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MECHANISM OF THE RADIOLYTIC TRANSFORMATION OF CELLULOSE.

II. CLEAVAGE OF THE GLYCOSIDIC BONDS

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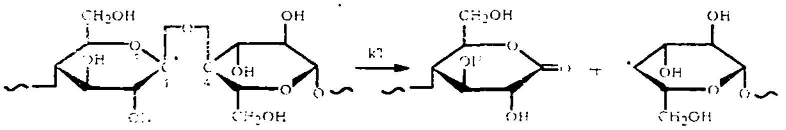
The radiation degradation of the cellulose macromolecule has been studied by viscometry and it has been shown that the cleavage of the glycosidic bonds of the irradiated polymer takes place as a result of the transformation of primary radicals with an unpaired electron at $C_{(4)}$. The values of G_d for temperatures of 77 and 300 K have been found to be 1.4 and 3.3, respectively. At 300 K, but not at 77 K, G_d reveals a dependence on the radiation dose, which is due to the presumed mechanism of the cleavage of the glycosidic bonds between the anhydroglucose units of the cellulose macromolecule as a result of γ-irradiation.

The history of the development of ideas on the radiation degradation of the cellulose macromolecule is reflected in [1-9, 11-16]. The opinion has been expressed [1] that the cleavage of the polymeric chain in irradiated cellulose takes place with the transformation of radicals having an unshared electron at $C_{(1)}$ and $C_{(4)}$ formed in the radiolytic disruption of the corresponding C−H bonds. However, the evolution of the scientific point of view in the world literature on the radiolysis of cellulose has been determined mainly by [2-5]. The results obtained were interpreted as arising from the direct depolymerization of the cellulose macromolecule, leading to the formation of radicals with an unshared electron at $C_{(1)}$ or $C_{(4)}$.

In recent years, radicals have been identified that arise in cellulose irradiated at 77 K with cleavage of the $C_{(1)}-H$ and $C_{(4)}-H$ bonds of the anhydroglucose units [6-9]. Secondary reactions of these radicals lead to the cleavage of the polymer chain or the breakdown of the unitary molecular structure of the cellulose [6]. Possible pathways of the transformation of the $\dot{C}_{(1)}$ and $\dot{C}_{(4)}$ radicals have been given in [7, 8], while it has been shown in [9] that only the $\dot{C}_{(4)}$ radical can be responsible for the cleavage of a glycosidic bond in the cellulose macromolecule.

The present work was devoted to a study of the cleavage of the glycosidic bonds between the anhydroglucose units of the cellulose macromolecule on γ-irradiation.

The radical products of the low-temperature γ-radiolysis of cellulose are represented by macroradicals the unshared electrons of which are localized on $C_{(1)}$, $C_{(4)}$, $O_{(2)}$, and $C_{(5)}$ [10]. Cleavage of the polymer chain of cellulose as the result of irradiation by ionizing radiation may, in principle, be due to the transformation of the $\dot{C}_{(1)}$ and $\dot{C}_{(4)}$ macroradicals, but the cleavage of the chain at a $C_{(1)}-O$ fragment of the glycosidic chain of radical II seems to us to be more likely than at the $C_{(4)}-O$ fragment of radical I.



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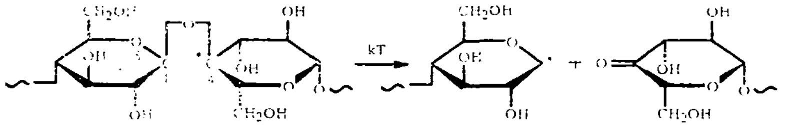

II

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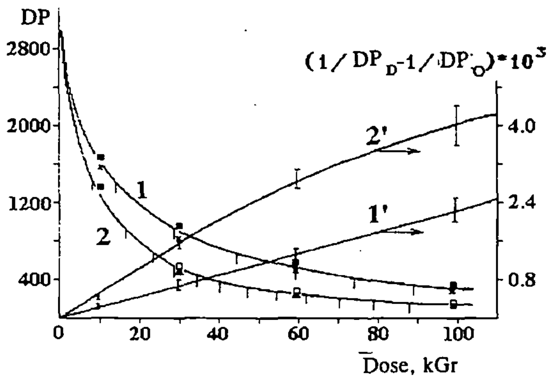

Fig. 1. Dependence of the values of the DP (*1, 2*) and of $1/\mathrm{DP}_D - 1/\mathrm{DP}_0$ (*1', 2'*) on the absorbed radiation dose for cotton cellulose with $\mathrm{DP}_0 = 2900$, γ-irradiated in vacuum at 77 K (*1, 1'*) and 300 K (*2, 2'*) with (x, Δ) and without (■, □) saturation by water vapor.

At first glance it may appear that the $C_{(4)}-O$ bond in radical I is weakened through the influence of the negative inductive effect of the $C_{(5)}-\dot{C}_{(1)}-O$ fragment. This does in fact take place, but the electron density on the $C_{(4)}-O$ bond is restored to some degree through the influence of the positive inductive effect of the carbon atoms adjacent to $C_{(4)}$. Because of this, transformation with cleavage of the $C_{(1)}-C_{(2)}$ bond is energetically favorable for radical I [10].

The situation is completely different in the case of radical II. Here, the $C_{(1)}-O$ bond is the most weakened, since the electron density of this bond is considerably delocalized through its drawing off to the $\dot{C}_{(4)}-O$ and $C_{(1)}-O_{(5)}$ fragments. The transformation of radical II with cleavage of the $C_{(1)}-O$ bond is therefore more realistic than the transformation of radical I with cleavage of the $C_{(4)}-O$ bond.

The radiation degradation of the cellulose macromolecule due to cleavage of the glycosidic bonds between the anhydroglucose units on irradiation is characterized by the magnitude G_{d}, which is called the radiation-chemical yield of degradation. It is determined from the dependence of the change in the degree of polymerization (DP) of the cellulose on the absorbed radiation dose.

It is known that the interrelationship of the DP of cellulose and the absorbed radiation dose is expressed by the traditional equation [11-13]:

$$1/\mathrm{DP}_D - 1/\mathrm{DP}_0 = K \cdot D^m, \tag{1}$$

where DP_0 and DP_D are the number-average DPs ($\overline{\mathrm{DP}}_n{}^s$) of the cellulose before and after irradiation, respectively; K is the probability of the cleavage of the glycosidic bond; D is the absorbed radiation dose; and m is a constant.

Since $m < 1$, the dependence of the difference in the reciprocal values of the DP on D is rectified in logarithmic coordinates:

$$\log\,(1/\mathrm{DP}_D - 1/\mathrm{DP}_0) = \log K + m \log D. \tag{2}$$

The value of K is found from the graphical dependence of $\log(1/\mathrm{DP}_D - 1/\mathrm{DP}_0)$ on $\log D$ by extrapolating the straight line to $\log D = 0$. The value of m is equal to the tangent of the angle of slope of this line.

According to Eq. (1), when the radiation dose is measured in Gr, K will have the dimensions Gr^{-m}. Then the value of G_{d} can be determined from the equation

$$G_{\mathrm{d}} = \frac{K \cdot n_0 \cdot 100}{\mathrm{d} \cdot D}, \tag{3}$$

where n_0 is the number of anhydro-β-D-glucose units in 1 g of cellulose, which is equal to $N_{\mathrm{A}}/162$; Э is the energy equivalent of 1 Gr, $6.24 \cdot 10^{15}$ eV; and D is the radiation dose, 1 Gr. (Equations for calculating G_{d} are also given in [14-17]).

For the calculations, as the DP_0 and DP_D given in Eq. (1) we used $\overline{DP}_v$ in place of $\overline{DP}_n$, assuming that the difference in the values of $\overline{DP}_v$ and $\overline{DP}_n$ will not be reflected in the result of the determination of the value of G_d corresponding to the "direct" cleavage of a glycosidic bond.

Figure 1 shows the dependence of the change in DP and in $1/DP_D - 1/DP_0$ on D for cotton cellulose irradiated at 77 K and 300 K both with and without saturation by water vapor. We carried out the irradiation of cellulose at 77 K specially. As was noted above, no cleavage of the glycosidic bonds occurs as a result of the irradiation of cellulose at 77 K. The cleavage of a glycosidic bond is apparently due to a transformation of a primary radical with the unshared electron at $C_{(4)}$. In this case, the number of cleavages of glycosidic bonds should rise linearly with an increase in the radiation dose in correspondence with the linear rise in the concentration of radicals at 77 K. This means that the value of G_d for cellulose irradiated at 77 K should remain constant in the dose interval that we used. The results obtained confirmed this – over the whole radiation dose interval the value of G_d was constant at 1.4 (Table 1).

Taking into account the fact that the cleavage of glycosidic bonds in cellulose irradiated at 77 K is due to the transformation of the primary radicals taking place with a rise in the temperature, while the presence of 10% of water and more in cellulose irradiated at 77 K [7] shifts the region of intense destruction of the radicals from 323-423 K to 163 K, we considered it necessary to investigate the influence of water on the change in the DP of cellulose irradiated at 77 K. In this case, the equilibrium amount of water sorbed by the cellulose reached 20%.

It was established in early investigations that the presence of sorbed moisture in cellulose has no appreciable influence on the decrease in its DP when irradiation is performed at room temperature [18, p. 50]. As can be seen from Fig. 1, we obtained similar results at 77 K. Thus, regardless of the temperature of irradiation, water sorbed by cellulose in an amount of $\leq 20\%$ has no appreciable influence on the act of cleaving glycosidic bonds.

The dependence of the change in $1/DP_D - 1/DP_0$ on D at 77 K given in Fig. 1 (curve 1′) is represented by a straight line. Consequently, for this case, $m = 1$, and the value of K is determined by the angle of slope of this straight line, which is $2.4 \cdot 10^{-8}$. Calculation of G_d from formula (3) gives a value of 1.4.

The dependence of the change in $1/DP_D - 1/DP_0$ on D at 300 K is not linear (Fig. 1, curve 2′). It is rectified in the coordinates of Eq. (2). The values of K and m that we determined from the graphical dependence of $\log(1/DP_D - 1/DP_0)$ on $\log D$ are $13.8 \cdot 10^{-8}$ and 0.9, respectively. Then $G_d = 8.2$, but this figure is considerably overestimated.

In view of the fact that the absorbed radiation dose was previously measured in Mrad (1 Mrad = 10 kGr = 10^4 Gr), the condition $\log D = 0$ was fulfilled at $D = 1$ Mrad. It can be shown that the value of K is equal to the tangent of the angle of slope of a straight line passing through the origin of coordinates and the point on the curve of the dependence of $1/DP_D - 1/DP_0$ on D corresponding to unit radiation dose. Therefore, with a decrease in the radiation dose in the series 1 Mrad, 1 kGr, and 1 Gr we obtained the following values of K and G_d, respectively: $5.6 \cdot 10^{-8*}$ and 3.3; $7.0 \cdot 10^{-8}$ and 4.1; and $13.8 \cdot 10^{-8}$ and 8.2. We may note that no such changes in the values of K and G_d are observed for cellulose irradiated at 77 K. This follows from the linear dependence of the change in $1/DP_D - 1/DP_0$ on D at 77 K.

Thus, to compare the values of G_d at 300 K that we have obtained and those known from the literature, one must use a value for G_d of 3.3 and one must recognize the fact that at 300 K, according to our results, the actual value of G_d is 3.3, and not 4.1 or 8.2.

It is known that at low radiation doses (up to 10 kGr) many properties of irradiated cellulose do not correlate with the properties that it exhibits when it is irradiated with higher doses [2, 19, 20]. Researchers ascribe this situation to the fact that at low radiation doses, in addition to degradation, a process of cross-linking takes place in cellulose. Usually, therefore, the dependence of a particular index of irradiated cellulose on the radiation dose is determined at doses of the order of 10 kGr and above. Then an extrapolation of this relationship may be obtained for low radiation doses.

However, as already discussed, the dependence of the change in $1/DP_D - 1/DP_0$ on D constructed in such a way does not permit an unambiguous evaluation of G_d on passing from Mrad to G_d as units of dose measurement. Here the technique of determining the value of K is not convenient for us and, consequently, this index must be replaced by one that could be determined directly from experimental results. A prerequisite for this is the fact that the product $K \cdot n_0$ in Eq. (3) gives the number of glycosidic bond cleavages in 1 g of cellulose – n_d – and that there is a direct link between n_d and the change in the DP on irradiation.

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*All values of K have the same dimensions – Gr^{-m}. If their values are given in terms of the dimensions corresponding to each unit of radiation dose, they amount to $5.6 \cdot 10^{-4}$ $Mrad^{-m}$, $7.0 \cdot 10^{-5}$ kGr^{-m}, and $13.8 \cdot 10^{-8}$ Gr^{-m}.

TABLE 1. Results of Calculations of the Values of n_d and G_d for Cotton Cellulose with DP 2900 Irradiated at 77 and 300 K

T	$\overline{\mathrm{DP}}_\nu$	n	$n_{\mathrm{DP}}\cdot 10^{-18}$, g^{-1}	$n_d\cdot 10^{-18}$, g^{-1}	$D\cdot 10^{-3}$, Gr	G_d
77 K	2900	(1)	1.3	0	0	-
	1450	2	2.6	1.3	14	1.5
	970	3	3.9	2.6	29	1.4
	720	4	5.2	3.9	45	1.4
	580	5	6.5	5.2	60	1.4
	480	6	7.8	6.5	75	1.4
	410	7	9.1	7.8	90	1.4
300 K	1450	2	2.6	1.3	8	2.6
	970	3	3.9	2.6	17	2.5
	720	4	5.2	3.9	24	2.6
	580	5	6.5	5.2	29	2.9
	480	6	7.8	6.5	35	3.0
	410	7	9.1	7.8	41	3.1
	360	8	10.4	9.1	48	3.1
	320	9	11.7	10.4	55	3.0
	290	10	13.0	11.7	63	3.0
	260	11	14.3	13.0	71	2.9
	240	12	15.6	14.3	80	2.9
	220	13	16.9	15.6	89	2.9

As a result, we obtained the following equation for calculating G_d

$$G_d = A\cdot D^{-1}\cdot(\mathrm{DP}_0/\mathrm{DP}_D - 1). \tag{4}$$

where A is a proportionality factor, which, in our case, was $2.1\cdot 10^4$; and D is the absorbed radiation dose measured in Gr.

A feature of this equation is the fact that G_d does not depend on the units of measurement of the absorbed radiation dose, which affects only the value of A.

Below, we give the results of the calculations performed for the derivation of Eq. (4).

When $K\cdot n_0$ is replaced by n_d, Eq. (3) assumes the form

$$G_d = \frac{n_d \cdot 100}{\text{Э} \cdot D}. \tag{5}$$

To determine the value of n_d from experimental results, we started from the fact that with an n-fold fall in DP_0 ($n = \mathrm{DP}_0/\mathrm{DP}_D$) the number of fragments formed from the cellulose macromolecule is $n\cdot(n_{\mathrm{DP}})_0$, where $(n_{\mathrm{DP}})_0$ is the number of macromolecules with DP = 2900 contained in 1 g of cellulose, which amounts to $N_A/\mathrm{DP}_0\cdot 162 = 1.3\cdot 10^{18}$. The total number of fragments of the cellulose molecule formed is connected with the number of cleavages in the following way:

$$n\cdot(n_{\mathrm{DP}})_0 = n_d + (n_{\mathrm{DP}})_0 \text{ or } n_d = (n_{\mathrm{DP}})_0\cdot(n - 1).$$

Hence, replacing n by $\mathrm{DP}_0/\mathrm{DP}_D$, we obtain:

$$n_d = (n_{\mathrm{DP}})_0\cdot(\mathrm{DP}_0/\mathrm{DP}_D - 1). \tag{6}$$

Substituting this value in Eq. (5), we obtain:

$$G_d = \frac{100 \cdot (n_{\mathrm{DP}})_0}{\text{Э}} \cdot D^{-1} \cdot (\mathrm{DP}_0/\mathrm{DP}_D - 1). \tag{7}$$

Equation (7) is identical with Eq. (4), where $A = \frac{100 \cdot (n_{\mathrm{DP}})_0}{\text{Э}}$.

Table 1 gives the results of calculations of values of n_d and G_d from Eq. (6) and (7), respectively. To simplify the calculations, we chose integers as n. Figure 1 gives the values of the DP corresponding to $\mathrm{DP}_D = \mathrm{DP}_0/n$, which have been marked on the curve of the dependence of DP on D by lines perpendicular to the axis of abscissae.

As can be seen from Table 1, the value of G_d calculated from Eq. (3) for 77 K is identical with the value of G_d calculated from Eq. (7). This witnesses the validity of the use of Eq. (7) in place of (3) for calculating G_d.

Calculation of G_d from Eq. (7) for 300 K showed that, at an arbitrarily selected small radiation dose for which it is possible to determine DP_D from the experimental curve (where $1 < n < 2$), G_d amounts to 2.6. This figure is close to the value of G_d found when the radiation dose is measured in Mrad. The observed discrepancy may be due only to the fact that the experimental value of DP_D for a dose of 10 kGr does not lie on the curve of the dependence of the change in the DP on D, and this must be regarded as experimental error. This is also shown by the values of G_d obtained for higher radiation doses.

As a rule, at 300 K G_d has the highest value for the initial doses, and with a rise in the latter it decreases. From this point of view it must be considered that G_d for cellulose irradiated at 300 K is 3.3. In just that case will it be possible to explain the decrease in G_d to 2.9 at radiation doses of 80-90 kGr.

The constancy of G_d at 77 K and its decrease at 300 K with a rise in the radiation dose follows from the mechanism of the cleavage of the glycosidic bonds: under the action of radiation no cleavages take place directly at 77 K, in view of which the number of cleavages determined after the sample has been brought to room temperature is proportional to the concentration of radicals found at 77 K*; at 300 K, cleavage of the glycosidic bonds begins from the moment of irradiation, and with a rise in the number of cleavages the probability of the localization of a radical in the middle of the chain, favoring continuation of the process, decreases somewhat.

It is known that at the most probable molecular mass distribution $\overline{DP}_n \sim \overline{DP}_v /2$ [17]. In such circumstances, for cellulose irradiated at 77 K and 300 K the value of G_d should be twice as great, i.e., 2.8 and 6.6, respectively, in place of the 1.4 and 3.3 that we found on the assumption that $\overline{DP}_v = \overline{DP}_n$. But, according to the literature, in irradiated cellulose, as well as the cleavage of glycosidic bonds there is also an accumulation in the main chain of the molecule of bonds that are sensitive to an alkaline medium and are readily cleaved, for example, when the irradiated cellulose is dissolved in cadoxene. While, as is shown in [14], the yield of cleavages is 3.0, the yield of bonds sensitive to alkaline media is 3.0-4.0. Consequently, on determining G_d from viscometric measurements the result obtained will be overestimated approximately 2-fold. It follows from what has been said that the values of G_d of 1.4 for 77 K and 3.3 for 300 K are closest to the values of G_d corresponding to the "direct" cleavage of cleavage of glycosidic bonds in irradiated cellulose. This opinion is also confirmed by the results of investigations [14-16] in which a value for G_d of 2.9 ± 0.1 was obtained from the results of measurements of $\overline{DP}_n$ for cellulose preparations irradiated at 300 K.

Thus, the cleavage of glycosidic bonds between the anhydro-*β*-*D*-glucose units of the cellulose macromolecule takes place as a result of the transformation of primary radicals with the unshared electron at $C_{(4)}$. At 300 K, but not at 77 K, the radiation-chemical yield of the degradation of cellulose reveals a dependence on the radiation dose that is explained by the mechanism of the cleavage of glycosidic bonds in irradiated cellulose.

EXPERIMENTAL

Cellulose obtained from cotton fiber of variety 108-F with an initial degree of polymerization of 2900 was investigated. Irradiation was conducted at 77 and 300 K with a Co^{60} γ-source at a dose rate of 5 Gr/sec. The viscosity-mean degree of polymerization $\overline{DP}_v$ of the samples was determined from the characteristic viscosities of solutions of the cellulose in cadoxene in accordance with the Mark-Houwink equation and published figures [21].

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*The dependence of the concentration of radicals on the radiation dose at 77 K is linear.

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