Photosensitivity of paramagnetic centers in radiolyzed solid hydrogen cyanide

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The photolysis of solid hydrogen cyanide and the effects of UV light on ^{60}Co-γ-irradiated HCN at 77 K were studied using an ESR technique. As in the case of radiolysis, the $H_2C=N^{\cdot}$ radical formed due to "sticking" of the H atom to the triple bond of the HCN molecule is the main radical product of low-temperature HCN photolysis. The $C{\equiv}N^{\cdot}$ radicals are accumulated at 77 K in insignificant amounts (~3 %). It was established that radical and ionic products stabilized in γ-irradiated HCN possess photochromism and under the action of UV light enter photochemical reactions leading to their decomposition. Upon photobleaching, the concentration of $H_2C=N^{\cdot}$ radicals first increases two- to threefold because of the decomposition of $H_2C=N^-$ ions and then decreases. The presence of radicals and ions formed upon the low-temperature radiolysis of HCN broadens the optical absorption band of the system, and the boundary of the action spectrum shifts from 280 nm (for nonirradiated HCN) to the visible region at 400—440 nm.

Key words: solid hydrogen cyanide, photolysis, radiolysis, free radicals, ions.

The interest of researchers in the mechanism of chemical transformations in solid hydrogen cyanide at low temperatures and weak radiation fields is associated with the presence of this compound in various cosmic formations (clouds of interstellar dust, comets, *etc.*). An important role of HCN in the pre-biological history of substance is also assumed. The first results on the studies of complex chemical transformations in solid HCN upon its low-temperature γ-radiolysis[1—3] and preliminary data on the types of paramagnetic centers (PMC) stabilized due to the radiolysis of the system[4] were obtained. It seems that the effect of UV light should be taken into account for modeling conditions of the cosmic space, in which HCN exists. Therefore, the purpose of the present work is to study the photolysis of HCN and the effect of UV light on PMC formed upon low-temperature radiolysis of solid HCN.

Experimental

The procedure of preparation and purification of HCN was described previously.[1,2] Radiolysis of HCN was carried out using γ-beams of ^{60}Co on a Gammatok setup. ESR spectra were recorded on a 3-cm-range radiospectrometer at a microwave field power of ~10^{-4} W and 77 K. A DRSh-1000 high-pressure mercury lamp was used for UV irradiation ($\lambda \geq 236$ nm, flux intensity with λ = 236—280 nm is $1.1 \cdot 10^{17}$ quantum cm^{-2} s^{-1}).

Results and Discussion

The low-temperature photolysis of the initial HCN at 77 K ($\lambda \geq 236$ nm, vacuum) is accompanied by the accumulation of PMC. In the ESR spectrum of the photolyzed hydrogen cyanide (Fig. 1, spectrum *1*), as in the spectra of the samples radiolyzed at 77 K,[4] a triplet of triplets of the radical due to the hydrogen atom "sticking" to the triple bond of the molecule predominates:

$$\mathrm{H{-}C{\equiv}N} + \dot{\mathrm{H}} \longrightarrow \underset{\mathbf{1}}{\mathrm{H_2C{=}\dot{N}}}\ . \qquad (1)$$

The main triplet is caused by the interaction of an unpaired electron with two β-H atoms of the methylene group ($a_\beta{}^{\mathrm{H}}$ = 8.7 mT, ratio of line intensities 1 : 2 : 1) and an additional triplet (a^{N} = 1.6 mT, ratio of line intensities 1 : 1 : 1), and HFC anisotropy appear due to interaction with the nitrogen nucleus. Anisotropic HFC constants correspond to the following values[4]: a_z = 3.2; a_y = 2.0; a_x = 1.2, and a_{iso} = 1.6 mT. The triplet HFC with ΔH = 0.5 mT is noticeable (and is more distinct than upon radiolysis[4]) in the central component of the overall spectrum of the UV-irradiated HCN. According to the literature data,[5] this HFC should

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be assigned to the $^{\cdot}$CN radical (**2**) formed due to the elimination of the H atom:

$$\mathrm{H{-}C{\equiv}N} \longrightarrow \dot{\mathrm{H}} + \underset{\mathbf{2}}{\dot{\mathrm{C}}{\equiv}\mathrm{N}} \,. \qquad (2)$$

The triplet of radical **2** with ratio of intensities 1 : 1 : 1 appears due to the interaction of the unpaired electron with the nitrogen nucleus (see Fig. 1, spectrum *1*, its components marked with asterisks). Judging from the computational simulation, the contribution of the signal from radical **2** to the total area of the spectrum is not more than 3 %. Therefore, as for the radiolysis, the main contribution to the overall spectrum is due to the signal of "sticking" radical **1**, and breakaway radicals **2** are stabilized to a considerably lesser extent. It is noteworthy that the intense spectra of radical **2** were obtained[5] upon vacuum UV photolysis of 1 % HCN in argon at 4.2 K. Probably, radical **2** is very unstable and disappears (in the reaction with the matrix or on recombination) already at $T \le 77$ K.

Two components of the doublet with line splitting $\Delta H = 6.8$ mT (see Fig. 1, spectrum *1*, marked with arrows D_1) can be observed between the central and side triplets. The same region of the overall spectrum of the radiolyzed HCN also exhibits a doublet, but with splitting $\Delta H = 8.4$—8.2 mT (see Fig. 1, spectrum *3*). Three probable structures were suggested[4] for this spectrum: a radical due to the "sticking" of the H atom to the nitrogen atom of the neutral molecule ($\mathrm{H{-}C^{\cdot}{=}NH}$), radical anion ($\mathrm{H{-}CN^{\cdot -}}$), and the growing polymeric chain radical ($\mathrm{R{-}CH_2{=}N^{\cdot}}$). The latter structure should be excluded due to the sharp decrease in the intensity of the doublet with increase in temperature of γ-irradiated HCN samples.[4] Since the formation of the $\mathrm{HCN^{\cdot -}}$ radical ion is highly improbable upon photolysis, the appearance of the lines of the doublet with splitting $\Delta H = 6.8$ mT upon UV irradiation of HCN can be related to either the second radical "sticking" of the H atom to the nitrogen atom of the HCN or the "sticking" of breakaway radical **2** to the carbon atom of the neutral molecule:

$$\mathrm{H{-}C{\equiv}N} + \dot{\mathrm{H}} \longrightarrow \underset{\mathbf{3}}{\mathrm{H{-}\dot{C}{=}N{-}H}} \,, \qquad (3)$$

$$\mathrm{H{-}C{\equiv}N} + \underset{\mathbf{2}}{\dot{\mathrm{C}}{\equiv}\mathrm{N}} \longrightarrow \underset{\mathbf{4}}{\mathrm{N{\equiv}C{-}CH{=}\dot{N}}} \,. \qquad (4)$$

Reaction (4) can be one of the channels of the disappearance of radicals **2**. The doublet spectrum also corresponds to the structure formed due to the addition of **2** to the nitrogen atom: $\mathrm{H{-}C^{\cdot}{=}N{-}C{\equiv}N}$ (**5**). However, the splitting value on the α-H atom would be[5] $\Delta H = 1.6$ mT, which does not agree with the experimental data.

The spectrum of radical **3** should be presented as a doublet of doublets with an additional splitting of each line to the triplet and with HFC anisotropy from the nitrogen nucleus. Perhaps, only two lines of the main doublet from the interaction of the unpaired electron with the β-proton on the nitrogen atom are observed in the complex spectra of irradiated HCN due to superposition with the triplet of radical **1**.

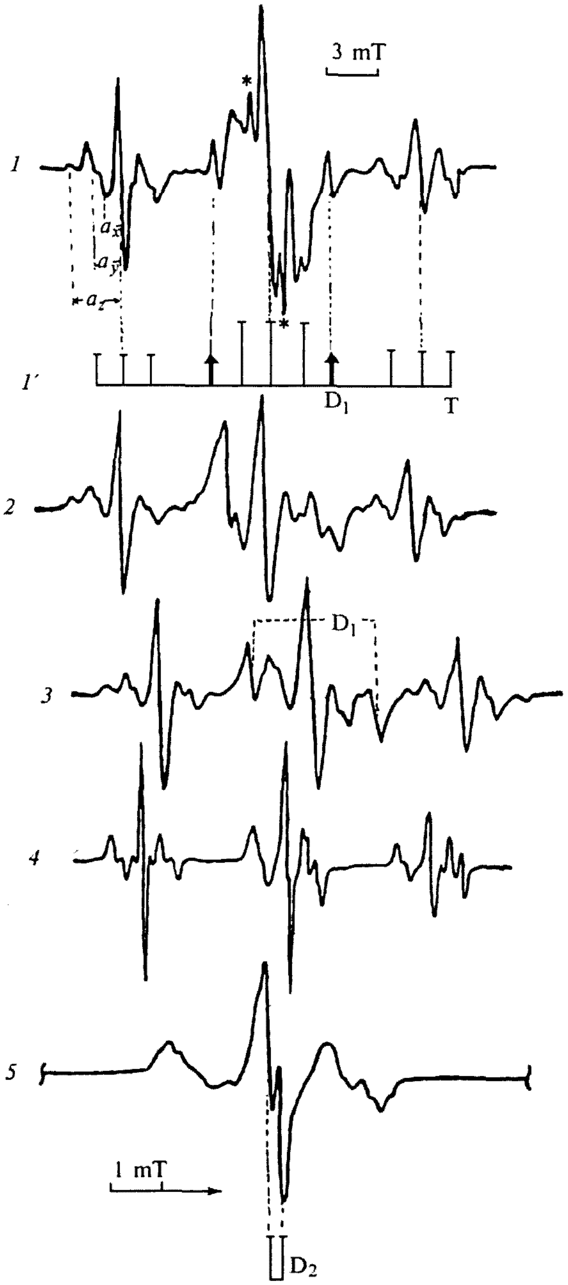

Fig. 1. ESR spectra of hydrogen cyanide irradiated at 77 K: *1*, UV irradiation (λ ≥ 236 nm) for 60 h; *1′*, theoretical scheme of triplet lines (T) of radical **1** and doublet lines (D_1) with splitting $\Delta H = 6.8$ mT; *2*, γ-irradiation with a dose of 30 kGy; after radiolysis sample **2** was irradiated with light with λ ≥ 440 nm (*3*), and then with light with λ ≥ 236 nm (*4*); *5*, center of spectrum *4* and theoretical scheme of doublet lines (D_2) from spin-nuclear interaction ("flip-flop").

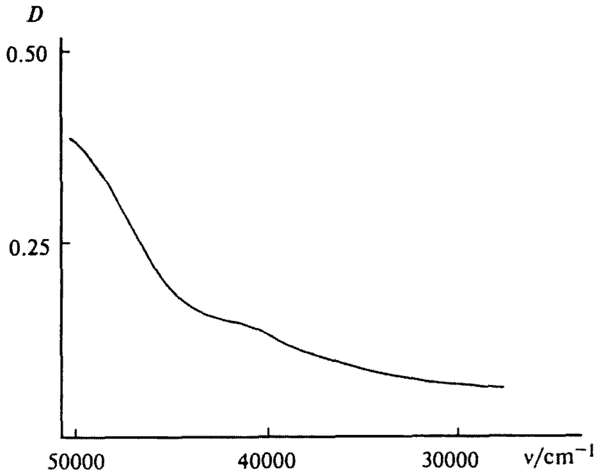

Fig. 2. Absorption spectrum of a 1-mm thick sample of HCN at 300 K.

The difference in the splitting values of doublets in UV- and γ-irradiated HCN is considerable: $\Delta H = 6.8$ mT and $\Delta H = 8.4$—8.2 mT, respectively. If the nature of the radical particles possessing the doublet spectrum is the same for radiolyzed and photolyzed HCN, this difference in ΔH is likely related to the different extents of reorientational relaxation of the radical, *i.e.*, to a change in the angle between the 2p(π)-orbital of the unpaired electron and the N—H or C—H bond. As the temperature of γ-irradiated HCN increases, this relaxation results in a decrease[4] in ΔH of the doublet to 7.8—7.6 mT.

It is likely that in photolyzed samples the relaxation occurs upon local heating of the matrix under the action of light, and the HFC constant of the doublet has a lower value of $\Delta H = 6.8$ mT, which is close to ΔH values for β-protons of organic radicals,[6] from the very beginning of the photolysis at 77 K. It is noteworthy that the contribution of the doublet signal to the spectrum of the photolyzed hydrogen cyanide does not exceed 15 %.

Photochemical peculiarities of HCN molecules are determined by the nitrogen atom and multiple bond. Spectra of compounds of this type exhibit a weak absorption band in the near-UV (or visible) region, which is related to the $n \rightarrow \pi^*$-transition of the antibonding electron of the nitrogen atom to the antibonding π^*-orbital of the multiple bond system.[7] The optical absorption spectrum of liquid hydrogen cyanide recorded at room temperature for a 1-mm thick sample (Fig. 2) is likely the edge of an intense band of the allowed transition, whose maximum lies in the vacuum UV-region. In the region from 240 to 260 nm, a weak band is observed that can be assigned to the forbidden $n \rightarrow \pi^*$-transition.

The boundary of the action spectrum for the formation of radicals upon low-temperature photolysis of HCN determined by ESR lies at 280 nm, while the position of the active light band in the total spectrum of the radiation of a DRSh-1000 lamp (λ = 236—280 nm) corresponds approximately to the band at 240—260 nm in the absorption spectrum of HCN (see Fig. 2). Therefore, free radicals are generated in HCN under the action of light with $\lambda \geq 236$ nm due to the intrinsic absorption of the matrix, and this process is not sensitized.

Since our attempt to obtain the absorption spectrum of HCN at 77 K was unsuccessful (due to strong scattering in the polycrystalline matrix), the quantum yield of accumulation of PMC upon low-temperature photolysis of HCN was estimated in the approximation of the complete absorption of active light by samples ~4 mm thick and was equal to $\varphi \approx 1.5 \cdot 10^{-5}$, which is typical of chromophoric centers with forbidden transitions.[7] When the temperature of photolyzed HCN samples increases, PMC begin to actively decay at $T > 150$ K.

The experiments on the effect of the action of light with $\lambda \geq 360$ nm on the radiolyzed HCN performed at 77 K on samples irradiated with doses of 200 and 800 kGy show that in both cases the concentration of PMC changed almost twice due to photoirradiation for 2 h (longer irradiation did not change the effect). The next series of experiments on photobleaching was performed using the full light of a DRSh-1000 mercury lamp ($\lambda \geq 236$ nm) on samples preliminarily irradiated with doses from 1 to 100 kGy. During the first 30—45 min of irradiation, the concentration of PMC in all samples increased 1.7—3.0-fold (Fig. 3). It should be mentioned that the increase in the PMC concentration during irradiation was ~$6 \cdot 10^{15}$ spin g^{-1} only due to photolysis, which is several orders of magnitude lower than the concentration of PMC formed due to radiolysis and the increase in the PMC concentration upon bleaching of the radiolyzed samples of HCN (10^{17}—10^{19} spin g^{-1}).

Then the boundary of the action spectrum for photobleaching was determined by ESR. Samples of HCN radiolyzed at 77 K were subjected to the action of filtered light, beginning from the red region, and the concentration of PMC was determined by the ESR spectra. Even the action of light with $\lambda \geq 500$ nm results in the disappearance of the initial bright-orange color of the irradiated samples and (depending on the dose of γ-irradiation) its changing to white (at doses lower than 20 kGy) or yellow (at doses of 30—90 kGy). Noticeable changes in the PMC concentration and in the pattern of the ESR spectra occurred at $\lambda \geq 400$—440 nm, and $\lambda \approx 440$ nm was accepted as the boundary wavelength of photolyzing light. Photobleaching with light ($\lambda \geq 400$ nm) results in the disappearance of asymmetry in the central region of the overall spectrum, and in low fields the first component of the doublet spectrum with $\Delta H = 8.2$—8.4 mT appears, then the two lines of the doublet become symmetric and narrow down, and splitting between them decreases to 7.6 mT (see Fig. 1, spectra *2* and *3*). It is likely that the

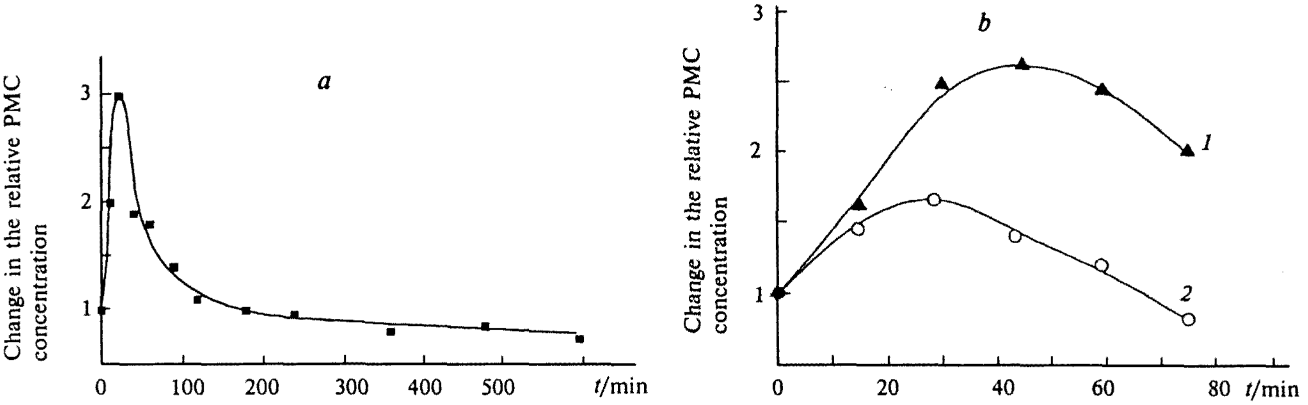

Fig. 3. Kinetics of changes in the concentration of paramagnetic centers of HCN (radiolyzed at 77 K) during photoirradiation ($\lambda \geq 236$ nm) at 77 K. *a*. Radiation dose 1 kGy (initial concentration of PMC $4.3 \cdot 10^{17}$ spin g^{-1}). *b*. Radiation dose 10 (*1*) and 100 kGy (*2*), initial concentrations of PMC $4.6 \cdot 10^{18}$ (*1*) and $3.3 \cdot 10^{19}$ spin g^{-1} (*2*).

narrowing of the doublet, which, according to the experiments on the photolysis, should be assigned to the radicals $\mathrm{H{-}C^{\cdot}{=}N{-}H}$ (**3**) or $\mathrm{N{\equiv}C{-}CH{=}N^{\cdot}}$ (**4**), and the disappearance of asymmetry of the overall spectrum is associated with the reorientational relaxation of radicals under the action of light. The total concentration of PMC gradually increases as the wavelength of bleaching light decreases. However, the fraction of particles **3** or **4**, which give the doublet spectrum up to $\lambda \geq 320$ nm, remains almost at the initial level (~25 %), and only at $\lambda \leq 300$ nm does the intensity of the doublet spectrum decrease noticeably, and the total concentration of PMC increases. The action of short-wave light ($\lambda \geq 280$ nm or $\lambda \geq 236$ nm) results in a ~2.7-fold increase in the total concentration of PMC (Fig. 4). Longer (1 h and more) irradiation with the full light of the mercury lamp results in a decrease in the PMC concentration, *i.e.*, the curves of PMC accumulation pass through maxima upon photobleaching. This character of the dynamics of changes in the PMC concentration was manifested by all samples irradiated with different doses, which is also demonstrated in Fig. 3, *a*, which shows a curve obtained upon prolonged bleaching of an HCN sample preliminarily irradiated with a dose of 1 kGy.

It follows from the results obtained that the components of the doublet spectrum decrease and the intensity of the triplet spectrum increases during photobleaching. Therefore, the total concentration of PMC increases due to generation of $\mathrm{H_2C{=}N^{\cdot}}$ radicals (**1**). In some experiments, an almost "pure" triplet of triplets with well-resolved HFC anisotropy (from nitrogen nuclei) on side lines of the central triplet, which are usually strongly deformed due to overlapping with the doublet lines, is observed after the disappearance of the doublet spectrum (see Fig. 1, spectrum *4*). The doublet with splitting $\Delta H = 0.25$—0.30 mT caused by the effect of spin-nuclear interaction between the electron spin and two nuclei in the $\mathrm{CH_2}$ group (so-called "flip-flop,"[6] see Fig. 1, spectrum *5*) is also observed on the central line of the overall spectrum. The appearance of the latter doublet is also associated with the disappearance of radicals with a broad doublet spectrum, whose lines screen a narrow doublet from the spin-nuclear interaction. For the first time, a distinct doublet caused by the effect of spin-nuclear interaction was observed[6] in the spectrum of radical **1** in the absence of spectra of other radicals upon photolysis of the HCN+HI system in an argon matrix at 4.2 K.

It follows from the experiments on photobleaching of radiolyzed HCN samples that two paramagnetic particles (radical **1** and radicals with the doublet spectra with $\Delta H = 8.4$ mT generated upon low-temperature radiolysis of HCN) possess photochromic properties.

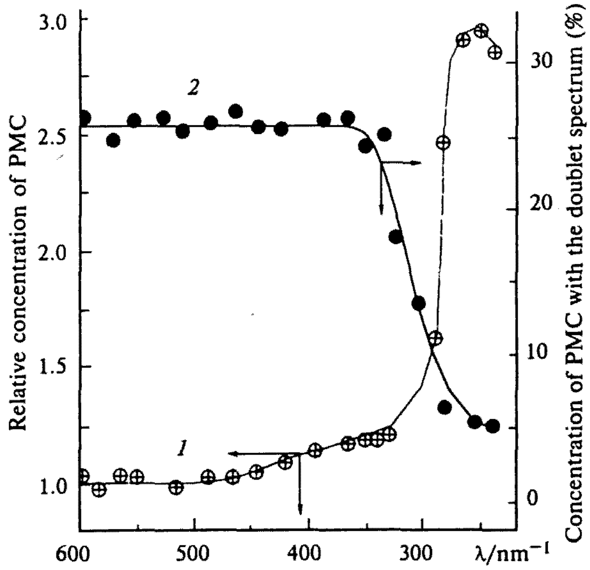

Fig. 4. Spectrum of action for photobleaching of radical ions of HCN γ-irradiated with a dose of 20 kGy (*1*) and change in content of the doublet spectrum (with $\Delta H = 6.8$ mT) at various wavelengths of photolyzing light (*2*). Samples were 2 mm thick, irradiation time at the specified wavelength is 15 min.

They are equally sensitive to the same wavelengths of photolyzing light and efficiently react under the action of light with $\lambda \leq 300$ nm. However, in the photolysis of radical **1**, an increase in the concentration is observed at first, and the radical with the doublet spectrum immediately disappears. It can be assumed that the increase in the concentration of radical **1** is related to "bleaching" of $H_2C=N^-$ anions formed upon radiolysis of the matrix due to capturing of an electron by the CN group. This particle is diamagnetic and does not give an ESR spectrum. Under the action of light, anions eliminate an electron to transform into radicals **1**.

The CN group possesses a high electron affinity (3.2—3.7 eV). Nevertheless, the energy of photons with a wavelength of 300—400 nm is sufficient to eject an electron from traps. The depth of these traps can be estimated from the action spectrum presented in Fig. 4. The minimum energy of photons, which causes the decomposition of anions, is 2.8 eV (λ = 440 nm), and the maximum energy is 5.2 eV (λ = 236 nm).

Due to the existence of the anions and their transformation into **1** the concentration of radical **1** upon photobleaching passes through a maximum, whose position is determined by the dose of preliminary γ-radiation. After conversion of a portion of the anions to radical **1**, growth of their concentration stops with further UV irradiation, and the photodecomposition of the radicals and decrease in their concentration become noticeable (see Fig. 3). The concentration of particles with the doublet ESR spectrum does not increase upon photobleaching at the expense of charged particles, and its decrease under the action of light occurs immediately upon UV irradiation of the radiolyzed HCN.

The experiments on photobleaching made it possible to establish that low-temperature radiolysis of HCN results in the accumulation of $H_2C=N^-$ ions along with the paramagnetic centers formed in a radiation yield $G \approx 8$ radicals per 100 eV of the absorbed γ-radiation energy.[4] These ions are bleached by light to transform into radicals. Therefore, 24 (not 8) paramagnetic centers are stabilized as a result of absorption of 100 eV of the γ-radiation energy in 1 g of solid HCN at 77 K. Since from 4.0 to 4.6 eV are consumed in the formation of one pair of radicals in this system, 50 to 55 eV out of 100 eV of the absorbed energy is stored as stabilized radicals. Therefore, when solid HCN is irradiated with γ-beams of ^{60}Co, more than 50 % of the absorbed energy of γ-radiation is accumulated in it only in the form of radicals. We do not know any other systems in which the γ-radiation energy would be stored so efficiently in the form of chemically active intermediates.

Thus, it is established by the ESR method that radicals and ions formed upon low-temperature (77 K) radiolysis of HCN possess photochromism and enter photochemical reactions resulting in their decomposition under the action of light with $\lambda < 400$ nm. At first, the concentration of radicals **1** increases two- to threefold probably due to the photobleaching of the $H_2C=N^-$ anions, whose concentration depends on the dose of γ-irradiation. Radicals with doublet spectra capture no electrons, decompose under the action of light, and their concentration immediately begins to decrease upon photobleaching. The presence of radical and ion products of low-temperature radiolysis in HCN broadens the optical absorption band of the system, shifting the boundary of the action spectrum from 280 nm (for nonirradiated HCN) to the visible range (400—440 nm for γ-irradiated HCN). Due to this shift, photochemical transformations of radicals and ions can occur under the action of longer-wave light than that necessary for the generation of primary radicals.

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