MECHANISM OF THE RADIOLYTIC TRANSFORMATIONS OF CELLULOSE.

1. FORMATION AND TRANSFORMATION OF RADICALS

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The formation (77K) and transformation (300K) of radicals in celluloses with various degrees of crystallinity under γ-radiation have been studied by the ESR method. The radical products of the low-temperature γ-radiolysis of cellulose formed in the polymer chain are macroradicals the unshared electrons of which are localized on $C_{(1)}$, $C_{(4)}$, $O_{(2)}$, and $C_{(5)}$. With a rise in the temperature to 300K they undergo substantial changes, which shows the dominating role of secondary reactions of macroradicals in the radiation-chemical transformation of cellulose.

We have undertaken a complex study of the radiolytic transformation of cellulose by physicochemical methods: ESR spectrometry, mass spectrometry, and viscometry. This approach is based on an analysis of literature reports showing a fairly strict directivity of the changes in the physicochemical indices of radiolyzed cellulose, regardless of the prehistory of the sample. At the same time, the processes of degradation and of the formation of free radicals and volatile products have previously been studied separately and, in the discussion of the results obtained, they have been considered autonomously, regardless of their connection with one another. The main concept of the investigations that we have performed consisted in the idea that any of the processes taking place in irradiated cellulose must be comprised within a single chain of transformations. The results of the investigations have permitted the construction of a strict chain of radiation-chemical transformations of cellulose under vacuum conditions.

In this paper we give the results of a study of radical-formation in γ-irradiated cellulose by the ESR method.

J. C. Arthur and his colleagues were the first to have studied the mechanism of the radiolytic transformation of cellulose by the ESR method [3-6]. They came to the conclusion that cellulose undergoes degradation on irradiation and, therefore, the most probable localization of the energy of the radiation is on the carbon atom in position 1 or 4 of an anhydroglucose unit, which must lead to the direct depolymerization of the cellulose macromolecule with the formation of radicals having the unshared electron on $C_{(1)}$ or $C_{(4)}$. Another opinion has existed, according to which $C-H$ bonds in the irradiated cellulose are cleaved [1], and the formation of radicals has been considered on this basis [2].

A reliable picture of the radical-forming process in γ-irradiated cellulose has been revealed in recent years [7-9]: Radicals arising at 77K with cleavage of $C-H$ bonds in positions 1 and 4 of the anhydroglucose units of the polymer have been identified by the ESR method.

The ESR spectra of ramie and cotton celluloses irradiated with doses of 10-80 kGy in vacuum at 77K each consists of seven lines (Figs. 1 and 2). These spectra, while having identical structures, differ by the relative intensities of the individual components and each consist of a superposition of five separate signals: two singlets with widths between the points of maximum slope (ΔH_i) of ~ 0.5 and 0.8 mT, two doublets with splittings between the components of (ΔH_s) of 2.5 and 13.0 mT, and a triplet with $\Delta H_s = 3.0$ mT.

The weak singlet with $\Delta H_i \sim 0.5$ mT, superposed on the weak-field side of the singlet with $\Delta H_i = 0.8$ mT, was due to captured electrons and rapidly disappeared when the sample was irradiated with visible light. Electron capture is characteristic for a wide range of polymers (see [10], p. 25).
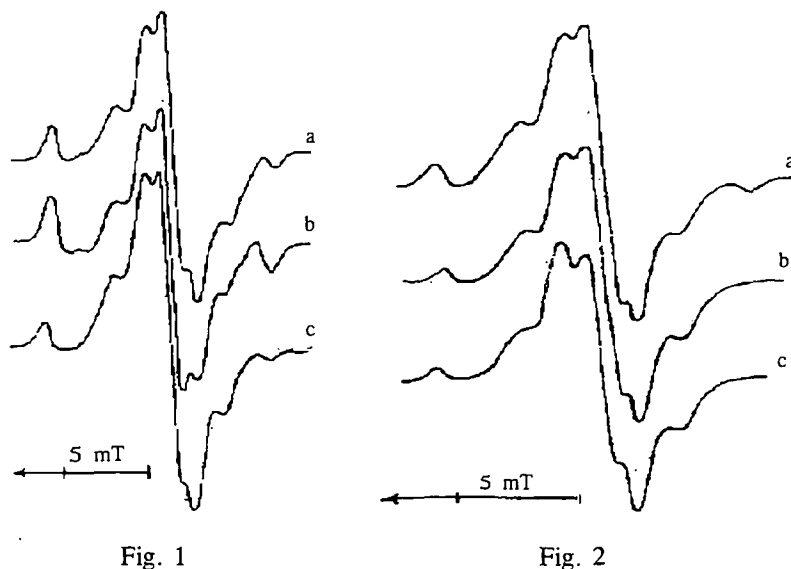

Fig. 1. ESR spectra of ramie cellulose γ-irradiated at 77K with doses of 10 (*a*), 40
(*b*), and 80 (*c*) kGy.

Fig. 2. ESR spectra of cotton cellulose with DCs of 80% (*a*), 61% (*b*), and 40% (*c*)
γ-irradiated at 77K with a dose of 80 kGy.

The central line in each spectrum is due to the singlet signal with $\Delta H_i = 0.8$ mT. It is characteristic that the intensity of this signal did not change appreciably as a function of the radiation dose (see Fig. 1) and of the degree of crystallinity of the cellulose (see Fig. 2). This means that the radicals responsible for the signal were formed in both the crystalline and the amorphous parts of the cellulose. According to our results [11], these radicals are formed in the dehydration of the $O_{(2)}-H$ bonds of the anhydroglucose units of cellulose.

A doublet with $\Delta H_s = 2.5$ mT and a triplet with $\Delta H_s = 3.0$ mT are due, respectively, to the radicals arising in irradiated cellulose with the cleavage of the $C_{(1)}-H$ and $C_{(4)}-H$ bonds [7-9].

An asymmetric doublet with $\Delta H_s = 13.0$ mT has not previously been reliably identified [12, 13]. For the samples investigated, the intensity of this signal passed through a maximum at doses of 40-50 kGy. We established its origin from a formyl radical by a mass-spectrometric study of the composition of the volatile products from the degradation of cellulose [14]. As can be seen from Figs. 1 and 2, the intensity of the asymmetric doublet increased with a rise in the DC of the cellulose. The amount of carbon monoxide in the products of the radiolysis of cellulose, the formation of which we connect with the transformation of a formyl radical, shows good correlation with the intensity of the asymmetric doublet.

The formation of a formyl radical is preceded by the cleavage of the $C_{(5)}-CH_2OH$ bond, as a result of which a radical with its unshared electron on $C_{(5)}$ also arises. However, no signal from these radicals appears in the observed spectra because of overlapping by the main signals.

To confirm the correctness of our interpretation of the ESR spectra of cellulose irradiated at 77K, we have constructed a theoretical ESR spectrum by the graphical superposition of individual signals: a triplet with an intensity ratio of 1:2:1 and $\Delta H_s = 3.0$ mT, a doublet with $\Delta H_s = 2.5$ mT, and a singlet with $\Delta H_i = 0.8$ mT, without taking into account the weak signal from captured electrons and the asymmetric doublet with $\Delta H_s = 13.0$ mT. As the individual signals we took the theoretically calculated [15] ESR spectra and the experimental ESR spectrum of paramagnetic lignin. The calculations showed that the arrangement of the lines of the experimental spectrum of irradiated cellulose can be obtained in two combinations of the superposition of the individual signals when they have identical intensities. But complete assignment of the structure of the experimental spectrum can be achieved when the relative positions of the signals with respect to their *g*-factors are taken into account. To solve this problem we recorded the ESR spectra of γ-irradiated cellulose and of DPPH simultaneously (Fig 3a).
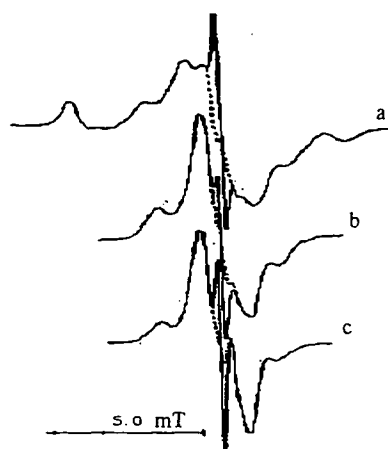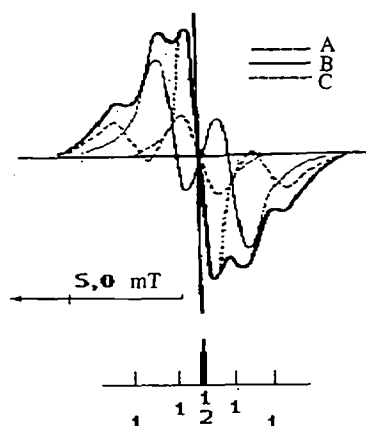
Fig. 3   Fig. 4

Fig. 3. ESR spectra of cotton celluloses with DC 80% (*a*, *b*) and 40% (*c*) γ-irradiated with a dose of 40 kGy at 77K (*a*) and 300K (*b*, *c*) recorded simultaneously with the ESR signal of DPPH.

Fig. 4. ESR spectrum obtained by graphical superposition of individual theoretically calculated spectra (*B*, *C*), and the ESR spectrum of paramagnetic lignin (*A*): *A*) singlet with ΔH_i = 0.8 mT; *B*) doublet with ΔH_s = 2.5 mT; *C*) triplet with ΔH_s = 3.0 mT.

The positions of the lines in the spectrum relative to the narrow line of DPPH showed that $g_{triplet}$ ~ $g_{singlet}$ < $g_{doublet}$ ~ g_{DPPH}. Figure 4 illustrates the theoretical ESR spectrum of γ-irradiated cellulose plotted in the light of the positions of the individual signals. The distance between the two groups of signals differing with respect to their *g*-factors amounts to ~0.15 mT, which corresponds to Δg = ~0.0009. Consequently, $g_{triplet}$ ~ $g_{singlet}$ ~ 2.0036 − 0.0009 ~ 2.0027 and $g_{doublet}$ ~ g_{DPPH} = 2.0036.

The results that we have obtained show that the main components of the ESR spectrum of cellulose irradiated at 77K are — together with a doublet having ΔH_s = 2.5 mT and a triplet having ΔH_s = 3.0 mT — a singlet with ΔH_i = 0.8 mT and an asymmetric doublet with ΔH_s = 13.0 mT.

To reveal the complete picture of the radiolytic transformation of cellulose it is necessary to follow by the ESR method the evolution of the radicals stabilized at 77K when they are allowed to warm to room temperature. The information in the literature relates mainly to the investigation of radicals in cellulose irradiated either at 77K or at 300K.

The resolution of the ESR spectra of cellulose irradiated at 300K depends on the temperature at which the spectra were recorded. At 77K an unresolved spectrum consisting of three lines is recorded. An identical spectrum is observed on the refreezing after their thermal annealing at 300K of samples irradiated at 77K (Fig. 5).

The resolution of the spectrum is better if it is recorded at 300K. Then, for a given sample, qualitatively identical ESR spectra are observed regardless of the temperature of irradiation (77 or 300K). For this reason, the ESR spectra of cellulose preparations irradiated at 300K may be regarded as the result of a 77→300K transition of the samples.

The poor resolution of the ESR spectra shown in Fig. 5 is due to the fact that at 300K radicals with α-protons are formed which, unlike radicals with β-protons, possess a considerable anisotropy of the HFS, and this depends on the orientation of the C_α−H bond in a magnetic field [16]. Therefore, at 77K the ESR spectra of radicals with α-protons represent a superposition of many lines corresponding to various orientations. This leads to a broadening of the lines and a smearing of the HFS of the spectra. At 300K the anisotropy of the HFS is averaged out because of the reorientation of the C_α−H bonds in the radicals relative to the magnetic field, and the ESR spectrum becomes more resolved.

Figure 6 shows the ESR spectra of ramie and cotton celluloses γ-irradiated at 300K and recorded at 300K. Each of these spectra consists of four lines, and they differ mainly by the positions of the central components. With an increase in the
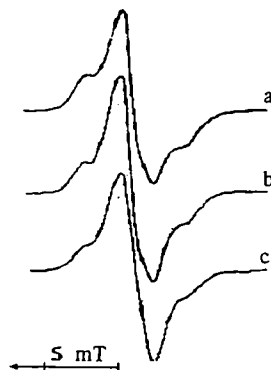
Fig. 5. ESR spectrum after the thermal annealing (3 min at 300K) of cotton celluloses with DC 80% (a), 61% (b), and 40% (c) irradiated at 77K. The spectra were recorded at 77K.
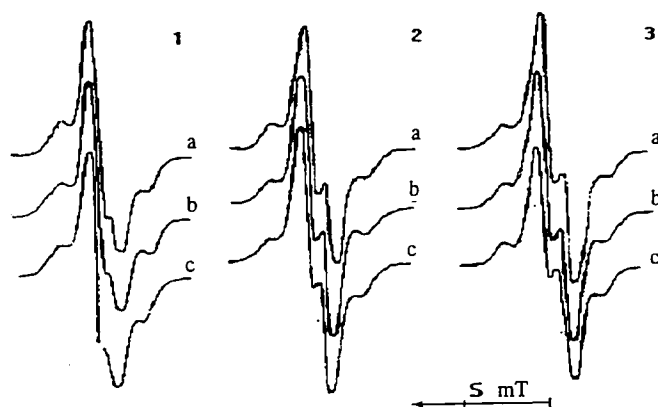

Fig. 6. ESR spectra of cellulose preparations γ-irradiated at 300K with doses of 10 (a), 40 (b), and 100 (c) kGy: 1) ramie cellulose and cotton cellulose with DC 80%; 2, 3) cotton celluloses with DC 61 and 40%, respectively.

absorbed dose from 10 to 100 kGy the form of the ESR spectra of the ramie and cotton celluloses with a DC of 80% did not change (see Fig. 6, curves 1a−1c), while for cotton celluloses with DCs of 61 and 40% the central components of the spectra tended to a more symmetrical position (see Fig. 6, curves 2a−2c and 3a−3c).

The dependence of the intensities of the individual lines on the DC of the preparation and the changes taking place in the spectra on storage of the irradiated samples and under the action of water vapor on a previously irradiated substrate showed that the ESR spectrum of γ-irradiated cellulose is formed by the superposition of three individual signals: a triplet with an intensity ratio of 1:2:1 and ΔH_s = 2.5 mT, a doublet with ΔH_s = 1.2 mT, and a singlet with ΔH_i = 0.8 mT. Figure 7 shows the theoretical ESR spectra constructed by the graphical superposition of the signals mentioned. It can be seen that the experimental ESR spectra are well described by a superposition of the three signals in various combinations of their intensities.

Many researchers have reported the appearance of an asymmetric ESR spectrum on the γ-irradiation of preparations of native cellulose. In the opinion of some of them, the asymmetry of the spectrum is due to the formation of radicals only in accessible regions of the cellulose [17]. The results that we have obtained agree with the opinion of Bernard et al. [2], who consider that the asymmetry of the spectrum is caused by the superposition of lines having different g-factors.

According to the theoretical spectra given in Fig. 7, the asymmetry of the observed ESR spectra of cellulose preparations is explained by the unsymmetrical superposition of the singlet. With a decrease in the intensity of the singlet the
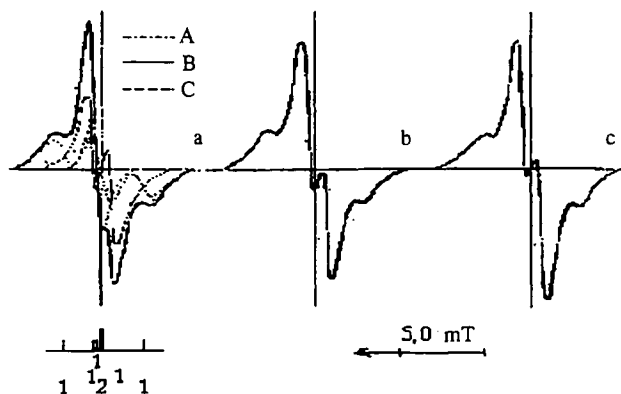
Fig. 7. ESR spectra obtained by the graphical combination of theoretically calculated spectra (B, C) and the signals of paramagnetic lignin (A) at $g_A < g_B = g_C$ (A being a singlet with $\Delta H_i = 0.8$ mT, B a doublet with $\Delta H_s = 1.2$ mT, and C a triplet with $\Delta H_s = 2.5$ mT): a) $I_A{:}I_B{:}I_C = 1.0{:}1.3{:}0.6$; b) $I_A{:}I_B{:}I_C = 1.0{:}4.0{:}1.5$; c) $I_B{:}I_C = 3.0{:}1.0$.
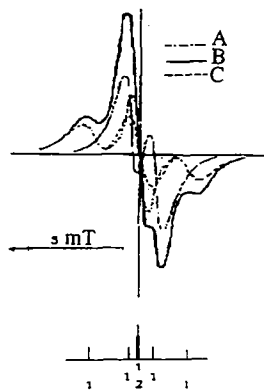

Fig. 8. ESR spectrum analogous to spectrum a in Fig. 7 but obtained at $g_A \sim g_C < g_C$.

spectrum acquires a more symmetrical form. Figure 7c illustrates the symmetry of the spectrum when there is no singlet signal, although this is not observed in the experimental spectra given here. A symmetrical spectrum arises on prolonged storage (40 days and more) of cellulose preparations that have been irradiated in vacuum [18].

We have reported the fact that the ESR spectrum of cellulose γ-irradiated at 300K consists of the geometric sum of three signals in [19, 20]. Here it was assumed that $g_{triplet} = g_{doublet} > g_{singlet}$ [20], as shown in Fig. 7. But the arrangement of the lines in the ESR spectrum of cellulose γ-irradiated at 300K relative to the line of DPPH showed that $g_{triplet} \sim g_{singlet} < g_{DPPH} < g_{doublet}$ (see Fig. 3b,c). Consequently, the theoretical spectrum in which an unsymmetrical superposition of the doublet, and not of the singlet, occurs must correspond to the structure of the experimental spectrum.

Figure 8 shows a theoretical ESR spectrum satisfying the condition $g_A \sim g_C < g_C$ and having $I_A{:}I_B{:}I_C = 1.0{:}1.3{:}0.6$, like the ESR spectrum given in Fig. 7a. The theoretical spectra shown in Fig. 7b,c can be reconstructed similarly with no change in the intensities of the individual signals. Then, as in Fig. 7, the asymmetry of the spectra will be due to the presence of the singlet signal, and with a decrease in its intensity the spectrum will become more symmetrical.

According to calculated figures obtained from Fig. 3b,c, the DPPH signal is observed in the middle between the centers of the triplet and the doublet. The distance between the centers of the triplet and the doublet is not less than 0.3 mT, which corresponds to $\Delta g \sim 0.0018$. Then $g_{triplet} \sim 2.0036 - 0.009 \sim 2.0027$, and $g_{doublet} \sim 2.0036 + 0.009 \sim 2.0045$.

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It is impossible to determine accurately the position of the line of the singlet relative to the DPPH line in Fig. 3b,c because of the superposition of the singlet on the triplet and the doublet. Its g-factor was assumed to be equal to the g-factor of the singlet with ΔH_i = 0.8 mT observed at 77K, since the singlet was due to one and the same radical in the two cases. But at 300K, in contrast to 77K, the $R\dot{O}_{(2)}$ radicals are stable only in the crystalline parts of the sample, being a kind of "indicator" of the physical structure of cellulose [21]. In the amorphous sections, these radicals are converted into radicals of the $O-\dot{C}H-O-$ type, giving a doublet with ΔH_s = 1.2 nTl.

We are the first to have assigned the doublet with ΔH_s = 1.2 mT in the ESR spectrum of cellulose γ-irradiated at 300K to radical (3) formed from a precursor — radical (1):
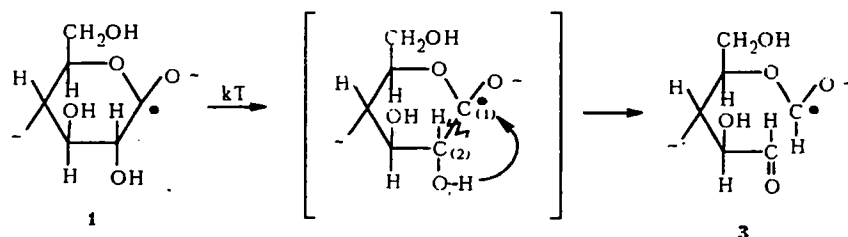
The smallness of the splitting in the doublet signal of radical (3) is due to the low spin density on the α-carbon atom linked to two $-OR$ groups, which, as is known [22], strongly draw off spin density.

The presence of a doublet signal in the spectrum of cellulose γ-irradiated at 300K has also been reported by other workers. According to their results, the value of ΔH_s was 1.0 [23], 1.3 [24], and 1.5 [25, 26] mT. These authors identified the radical from their own considerations of the course of the γ-radiolysis of cellulose.

The triplet with ΔH_s may relate to the terminal radical (4) formed as a result of the transformation of radical (2):
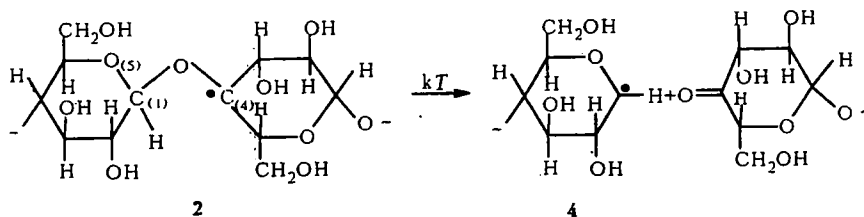
At the same time, according to our results, in irradiated cellulose several types of radical (4) may exist that differ from one another by their environment — the combination and density of intramolecular and intermolecular hydrogen bonds.

For the radical with the unshared electron at $C_{(5)}$, the most probable transformation pathway may be the splitting out of β-hydrogen:
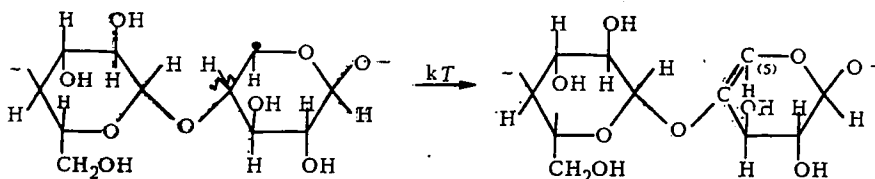
Thus, the radical products of the low-temperature radiolysis of cellulose, formed from the polymer chain, are macroradicals the unshared electrons of which are localized on $C_{(1)}$, $C_{(4)}$, $O_{(2)}$ and $C_{(5)}$. With a rise in the temperature to 300K they undergo substantial changes, which shows the dominating role of secondary reactions of the macroradicals in the radiation-chemical transformation of cellulose.

EXPERIMENTAL

Ramie and cotton celluloses and two amorphous samples of cotton cellulose having degrees of crystallinity, according to x-ray diffraction results, of 83, 80, 61, and 40%, respectively, were investigated. Samples of cellulose weighing 20-30 mg, in quartz tubes, were carefully degassed in a high-vacuum apparatus at a residual pressure of $1.33 \cdot 10^{-2}$ Pa. Irradiation was conducted at 77K and 300K with a Co^{60} γ-source at a dose rate of 2 Gy/sec. ESR spectra were recorded on a radiospectrometer of the RÉ-1301 type at the same temperature as that used for irradiation (77 or 300K).

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