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The Formation of Molecular Compounds following Radiolysis of Solid Hydrogen Cyanide

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Low-temperature HCN radiolysis (conditions close to those in cosmic space) leads to formation of different molecular compounds; conjugated polymers $[C{=}N{-}C{=}N]_n$, with conjugated chain growth, are formed (colour change orange → brown → black). The polymer gives a singlet EPR signal typical of polyconjugated systems, and crystals of 1,2-diaminomalonodinitrile are also formed. Electrical breakdowns and glow are observed on freezing the HCN; this is connected with a brittle fracture of HCN crystals leading to electrical charge separation. The freezing out of HCN onto grains of interstellar dust under cosmic conditions would lead to effective coagulation of the dissipated substance at the expense of electrostatic attraction.

The molecular formation of HCN is very abundant in cosmic space: in gigantic clouds of comets, protoplanet clouds, interstellar dust and other galactic structures. The HCN molecule is believed to be the basis for further chemical evolution, since its conversion is a direct pathway to the formation of proteins and other macromolecules.[1–5] It has been suggested[6] that the chain length of the cyanopolyene macromolecules arising during HCN condensation might be used as an inner clock with which to date interstellar dust clouds. Other astrophysical items concerning the chemical transformation of HCN are actively being studied now.[7,8] However, it is not clear the mechanism by which the chemical activation of HCN takes place under cold cosmic conditions. The liquid HCN is assumed to be polymerized by an anionic mechanism effected by γ-radiation, giving a complex mixture of azulmic compounds.[9] Facts about the radiolysis of HCN in the literature are scanty[10–12] and studies on the chemical changes after radiolysis of solid HCN are completely absent.

In this connection, it is of interest to study the chemical behaviour of this simple molecule under conditions close to cosmic (low temperature and radiation) and its role in the 'cold' chemical evolution of the Universe. This initial study of the formation of molecular compounds due to low-temperature radiolysis of solid hydrogen cyanide discussed below is only a part of our cosmochemical studies.

Hydrogen cyanide was obtained by the technique taken from ref. 13. The resulting product was additionally purified by low-temperature fractional distillation: T_b 298.6K, T_m 260 K. An appropriate amount of HCN was placed in a glass ampoule, carefully evacuated and sealed. In order to study the phase state of the system and the dynamics of the chemical conversion, a well-known calorimetric technique was used.[14] The radiolysis was carried out by ^{60}Co γ-irradiation.

On cooling HCN to 77 K it passes to a crystalline state. The calorimetric curve of heating HCN cooled to 77 K shows an H-type crystal-crystal phase transition (classification from ref. 15) at 248 K with melting at 260 K. The melting heat of HCN, $\Delta H = 8.4 \pm 0.4$ kJ mol^{-1}, agrees well with the literature data.[16,17]

A very interesting physical phenomenon is observed on freezing the HCN. Solidification of the liquid HCN sealed in an ampoule is followed by an effective attraction of the ampoule to the Dewar walls, evidently due to electrostatic forces. On storage of the ampoule in liquid nitrogen the force of this attraction diminishes quickly. In the dark, electrical break-downs and glow are observed in the ampoule with the HCN cooled to 77 K. We supposed that on freezing the HCN a brittle fracture of its crystals takes place and that this is the cause of the electrical charge separation. The nature of this phenomenon obviously requires special study but it is clear that freezing out of HCN on the grains of interstellar dust would led to effective coagulation of the dissipated substance at the expense of the electrostatic attraction.

Calorimetric measurements in the immediate field of γ-radiation at 77 K have shown the absence of marked heat

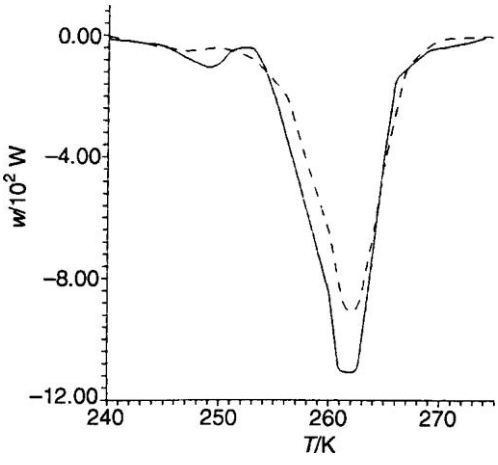

Fig. 1 Calorimetric curves (heat power *w vs. T*) for HCN unfreezing: (*a*) non-irradiated sample (—); (*b*) sample irradiated with ^{60}Co γ-rays, dose 725 kGy(---).

release associated with chain polymerization. On heating HCN-radiolysed at 77 K, polymerization occurred in the melting region. The calorimetric curve of heating shows a decrease in the melting peak area (superposition of the exothermal polymerisation process on the melting endothermicity) (Fig. 1). The polymerization heat of HCN $\Delta H \approx 44.0 \pm 6.3$ kJ mol^{-1}; this experimental value is in less than that calculated in ref. 18.

The yield of the polymer formed on heating the HCN samples irradiated at 77 K to room temperature increases with pre-irradiation dose and reaches 2.5% for a dose of 725 kGy. The radiation-induced polymerization of liquid HCN at 273 K occurs much less effectively. Liquid HCN has proved to be stable in storage, and prolonged storage of HCN in sealed, evacuated ampoules at room temperature does not lead to any changes in its colour or any formation of polymeric products. At the same time, the storage of HCN radiolysed at 77 K at room temperature leads to a change in colour (from orange to nearly black) with formation of polymer products. The polymeric product yield rises with storage time and reaches 33.5% within 750 h. Therefore, formation of the polymer in storage is initiated by radiolysis products, presumably by the polymer formed on sample melting.

The polymer products obtained under various polymerization regimes differ in appearance and characteristics. The polymer formed on melting a radiolysed sample and isolated immediately after the melting is orange and soluble in acetone and ethanol. This product is, however, markedly unstable. On prolonged storage at room temperature, the polymer turns dark. An analysis of the IR spectra of a freshly prepared 'orange' polymer showed, together with the absorption bands of the C≡N bond (2100–2200 cm^{-1}), absorption bands appearing in the range 1600–1700 and 1200–1250 cm^{-1} obviously related to the stretching vibration of the C=N and C–N bonds, respectively.

The IR absorption spectrum of the 'black' polymer (conversion from the orange to the black polymer during post-polymerisation at room temperature) shows no appreciable changes as compared to the 'orange' polymer spectrum. It is evident that on keeping the system at room temperature the polymer product, as well as increasing in quantity, undergoes a change in structure. Redistribution of the band intensities in the region of 1250 and 2200 cm^{-1} and an increase in the background in the region of 1700–2200 cm^{-1} are observed; however, all the main absorption bands remain.

Differential thermal and thermogravimetric analyses of the 'orange' polymer have been carried out. The polymer is stable up to 700 K and only in the range 750–950 K is an exothermal process (maximum at 780 K), presumably of oxidation, observed and 95% of the weight is lost. The electroconductivity of the 'black' polymer is typical of most dielectrics $\sigma = 3 \times 10^{-5}$ Ω^{-1} cm^{-1}. According to the X-ray data both the polymers are amorphous. The polymer gives a singlet EPR signal typical of polyconjugated systems.

Polymerization processes initiated by radiation[10] and electrolysis of cyanides in alkaline solutions[11] lead to formation of a mixture of substances of general formula $C_4H_5N_5O$. In our case, the formation of such compounds is probably impossible, since no admixed oxygen or water are present in the reaction mixture. It is assumed[12] that HCN polymerization proceeds by an anionic mechanism *via* a cyanide anion CN^-. This scheme also suggests that the tetramer of HCN is formed at the tetramerization stage through abstraction of the cyanide-anion.[12]

During polymerization of HCN the formation of brownish, needle-shaped crystals takes place. The yield of these crystals is appreciably lower than that of the polymer, and they are formulated as 1,2-diaminomalonodinitrile by X-ray structure measurements.

It may be assumed that the abstraction of a hydrogen atom with its subsequent addition to the C≡N triple bond and stabilization of the $H_2\dot{C}-N$ or $H\dot{C}=NH$ radicals in the solid matrix occurs in the course of low-temperature radiolysis of the solid HCN. The ·CN radical cannot be stabilized in the matrix at 77 K.[17]

The radical $H_2\dot{C}=NH$ is stabilized at 77 K.[18] The stabilized radicals acquire translation mobility and initiate $H_2C=N-[HC=N]_n$ macroradical propagation in the course of heating the radiolysed sample of solid HCN in its melting region.

The colouring of the polymer and its darkening (to black) during its conversion by the radical scheme can be more naturally explained as a consequence of the –C=N–C=N– conjugation chain formation. A more natural explanation can be used for the IR-spectroscopic data of the polymeric product.

The formation of needle-like crystals of HCN tetramer may be also connected with the formation of the biradical amino-cyanocarbene,[21] the dimerization of the latter leading to the tetramer, reaction (1).

$$4\,HCN \longrightarrow 2[NC-\ddot{C}-NH_2] \longrightarrow \begin{matrix} H_2N-C-CN \\ \| \\ H_2N-C-CN \end{matrix} \qquad (1)$$

Formation of the aminocyanocarbene was first observed in ref. 22. This biradical is in the ground singlet state, $H_2N^{\delta+}-C-C=N^{\delta-}$; the tetramer of HCN is formed on its dimerization.[22] The formation of appreciable quantities of tetramer in our experiments on radiation polymerization allows us to believe that the above mechanism takes place here. It may be assumed that the aminocyanocarbene initiates further propagation of the polymerization chain of HCN. It is not improbable that the aminocyanocarbene in general plays the key role in prebiological organic synthesis since hydrolysis of the dimer aminocyanocarbene gives an aminoacid.

The following conclusions can be drawn from this work. (*a*) Under conditions close to those in cosmic space (low temperature and radiation), different molecular compounds can be formed in HCN. Conjugated polymers $[C=N-C=N]_n$, with conjugated chain growth are formed (colour change orange → brown → black). The polymer gives a singlet EPR signal typical of polyconjugated systems, and crystals of 1,2-diaminomalonodinitrile are also formed.

(*b*) A very interesting physical phenomenon is observed on freezing the HCN. In the dark, electrical breakdowns and glow are observed; this is connected with a brittle fracture of HCN crystals leading to electrical charge separation. This phenomenon obviously requires special study but it is now clear that the freezing out of HCN on the grains of interstellar dust under cosmic conditions would lead to effective coagulation of the dissipated substance at the expense of the electrostatic attraction.

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