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Intermediate paramagnetic centres stabilized in γ-irradiated solid hydrogen cyanide

Svetlana I. Kuzina, Pavel S. Mozhaev,* Dmitry P. Kiryukhin, Alfa I. Mikhailov and Igor M. Barkalov

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 938 2156

The low temperature radiolysis of HCN gives high yields of the paramagnetic centres C≡N and, mainly, $H_2C{=}\dot{N}$ radicals which upon subsequent heating to room temperature are shown to polymerise to polyene radicals.

Hydrogen cyanide is a widely distributed molecule in outer space, being found in gigantic clouds of dust mists, interstellar dust, comets and other cosmic structures, and its chemical conversions lead to the formation of purines, pyrimidines and amino acids.[1–5] The astrophysical aspects of the chemical conversion of hydrogen cyanide are well developed.[6–8]

We have begun a series of investigations on the chemical conversions occurring in solid HCN irradiated by ^{60}Co γ-rays.[9,10] The formation of various highly active intermediates and their IR spectra in the photolysis of solid HCN have been studied with the matrix isolation technique.[11] No studies on the intermediate centres arising during low-temperature radiolysis of solid hydrogen cyanide are known to us. This communication presents the results of a study on the dynamics of the formation of paramagnetic centres and the mechanism of their conversion in solid, radiolysed HCN.

The technique of preparing and purifying of HCN is given in refs. 9 and 10. The HCN radiolysis was carried out using ^{60}Co γ-rays on a 'Gammatok' set-up at 77 K. The EPR spectra were recorded on a 3 cm band ESR-21 spectrometer with a SHF-field power of $\approx 10^{-4}$ W at 77 K. The radical concentration was determined conventionally from the EPR spectra, by using a sample of the nitroxyl radical $R\dot{N}O$ containing a known number of spins as a reference. The absolute error of measurement involving both the recording and double integration of spectra was ±15%, which is normal for the EPR technique.

The radiolysis of hydrogen cyanide at 77 K is followed by accumulation of paramagnetic centres (PMC) with a radiation yield of $G = 8$ (per 100 eV of absorbed energy). The kinetics of PMC accumulation and their thermal stability have proved to be unusual. Up to a dose of 3000 kGy (at a concentration of $\approx 4 \times 10^{20}$ spin g^{-1}) the highest concentration is not reached. With an increase in the radiolysed HCN temperature, an effective decomposition of the PMC occurs in the range 140–160 K, *i.e.* 100 K below the melting point of HCN (260 K).

The PMC remaining after melting ($\approx 0.2\%$ of the initial concentration) are present in the radiolysed HCN samples for a long time.

The EPR spectrum of the paramagnetic intermediates and its transformation with the increasing dose and temperature are shown in Figure 1. The spectrum of the radiolysed HCN, as well as that of the photolysed [HCN + HI] system, investigated at 4.2 K,[13,14] shows a predominance of a triplet of triplets due to the addition of atomic hydrogen to the triple bond in the hydrogen cyanide molecule:

$$HCN + \dot{H} \longrightarrow H\text{–}\underset{H}{\overset{|}{C}}\text{=}\dot{N}$$

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(H atoms are produced by γ-radiolysis of solid hydrogen cyanide). The main triplet splitting, with a binomial integral intensity ratio (1:2:1) in the radical **1**, is due to hyperfine interactions with two equivalent β-protons of the methylene group ($a_\beta^H = 8.7$ mT). The additional triplets and the hyperfine interaction anisotropy (HIA) are due to an interaction with the nitrogen nucleus.[13,14] At early stages of radiolysis, we succeeded in obtaining well-resolved spectra with pronounced HIA on the outer lines of the secondary triplets and in determining the anisotropic constants: $a_z = 3.2$ mT; $a_y = 2.0$ mT; $a_x = 1.2$ mT and $a_{iso} = 1.6$ mT. The integral shape of the spectrum allowed us to conclude that the intensity ratio of the secondary triplets components was close to 1:1:1 (Figure 1, spectrum 1, scheme of lines T_1).

The spectrum of the Ċ≡N radical **2** (formed *via* hydrogen abstraction), in agreement with ref. 13, is also a triplet with a hyperfine splitting (HFS) constant of $a^N = 0.46$ mT and anisotropy due to the nitrogen atom. Some features of the triplet with $H = 0.43$–0.46 mT, which should be derived from the Ċ≡N radical, are observed on the central line of the main

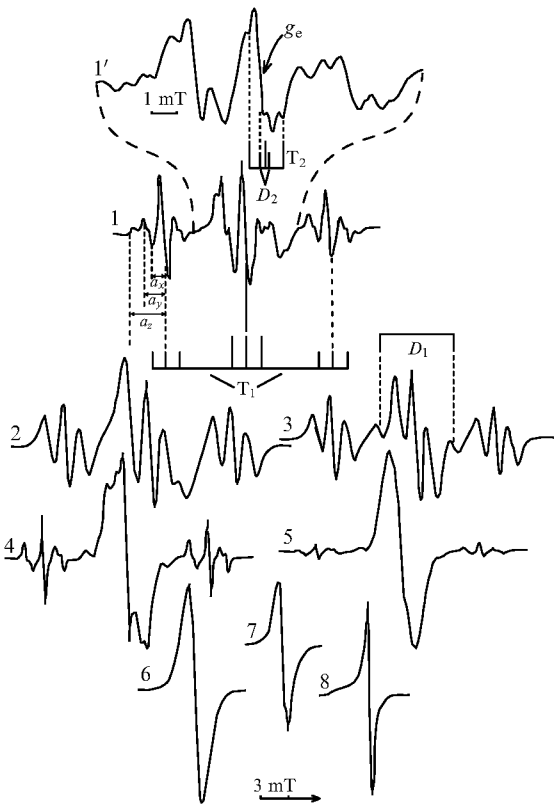

Figure 1 EPR spectra derived from γ-irradiated (77 K) HCN with a dose of 1 (1′); 40 (1); 800 kGy (2) and theoretical schemes of triplets of radicals $H_2C{=}\dot{N}$ (T_1); Ċ≡N (T_2); doublet D_1 (with $H = 8.0$ mT) and doublet D_2 (with $H = 0.3$ mT). After irradiation the sample (2) was warmed up 130 (3), 160 (4), 170 (5), 230 (6), 255 (7) and 273 K (8). Recording of spectra at 77 K.

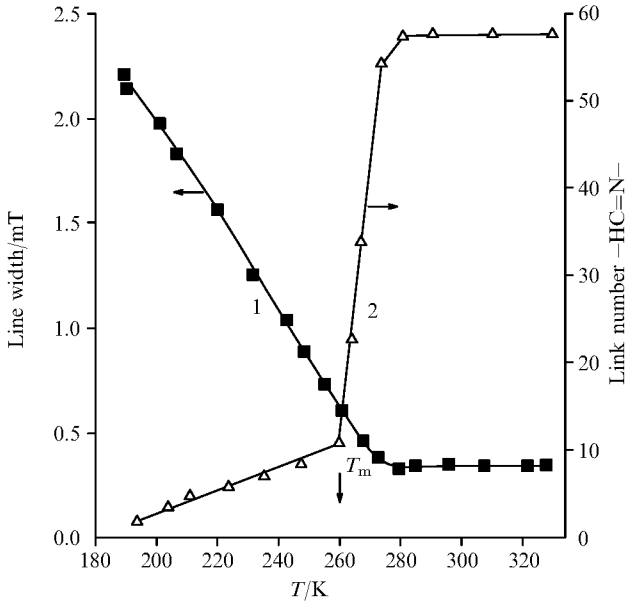

Figure 2 Change of the EPR singlet line width (1) and the number of –CH=N– links of the polyene radical chain (2) during heating of the radiolysed sample of HCN.

triplet when recording the general spectrum after a dose of 1 kGy (Figure 1, spectrum 1′, scheme of lines T_2). A narrow doublet with the splitting $H = 0.26$ mT (Figure 1, spectrum 1′, scheme of lines D_2), which, according to ref. 13, appears because of spin–nuclear interaction with the CH_2 group protons is observed in the very centre of the spectrum derived from the $H_2C{=}\dot{N}$ radical.

When the dose is increased, the EPR spectra show a decrease and then a complete disappearance of the HFI anisotropy on the outer lines of the secondary triplets, while the lines themselves become about two times wider. The symmetry of the spectrum is increased and, between the triplets, the doublet EPR spectrum, with line splitting $H = 8.2$ mT and intensity ratio close to 1:1, becomes marked and, at 130 K, is completely resolved (Figure 1, spectra 2,3, scheme of lines D_1).

In principle, the doublet spectrum can be derived from the following PMC:

(i) The radical of an H atom addition to the N atom of the hydrogen cyanide molecule, H–Ċ=NH **3**. However, a doublet spectrum has no HFS features due to α-hydrogen ($a_\alpha^H = 1.6$ mT [14]) and no HFI anisotropy due to the nitrogen nucleus (this may be because of the multiple line overlapping in the central part of the spectrum).

(ii) An electron 'sticking' to the CN group of the neutral molecule to give an anion-radical, $H{-}\dot{C}N^-$.

(iii) The radical of a propagating polymer chain. If the polymerization is initiated by radical **1**, then the oligomer or polymer radical will have the $RHC{=}\dot{N}$ structure, similar to radical **1**. But this assumption is not consistent with the decay of the doublet spectrum upon increasing the temperature of the radiolysed HCN. Already at 120–130 K the intensity of the doublet is decreased by a factor of 2.5–3.0 (Figure 1, spectrum 3).

The PMC with a doublet spectrum are accumulated at a constant rate and are about 25% of the total PMC concentration. The quantitative estimation was made from the difference between the general spectrum area and the $H_2C{=}\dot{N}$ radical triplet area calculated from the areas of the outer components. The given value ($\approx 25\%$) is obviously overestimated as it was difficult to allow for the abstraction radical **2** spectrum area and, probably, other PMC too, whose signals are situated in the centre of the general spectrum.

At 160 K, the HFS of the central spectral region became less defined due to overlapping with the singlet line, and after

complete disappearance of the triplet components (190 K) only a singlet with the width $H = 2.2$ mT and g-factor of 2.0023 is recorded (Figure 1, spectra 4–6). On raising the temperature further, a gradual narrowing of the spectral line to 0.3 mT at $T_m = 262$ K is observed (Figure 1, spectrum 8). It should be noted that on the spectral line in the pre-melting range (256 K) there appears a twist which is obviously related to the superposition of two singlets with different g-factors: one singlet with $g = 2.0023$ and another with $g = 2.0009$ (Figure 1, spectrum 7). After melting, the signal turns again into an isotropic singlet with $H = 0.3$–0.4 mT (Figure 1, spectrum 8). The sample colour after melting is yellow. On warming to ambient temperature and above (up to 360 K) the singlet shape and its intensity do not change.

The appearance of a narrow singlet line with a g-tensor close to the g value of the free electron confirms the formation of polyene radicals having a system of conjugated double bonds. The observed narrowing of the singlet line (from 2.2 to 0.3 mT) is connected with an increase in the degree of delocalization of the unpaired electron. The formation of polyene radicals, in turn, testifies that the polymerization of the γ-irradiated hydrogen cyanide takes place after the temperature of the radiolysed samples is raised. Actually, an investigation on a calorimetric set-up[12] has shown that the radiolysed HCN polymerization occurs in its melting region.[9,10]

The molecular mass of the polymer can be obtained by dividing the polymer weight by the concentration of free radicals in it. This value was found to equal 1350 ± 40. On the other hand, we can estimate the degree of delocalization of the spin density (hence, the lower boundary of the number of –CH=N– links in the polyene radical chain) through an effective width of the EPR singlet line by using the formula $n \geqslant 1 + (H_0/H)^2$; n is the number of –CH=N– links; H is an effective width of the EPR singlet line, mT; $H_0 = 2.25$ mT is a HFS constant on C–H.[15] As is seen from Figure 2, the delocalization degree increases linearly with temperature up to sample melting (260 K) and subsequently reaches 57 links (the width of the EPR singlet line is $H = 0.3$ mT). This corresponds to the molecular mass 1540 ± 50, which agrees satisfactorily with the above estimates. At a further rise of temperature or after prolonged storage of samples the singlet width (hence, the delocalization degree as well) does not change.

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