not obtain urea by heating ammonium cyanate. His 1828 paper[2] makes it quite clear that he was actually trying to prepare ammonium cyanate, first by combining cyanic acid with ammonia in solution, then by the reaction of silver cyanate with ammonium chloride solution, and then again by reacting lead cyanate with ammonia. All of these reactions led not to the desired product ammonium cyanate but to a crystallizable white substance that Wöhler was able to identify as urea.[3] It was only two years later that Liebig and Wöhler[4] succeeded in preparing ammonium cyanate as a fluffy, white powder by the direct union of dry ammonia and cyanic acid. In a sealed vessel under ammonia, the powder could be kept essentially unchanged; open to the atmosphere, it transformed in 2 days into urea.

The transformation of ammonium cyanate into urea thus takes place both in solution and in the solid state. It has been studied by many authors for more than a century.[5] Much information about the rate and equilibrium in solution has been accumulated, but details of the reaction in the solid state are sparse. The careful study of Walker and Wood a century ago[6] was necessarily restricted by the limited choice of methods then available, and little seems to have been done in this area since then. Thus, even the crystal structure of ammonium cyanate has been unknown until now. We therefore decided to take up the study of this reaction anew—to prepare solid ammonium cyanate, determine its crystal structure, and obtain information by modern methods about its transformation to urea. This paper reports our first explorations in this area.

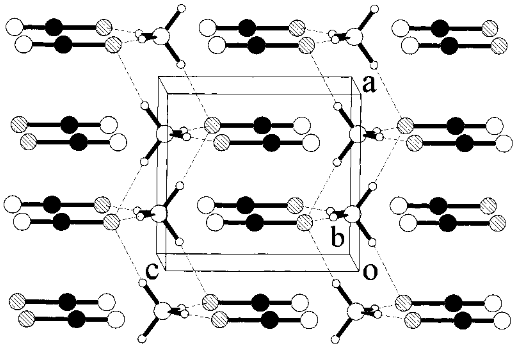

Figure 1. Crystal structure of ammonium cyanate viewed almost along the *b*-axis [N, large open circles; H, small open circles; C, filled circles; O, shaded circles]. The dashed lines represent hydrogen bonds (H···O, 2.07 Å; N−H···O, 177°; N−H, 0.98 Å).

Ammonium cyanate was synthesized by ion exchange between tetraethylammonium cyanate and ammonium thiocyanate with use of a modified version of the procedure described by Dieck et al.[7,8] The sample was collected as a microcrystalline powder, from which we have been unable to obtain single crystals. The powder X-ray diffraction pattern[9] was indexed in terms of a tetragonal unit cell: $a = b = 5.15$ Å, $c = 5.56$ Å, space group $P4/n$. With two formula units NH_4NCO per unit cell, the linear NCO^- anions must lie along 4-fold axes and the N atom of the ammonium cation must sit on a site of $\bar{4}$ symmetry. Rietveld refinement with the GSAS program package,[12] with standard geometric restraints applied to bond lengths and isotropic displacement parameters refined for all atoms (assuming a common value for all non-hydrogen atoms), led to the structure shown in Figure 1. The parameters listed in Table 1 give an excellent fit to the powder diffraction profile (Figure 2).

Each NH_4^+ cation is surrounded by eight NCO^- anions (see Figure 1). The local geometry around the NH_4^+ cation is that of a slightly distorted cube, with O and N atoms at alternate corners. Each H atom engages in a nearly linear N−H···O hydrogen bond (H···O, 2.07 Å; N−H···O, 177°). There are no analogous N−H···N interactions. Although the two ends of the NCO^- anion have similar scattering power, the assignment of the O and N atoms is readily made on bond distance criteria (C−O, 1.278 Å; C−N, 1.172 Å) corresponding to the valence bond description

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(1) Encyclopaedia Britannica, article on CHEMISTRY, Benton, Chicago, 1964.

(2) Wöhler, F. *Pogg. Ann.* **1828**, *12*, 253.

(3) Many authors have drawn attention to the incorrectness of the traditional textbook account. For a recent contribution to the subject see: Cohen, P. S.; Cohen, S. M. *J. Chem. Educ.* **1996**, *73*, 883.

(4) v Liebig, J.; Wöhler, F. *Ann. Phys. Leipzig, Ser. 2* **1830**, *20*, 369.

(5) See chapter on ammonium (iso)cyanate in Gmelin and also the following review: Shorter, J. *Chem. Soc. Rev.* **1978**, *7*, 1.

(6) Walker, J.; Wood, J. K. *J. Chem. Soc.* **1900**, *77*, 21.

(7) Dieck, R. L.; Peterson, E. J.; Galliart, A.; Brown, T. M.; Moeller, T. *Inorg. Synth.* **1976**, *16*, 131.

(8) The ion exchange reaction was conducted under normal laboratory conditions in standard glassware and kept under a nitrogen atmosphere rather than a drybox (as described in ref 7). Furthermore, prior to drying in vacuo, the filtered solid was washed twice with ether to remove traces of acetonitrile. In earlier attempts to crystallize ammonium cyanate from dioxane solution we obtained single crystals of a 1:1 urea:dioxane cocrystal (monoclinic, $a = 6.751$ Å, $b = 4.547$ Å, $c = 12.634$ Å, $\beta = 95.145°$, space group $P2/c$, $Z = 2$), the structure of which will be reported elsewhere.

(9) The powder X-ray diffraction pattern of a ground sample was recorded at 22 °C in transmission mode on a Siemens D5000 diffractometer, using Ge-monochromated Cu Kα_1 radiation and a linear position-sensitive detector covering 8° in 2θ. The total data range was $3° \leq 2\theta \leq 90°$, measured in 0.02° steps, and collected over 12 h. The diffractogram was indexed by using the program TREOR[10] on the basis of the first 20 observable reflections. Tetragonal cell dimensions reported previously[11] [$a = b = 3.64$ Å, $c = 5.58$ Å] correspond to a sub-cell.

(10) Werner, P.-E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 360.

(11) Waddington, T. C. *J. Chem. Soc.* **1959**, 2499.

(12) Larson, A. C.; Von Dreele, R. B. Los Alamos Lab Report No. LA-UR-86-748, 1987.

10.1021/ja983285c CCC: $15.00

Table 1. Fractional Coordinates for the Crystal Structure of Ammonium Cyanate at Ambient Temperature [$P4/n$; $a = b =$ 5.1431(1) Å, $c =$ 5.5552(2) Å; Origin at $\bar{1}$]

atom	x	y	z	U_{iso}/Å^2
N(1)	0.25	0.75	0	0.02(1)
H(5)	0.245(1)	0.908(1)	0.100(1)	0.03(1)
O(2)	0.25	0.25	0.296(1)	0.02(1)
C(3)	0.25	0.25	0.526(1)	0.02(1)
N(4)	0.25	0.25	0.737(1)	0.02(1)

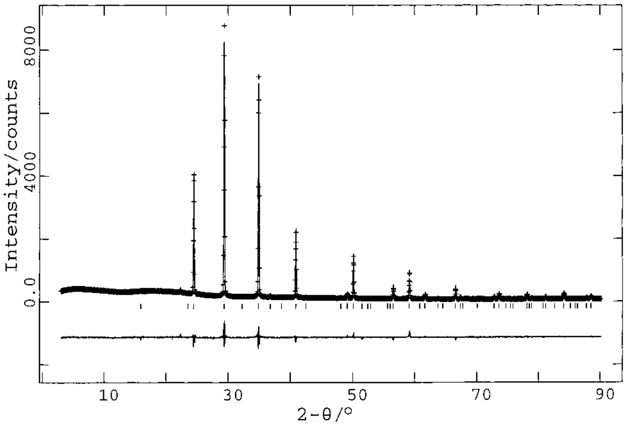

Figure 2. Experimental (+ marks), calculated (solid line), and difference (bottom) powder diffraction profiles for the Rietveld refinement of ammonium cyanate (R_{wp} = 6.4% and R_p = 4.7%). Reflection positions are marked.

N≡C−O$^-$. Reorientation of the NH_4^+ cation to point the N−H bonds toward the other four corners of the cube (to form N−H···N interactions) gives significantly worse agreement with the powder diffraction data. In contrast to the observed preference for N−H···O hydrogen bonding in ammonium cyanate, cyanic acid exists overwhelmingly as H−NCO rather than NCO−H.[13,14]

The preference for N−H···O rather than N−H···N hydrogen bonding in the crystal is corroborated by our results of periodic Hartree−Fock calculations (basis set 6-31G**) using the CRYSTAL95 program.[16] The experimental structure was found to be more stable (by about 10 kcal mol^{-1}) than the alternative structure with inverted orientation of the NH_4^+ cation.

We have made a preliminary study of the solid-state transformation to urea at 50 °C by in situ synchrotron X-ray powder diffraction[17] (Figure 3). In the course of about 6 h, microcrystalline ammonium cyanate transforms completely to microcrystalline urea. There is no evidence for any crystalline intermediate phase during the transformation, and no significant amounts of amorphous material are produced. The loss of starting material is approximately zeroth order, the rate constant increasing with temperature. On melting, the reaction goes almost instantly to completion.

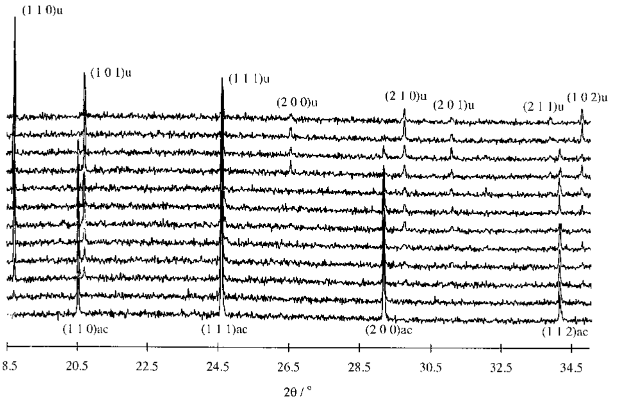

Figure 3. Synchrotron X-ray powder diffractograms (λ = 1.300 Å, calibrated against Si standard) recorded for ammonium cyanate at 50 °C as a function of time (bottom to top, with recording time per diffractogram ca. 30 min). Selected peaks characteristic of ammonium cyanate (subscript ac) and urea (subscript u) are marked.

Indeed, differential scanning calorimetry shows that a strongly exothermic process, accompanied by melting, occurs between 80 and 90 °C, depending on the scanning rate.[18] Thermogravimetric analysis shows loss of volatile material (presumably ammonia) in this region. The sudden rate increase on melting suggests that the solid-state reaction is not topochemical.[19−21] In any case, according to the standard mechanism involving initial proton transfer from NH_4^+ to the N of NCO^-, dynamic orientational disorder of the cation would seem to be a prerequisite for the onset of the chemical reaction in the crystal. Further in situ powder diffraction and solid-state NMR studies are under way to clarify these issues.

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(13) Belson, D. J.; Strachan, A. N. *Chem. Soc. Rev.* **1982**, *11*, 41.

(14) According to our MO calculations at the Hartree−Fock limit (basis set 6-31G**) using the SPARTAN program[15] on the molecules NCOH and HNCO, the latter is more stable by 23 kcal mol^{-1}.

(15) SPARTAN, Wave function Inc., Irvine, CA, USA (SGI Version 4.0.4 GL).

(16) Dovesi, R.; Saunders, V. R.; Roetti, C.; Causà, M.; Harrison, N. M.; Orlando, R.; Aprà, E. *CRYSTAL95 User's Manual*; University of Torino: Torino, Italy, 1996.

(17) A sample of ammonium cyanate was gently ground, loaded into a capillary (0.5 mm diameter), and mounted on the high-resolution powder diffractometer on Station 2.3 at the Synchrotron Radiation Source (Daresbury Laboratory). Powder X-ray diffraction data (λ = 1.300 Å) were recorded at 50 °C in 30 min scans over the range $18.5° \leq 2\theta \leq 40°$ in steps of 0.015°.

(18) The heat of reaction has been estimated[6] as 4.9 kcal mol^{-1}.

(19) Kohlschütter, V. *Z. Anorg. Chem.* **1919**, *105*, 1.

(20) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996.

(21) Thomas, J. M. *Philos. Trans. R. Soc.* **1974**, *277*, 251.