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The Radiation Chemistry of Cellulose

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The radiation-chemical transformations of cellulose and the influence of various factors on the efficiency of these processes have been examined. Ionising radiation has a significant influence on the structural-morphological state of the polymer; the nature of the primary radical-ion radiolysis products has been discussed, and a quantitative description of the radiation degradation of cellulose has been given. The mechanism of the radiation-chemical transformations of cellulose, which provide a promising method for treating cellulose-containing raw material for the production of valuable products, has been discussed. The bibliography contains 131 references.

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I. INTRODUCTION

Cellulose is one of the most widely encountered natural polymers, being the principal component of plant materials. The study of the radiation chemistry of this compound is therefore of considerable theoretical and practical importance. The use of penetrating ionising radiation can radically alter the technology of the treatment of plant raw material, since it facilitates considerably the conversion of the carbohydrate complex into the soluble state or increases its sensitivity to other methods of treatment, such as enzyme hydrolysis.

The use of radiation with a high penetrating power (γ-rays, X-rays, accelerated electrons) makes it possible to bring about chemical transformations in the bulk of the substance, and this, in particular, has found extensive practical application as a method for modifying polymers.[1-5] Not all the reactions taking place when a substance is irradiated are specific for radiation chemistry. Many of them also apparently take place under the influence of light, an electric discharge, cavitation processes, etc. Thus the study of the radiation-chemical reactions is also important for establishing the mechanism of the chemical reactions taking place after initiation by other methods.

Considerable attention has been and is being paid to the problem of the influence of penetrating ionising radiation on cellulose and cellulose-containing materials. This is due to a number of factors, among which the following are of primary importance. The physical and chemical properties of cellulose fibres can be changed in a directed fashion by the radiation grafting of various polymers on to them.[6,7] Penetrating radiation achieves effective sterilisation of cellulose-containing materials for medical purposes, and the conservation of good and animal feedstuffs.[8-10] Irradiation is used to accelerate and optimise the processes involved in the thermochemical and enzyme treatment of wood,[11-17] cellulose,[18-20] and cellulose-containing waste products,[21-23] to modify the physicomechanical properties of wood and to create new materials based on it,[24-26] to intensify the production of yeast[27-31] and cellulose paper production.[32-35] Finally, ionising radiation may find application in the technology of the treatment of non-edible plant materials (chiefly the waste products from the wood processing industry and agriculture) to obtain animal feedstuffs and food products.[21,36-38]

A systematic analysis of data on the radiation chemistry of cellulose was last carried out in the 1970's.[39] The present review summarises the experimental data obtained in recent years, discusses the influence of radiation on the properties of cellulose, and examines the main trends in radiation-chemical transformations of this important natural polymer. Since the final products of the radiation-chemical transformations of cellulose have not been studied in detail, because of the fundamental difficulties involved in the chemical analysis of the long polymer fragments, the possible mechanisms of the transformations will be discussed using available data on the radiolysis of various simple carbohydrates and oligosaccharides, which can (in a certain sense) be regarded as model compounds of cellulose.

II. INFLUENCE OF IRRADIATION ON THE STRUCTURE OF CELLULOSE

Each monomeric unit in cellulose has three hydroxyl groups, which form intra- and intermolecular hydrogen bonds. The presence of the branched system of hydrogen bonds determines to a considerable extent the physicochemical and mechanical properties of the polymer.

Cellulose is one of the polymers whose crystallographic characteristics have been studied most intensively for several decades. Nevertheless, there is still lack of agreement about the phase compositions of cellulose. As early as the 1930's, Kargin[40] suggested that the amorphous state of cellulose is thermodynamically stable and the only state possible. Later, he drew attention to the main indications confirming this viewpoint.[41] At the present time, however, the more generally accepted approach regards cellulose as a material with a crystalline structure containing quantities of an amorphous phase. Different models of the crystallographic lattices of cellulose and theories of the crystallinity of this polymer exist. In particular, four structural forms of cellulose have been established, of which the natural material is described as cellulose I.

The structural state of cellulose has been described in detail.[42-44] It is suggested that cellulose consists of small crystallites, made up of microfibrils, which are surrounded by regions of amorphous and polycrystalline phases.[45,46]

The dimensions and orientation of the crystallites and the ratio of the phases are determined by the nature of the previous treatment of the materials. The length of the polymer chains is appreciably greater than the size of the crystallities, so that the macromolecules are present in alternating regions with crystalline and amorphous structures.

The complex amorphous–crystalline system can be characterised by the degree of crystallinity and the degree of orientation. The crystalline phase is more closely packed, so that the rates of hydrolytic splitting differ considerably for these phases. Different methods for determining the degree of crystallinity of cellulose generally give different results. This is because the methods used make it possible to study different aspects and manifestations of the structural state. For example, X-ray diffraction characterises the degree of order of the polymer, whereas methods involving chemical reaction determine the accessibility of the different regions to the reactions, that is they characterise its structure only qualitatively. Nevertheless, it is assumed[42–46] that cotton cellulose contains ~65–75% crystalline fraction and ~25–35% amorphous fraction.

The different manifestation of structurally sensitive properties in different regions of cellulose, however, is not sufficient to enable them to be characterised as amorphous or crystalline phases. It is apparently more correct to say that cellulose contains regions with different ratios of intra- and intermolecular ordering.[47] From this viewpoint, cellulose is regarded as a single-phase system, in which, if an amorphous phase is present, its concentration does not exceed ~5%.[48–50] According to this hypothesis, cellulose contains imperfect regions, and its structure can be regarded as "liquid-crystalline" or "paracrystalline".[48–50] The indeterminacy of the interpretation of the structural state of the original cellulose makes it difficult to explain the data obtained after it has been exposed to ionising radiation.

The structure and intensity of the infrared spectra of cellulose is preserved after its irrdiation up to an absorbed dose of ~100 kGrad,[51] from which is was concluded that its structure is preserved under these conditions. X-Ray diffraction has shown that the phase state of cellulose[52,53] and cotton lint[54] remains unchanged at much higher doses.

Infrared (IR) spectroscopy is most convenient for the study of the structure of cellulose if the phase changes are not accompanied by a significant change in the chemical state. On irradiation, however, the process with the greatest influence on the IR spectra is the chemical transformation of cellulose, that is the formation of carbonyl and carboxyl groups, dehydrogenation, and dehydration. In the study of the influence of radiation on the structure of cellulose, the strong band in the range 3600–3000 cm^{-1}, due to OH group stretches, is of particular interest. It can be used to characterise the redistribution of OH groups with respect to hydrogen bond strengths. With interest in the absorbed dose, the maximum of the band due to the OH groups in the infrared spectrum of cellulose is displaced from 3400 cm^{-1} to 3440 cm^{-1}, accompanied by a change in the shape of the band.[53] Table 1 gives the values of ν_{OH}, and also the symmetry index of the band a/b, that is the ratio of the right-hand and left-hand parts of the half-width of the band due to the OH groups. The observed changes show that irradiation leads to breakdown of the ordered system of intermolecular hydrogen bonds, as a result of which the hydroxyl groups are involved in less stable hydrogen bonds.[55] The distribution of OH groups with respect to bond strengths becomes statistically less uniform (the value of a/b changes from 0.72 to 0.58). The irradiation of cellulose leads to the production of carbonyl and carboxyl groups. The intensity of the corresponding bands in the infrared spectra (bands at 1740 cm^{-1} for CO and at 3400 cm^{-1} for COOH) increases with increase in the absorbed dose, and the change in their ratio (D_{1740}/D_{3400}) indicates the preferential formation of carbonyl groups (Table 1).

The changes in the structure of cellulose brought about by the action of γ-radiation have been characterised not only by IR spectroscopy but also by X-ray diffraction.[52,53] Up to absorbed doses of 480–1180 kGrad, the structure of cellulose remains practically unchanged[52] (since the values of the crystallinity indices, determined by the published method,[56] remain unchanged). At absorbed doses greater than 2000 kGrad, the crystallinity index decreases considerably (Table 2), and at a dose of 9400 kGrad, X-ray diffraction indicates that cellulose can be characterised as having an amorphous structure.

Table 1. Changes in the infrared spectra of cotton cellulose γ-irradiated in a vacuum.[53]

Dose, kGrad	ν, cm^{-1}	a/b	D_{1740}/D_{3400}
0	3400	0.72	0
480	3410	0.67	0.4
2560	3420	0.65	1.1
9400	3440	0.58	3.7

Table 2. Physicochemical properties of γ-irradiated cotton cellulose.[53]

Dose, kGrad	β, %	$\overline{DP}_\nu$	c_s, %	$\overline{DP}'_\nu$	β′, %
0	73	911	10.3	205	78
5	73	575	10.9	189	78
10	73	505	11.3	159	78
32	73	269	11.9	139	78
170	73	94	17.0	80	78
480	73	49	21.2	48	76
680	—	40	22.0	28	73
800	—	32	27.8	10	72
1680	69	14	43.7	5	68
2560	63	8–9	100	—	—
9400	0	4–5	100	—	—

Notes: β is the crystallinity index of the original cellulose, $\overline{DP}_\nu$ its viscosity-average degree of polymerisation, c_s the quantity of soluble fraction in the ethanolysis of the cellulose (% of the mass of the original specimen), $\overline{DP}'_\nu$ the viscosity-average degree of polymerisation of the insoluble residue, and β′ its crystallinity index.

γ-Irradiation leads to the degradation of cellulose, revealed by a decrease in its degree of polymerisation. The changes in the degree of polymerisation of cellulose and in its solubility take place much more effectively (see Table 2) than the changes in the structure observed on the X-ray diffraction patterns. This apparently represents a situation where the method for the experimental determination of the degree of ordering of a substance in practice makes it possible to estimate only a certain particular characteristic. Thus X-ray diffraction indicates the existence of a highly ordered structure in cellulose up to high absorbed doses. At the same time, chemical methods for the analysis of the structure of cellulose, which to a large extent characterise the accessibility of the different parts of its molecule with respect to the reactions and breakdown of the system of intermolecular hydrogen bonds, indicate that γ-irradiation leads to the production of disordered defect regions. There is no contradiction here, however. X-Ray diffraction shows that

in the dose range studied, the structure of the primary crystals and the overall degree of crystallinity of cellulose remain unchanged. The increase in the ability of γ-irradiated cellulose to dissolve, however, is related to an appreciable decrease in its degree of polymerisation, and also to the formation of active chemical groups, i.e. carbonyl and carboxyl groups, which facilitate the conversion of the macromolecules to the dissolved state. Thus when irradiated cellulose is brought into contact with water, the products transferred preferentially to the solution are those containing acidic and aldehydic groups, and the total extractability increases with increase in the absorbed dose.[57]

The change in the degree of order of the cellulose structure on irradiation has been characterised by IR spectroscopy.[58] The parameter of the degree of ordering (φ) (the term "index of paracrystalline regularity" is used in the work cited) was the ratio of the intensities of the bands at 1370 cm^{-1} and 890 cm^{-1}. The parameter φ decreases almost exponentially with increase in the absorbed dose, and for a dose of ~2400 kGrad it decreases by a factor of *e*. Infrared spectroscopy apparently determines the degree of ordering of the largest macromolecules of cellulose, and it shows a closer correlation, compared with X-ray diffraction, with chemical methods for estimating its structural state. The observed character of the decrease in the degree of ordering of the cellulose structure with increase in the absorbed dose agrees with the decrease in its degree of crystallinity determined in Ref.59.

In the γ-irradiation of cotton fibres, even at an absorbed dose of ~10 kGrad, scanning electron microscopy detects unambiguously the breakdown of their morphologicaly structure.[58] Cracks lying parallel to the twisting axis of the fibre appear, and show a significant increase in their length and depth with increase in the absorbed dose. This process is apparently due to the rupture of intermolecular bonds in the fibrils and to a decrease in the strength of the surface interactions between them. Various problems of the morphology on irradiated cellulose materials were examined in Ref.34. The physicochemical processes taking place when cotton fibres are exposed to radiation lead to an appreciable decrease in their mechanical strength.[58,59]

Thus the action of ionising radiation leads to a decrease in the intra- and intermolecular ordering in cellulose, due to the breakdown of the system of intermolecular hydrogen bonds and to chemical transformations of the polymer.

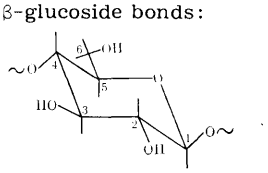
III. RADICAL RADIOLYSIS PRODUCTS OF CELLULOSE

The radicals produced by the radiolysis of cellulose have been studied many times by EPR.[39,60,70] In spite of this, there was lack of agreement on their nature until recently. This was due to the fact that the studies were carried out under different conditions (temperature of irradiation, moisture content of the cellulose, absorbed doses etc.), and in the interpretation of the EPR spectra, no allowance was made for the actual conformation of the monomeric fragment of the polymer. As a result, the EPR spectrum of γ-irradiated cellulose was examined in different studies as, for example, consisting of a triplet and a quintet[39] or a quadruplet and a singlet.[69]

The radicals in γ-irradiated cellulose, and the kinetics of their accumulation and thermal transformations, have been studied.[71,74] Natural cotton cellulose, purified and dried for a long time at 313 K (in the presence of P_2O_5) and at 378 K, and also moist cellulose, containing two water weight fractions, were used. Cellulose hydrate (technical cellophane) and holocellulose were also studied. The most interesting data were obtained on the radicals obtained by irradiating cellulose at a low temperature (77 K). It may be assumed that under these conditions the species stabilised are the primary radical–ion products, whose subsequent chemical transformations determine the entire range of changes in the physicochemical state of cellulose. Specimens of natural and regenerated cellulose irradiated at 77 K acquire a bluish colour,[71,72] typically observed when electrons are captured by intermolecular traps in polar substances.[73–75] The colour disappears rapidly under the influence of visible light or when the specimen is heated to ~173 K. The changes which then take place in the EPR spectrum indicate the disappearance of the narrow singlet, due to the captured electron, with a *g* value equal to that for the free electron. The optical absorption maximum for the captured electron (e_{capt}) in cellulose hydrate lies at 540 ± 20 nm, and the half-width of the absorption band is 1.3 1 0.1 eV, which are close to the characteristics of the optical spectra of e_{capt} in vitreous polyhydric alcohols[75–78] and concentrated aqueous solutions of carbohydrates.[79,80] In this case, the stabilisation apparently takes place in the water micro-phase in cellulose with a vitreous structure, and also in the amorphous regions of cellulose in the electrostatic field of the oriented OH groups. The yield of this species is much lower than that of the other radicals.

The EPR spectra of natural cellulose and cellulose hydrate are practically identical, and (in addition to the e_{capt} signal) consist of the superposition of a triplet (component ratio close to 1 : 2 : 1), splitting between the components 2.6 ± 0.1 mT), a doublet (splitting 3.0 ± 0.2 mT), and a singlet with a low intensity.

The cellulose macromolecule includes *D*-glucose repeat units, joined by 1,4-β-glucoside bonds:



The three-dimensional structure of the *D*-glucose unit in the macromolecule is characterised by a pyranose ring with axially arranged hydrogen atoms. An analysis of the splitting constants indicates that the signals with the doublet and triplet HFS are due to radicals with a pyranose ring, formed as a result of the rupture of the C–H bonds in positions 1, 2, 3, or 4. This follows from the fact that the spectrum does not show the signals with splitting constants 1.7–1.9 mT, characteristic of radicals with α-protons.[81–83] Splitting values of 2.5–3.0 mT are characteristic of carbohydrate radicals with axial β-protons.[84–87] As a result of the removal of the hydrogen, the hybridisation of the carbon atom changes from sp^3 to sp^2, and the unpaired electron is transferred to the $2p_z$ orbital; in this position, it interacts effectively with the axial β-hydrogen atoms. The doublet signal must be due to the radical formed by the rupture of the C–H bond in position 1. In principle, the triplet signal may be due to any of the radicals produced as a result of the rupture of a C–H bond in positions 2, 3, or 4; it may also represent the superposition of EPR signals from three radicals produced in this way, differing little from one another. The most probable position for the localisation of the excitation energy, however, is the C(4) atom. This conclusion agrees with the fact that the C–H bonds broken are those in positions 1 and 4, which are weakened to the greatest extent as a result of the withdrawal of the electrons to the 1,4-β-glucoside bonds and the ring oxygen atom. A similar interpretation was proposed for the EPR spectra obtained in the sensitised photolysis[88] and radiolysis[89] of cellulose.

The appearance of the singlet signal can apparently be related to the presence of residual lignin in the cellulose. Thus the intensity of this signal is much greater in the EPR spectra of holocellulose and wood γ-irradiated at 77 K.[71] Unlike cellulose, these materials contain considerable quantities of lignin (particularly wood). Lignin γ-irradiated at 77 K gives a narrow symmetrical singlet with line width 1.0 ± 0.1 mT, which coincides with that observed for cellulose and wood.[72] This may indicate that the singlet signal in the spectrum of irradiated cellulose is due to a radical of the "lignin" type. The yields of the radicals, calculated for a linear accumulation section (G), are 3.4 radicals and 1.6 radicals per 100 eV for the γ-irradiation of specimens at 77 K and 300 K respectively.[71] The kinetics of the accumulation of the radicals is described effectively by the equation:

$$[R] = [R]_{lim}(1 - e^{-K_d D})$$

where the limiting concentration of the radicals $[R]_{lim} = G/K_d$ (K_d is the constant for the radiation disappearance of the radicals), and the absorbed dose $D = It$ (I is the dose power, and t the irradiation time). The values $K_d = 7.7 \times 10^{-3}$ kGrad^{-1}, calculated from this equation using published data,[71] are the same, within experimental error, for γ-irradiation at 77 K and 300 K, apparently indicating that the mechanisms of the annihilation of the radicals by radiation at these temperatures are the same. This value of K_d is characteristic of compounds with saturated bonds,[90] and indicates that there is no effective migration of the excitation in cellulose.

Thus when cellulose is exposed to ionising radiation, some of the "ejected" electrons, after thermalisation, are stabilised in intermolecular traps. Because of the "crystal-like" character of the structure of cellulose, however, the concentration of these traps is apparently insufficient to suppress effectively the recombination of the "electron-hole" ion pairs, bound to Coulombic interaction. The excitations produced as a result of the recombination are localised, leading to the rupture of the C–H bonds in the weakened positions 1 and 4 [$R_{C(1)}$ and $R_{C(4)}$ radicals respectively are formed]:

$$(RH)^* \rightarrow \dot{R} + H\ .$$

The hydrogen atoms dehydrogenate the elementary monomeric units of cellulose, again in positions 1 and 4. Another important fact is noteworthy. In very moist cellulose, γ-irradiated at 77 K, OH radicals are stabilised, and with increase in temperature these disappear, removing preferentially the hydrogen atoms in positions 1 and 4 of the carbohydrate fragment.[71,72] Thus the point of attack by the radical coincides with the point of rupture of the C–H bonds in the direct action of radiation on cellulose:

$$RH + H(OH) \rightarrow R_{C(1)}\,(R_{C(4)}) + H_2(H_2O).$$

The large amount of information on the EPR study of cellulose γ-irradiated at room temperature is fairly contradictory. Thus it has been reported[65] that the spectrum consists of the superposition of a singlet and a triplet. In Refs. 63, 64, and 67 it is reported that the EPR spectra of dried cellulose I and II after γ-irradiation are extremely similar, and consist of poorly resolved triplets. The EPR spectra produced when the dry specimens are brought into contact with water, and the spectra of specimens containing residual moisture, consist of three components for cellulose I, and five lines for cellulose II. An EPR spectrum containing five components was recorded in Ref.60. Under certain conditions, preliminary treatment of cellulose in the absence of oxygen gives signals with a doublet structure.[67,68]

The present authors[71,72] established that the EPR spectra of very moist cotton cellulose and cellulose hydrate, γ-irradiated at 77 K and then heated to 300 K, and also specimens γ-irradiated directly at 300 K, are practically identical and consist of a triplet with splitting between the components ~2.8 mT. When the specimens are subsequently heated, the total concentration of radicals decreases, the structure of the EPR spectrum changes, and there are grounds for assuming that it consists of the superposition of the EPR signals from several radicals (singlet, doublet, and triplet). At 330 K, a doublet signal with a splitting less than 1.5 mT predominates in the EPR spectrum.

These differences in the structures of the EPR spectra observed in cellulose γ-irradiated at room temperature are apparently due to the appreciable influence of the structure of the cellulose, its moisture content, and other factors, which are not taken into account in the preparation of the cellulose specimens and which influence the thermal stability of the radicals. As a result, at a given temperature (room temperature), radicals of several types, but with different concentration ratios, are stabilised in different specimens, leading to appreciable differences in the form of the EPR spectra.

Thus a study of the thermal stability of cellulose macroradicals[39,61–64,69,89] showed an appreciable increase in the rate of their disappearance or transformation in the presence of water, aqueous solutions of acids and alkalis, ammonia, etc. In thoroughly dried cellulose, the temperature of the intensive disappearance, corresponding to a decrease in the original concentration of radicals by a factor of two, corresponds to ~370 K, whereas in the presence of 2, 7, 11, and 24 mass % water it is displaced to 310, 260, and 210 K respectively.[89] This effect is attributed to the plasticising action of water on cellulose, leading to an increase in the molecular mobility in the polymer. The disappearance of the radicals is then limited by the mobility of the macrochains in the cellulose, and the actual nature of the radicals apparently has no significant influence on the rate of their disappearance. The thermal stability of ~15% of the macroradicals is independent of the water concentration, apparently because they are localised in crystalline regions which are not accessible to water.[89]

The disappearance of the macroradicals is characterised by a kinetic arrest; thus when a certain temperature is reached, the concentration of the particles, for a limited observation time, can be regarded as "stationary". Thus the disappearance of the radicals takes place as it were "in stages". The polychromatic kinetics are due to the physical non-uniformity of the polymer matrix, as a result of which a number of chemically identical processes with different values of the rate constants of the limiting stages take place, that is there is a distribution of the rate constants with respect to activation energies (from E_{min} to E_{max}). Analysis of the results established[89] that for dried cellulose, the pre-exponential factor in the Arrhenius equation is ~10^{-5} cm^3 s^{-1}, E_{min} = 96 ± 8 kJ mole^{-1}, and E_{max} = 155 ± 12 kJ mole^{-1}. For specimens containing ~50% water, the pre-exponential factor decreases to ~10^{-13} cm^3 s^{-1}, and E_{min} and E_{max} have the values 29 ± 2 kJ mole^{-1} and 46 ± 2 kJ mole^{-1} respectively.[89] A noteworthy feature is that in cellulose there may be a compensation effect, involving a decrease in the activation energy of the process with increase in temperature.[91] This feature leads to a decrease in the observed values of the activation energies for the disappearance of the radicals.

When cellulose is plasticised by water, the diffusion mobility of the macro-radicals increases by several orders of magnitude. The elementary act of their diffusion apparently involves the movement of the pyranose unit, in which the

radical state is localised, relative to the other units of the polymer. In dry cellulose, each unit is joined to its neighbours by three hydrogen bonds, but when water is introduced, these bonds are broken, leading to a decrease in the strength of the bonding to the polymer macromolecules. This is responsible for the plasticising action of water or other low-molecular substances on cellulose.

The results of the experimental study of the EPR spectrum show that no appreciable rupture of C–OH, C–C, or C–O–C bonds takes place when cellulose is γ-irradiated. The secondary reactions of the radicals obtained by the rupture of the C–H bonds in positions 1 and 4 lead to the rupture or breakdown of the molecular structure of cellulose.

IV. RADIATION-CHEMICAL DEGRADATION OF CELLULOSE

When polymers are irradiated, two opposed processes take place: cross-linking of the polymer chains, leading to an increase in the average molecular mass $\overline{M}$, and also their degradation, leading to a decrease in the value of $\overline{M}$.[1–5] These processes most frequently take place simultaneously, and polymers may undergo cross-linking or degradation, depending on which process predominates. Cellulose undoubtedly belongs to the second group; degradation is the main result of the action of ionising radiation on cellulose.[7,11,17,19,51,53,92–103]

1. Degradation of the Polymer According to a Random Law

Since the radiation-chemical processes involved in the rupture and cross-linking of polymer chains take place according to a random law, the changes in the molecular mass distributions of the macromolecules are described using statistical methods. The regular statistical features of the processes of cross-linking and degradation, taking place under the influence of ionising radiation, have been discussed in detail.[1,3,5] If the original polymer has a distribution with respect to degrees of polymerisation close to the most probable distribution, the degree of polymerisation will decrease during disordered degradation, but at the same time the most probable distribution will be preserved. For this case, the following equation is applicable:

$$\overline{DP}_n/\overline{DP}_n^0 = \overline{DP}_w/\overline{DP}_w^0 = 1/(1+s) \qquad (1)$$

where $\overline{DP}_n$ and $\overline{DP}_w$ are the number-average and weight-average degrees of polymerisation, $\overline{DP}_n^0$ and $\overline{DP}_w^0$ the corresponding original degrees of polymerisation, and s the number of ruptures taking place in the original polymer molecule. For the most probable distribution, $\overline{DP}_w = 2\overline{DP}_n$.

A system with a broader original distribution of the polymer with respect to degrees of polymerisation, compared with the most probable distribution, shows a slight deviation from relationship (1). It should be emphasised, however, that the most probable distribution in real situations is reached in the initial range of absorbed doses, used for the analysis of the dependence of the degree of polymerisation on the number of ruptures, that is on the absorbed dose, according to Eqn. (1). The number of bond ruptures s for a molecule with a degree of polymerisation $\overline{DP}_n$ is given by the equation

$$s = \frac{D\,\overline{DP}_n^0 m}{N_A E_d} \qquad (2)$$

where m is the molecular mass of the unit fragment of the polymer, and E_d is the energy required for the rupture of one bond. Eqn.(1) can be transformed as follows:

$$\frac{1}{\overline{DP}_n} - \frac{1}{\overline{DP}_n^0} = \frac{G^0 m D}{N_A} \qquad (3)$$

Here, G^0 is the initial radiation-chemical yield of the process of polymer degradation, that is the number of macromolecule ruptures corresponding to 100 eV of absorbed energy.

The molecular masses of polymers (M) or their degrees of polymerisation are determined by measuring the viscosity of their dilute solutions. For an unbranched polymer (in particular cellulose[104,105]), the following empirical relationship is applicable:

$$[\eta] = KM_v^\alpha \qquad (4)$$

where K and α are the parameters which depend on the chemical structure of the polymer, temperature, and the solvent used, and $[\eta]$ the characteristic viscosity. Depending on the configuration of the polymer macromolecule in the solution and the nature of the bonds formed with the solvent, the values of α vary in the range 0.6–1.0, corresponding to changes of only 1.82–2.0 in the expression in braces in Eqn.(5).[3] The value of M_v is related to the number-average molecular weight M_n by the expression

$$M_v = M_n\{(\alpha+1)\Gamma(\alpha+1)\}^{1/\alpha} \qquad (5)$$

where $\Gamma(\alpha+1)$ is the γ-function of α.

Thus the experimentally determined value of M_v and Eqns. (3) and (5) can be used to determine the yield of the degradation of the polymer G.

2. The Radiation Degradation of Cellulose

The first systematic study of the degradation of cellulose under the influence of a beam of accelerated electrons with an energy of 0.8 meV (for sulphite cellulose and cotton linter) was described in Ref.11. The degree of polymerisation was determined from the characteristic viscosity of the irradiated specimens in solutions of the complex of copper(II) with ethylenediamine. A regular decrease in the viscosity, which was practically the same for the specimens indicated, was established, that is the degree of polymerisation decreased with increase in the absorbed dose.

Since the determination of $\overline{DP}_v$ in Ref.11 was inaccurate, because of the absence of a reliable relationship between η and M in Eqn.(4), another method of calculation was proposed,[92] which did not use any direct relationship between η and M. This gave the following final expression relating η and the absorbed dose d:[92]

$$\eta = A(D+D_0)^\alpha \qquad (6)$$

where D_0 is the absorbed dose corresponding to the attainment of the most probable distribution of the polymer with respect to molecular masses, α the coefficient in Eqn.(4), and A a constant determined from the experimental dependence of η on $D + D_0$ in accordance with Eqn.(6). Treatment of the data from Ref.11 showed[92] that $\alpha = 0.71$ and $A = 4.9$. The value of K in Eqn.(4) was then taken as 5.9×10^{-4}, which gave a value of 10 for the cellulose degradation yield†.

The approach proposed in Ref.92 has the same disadvantages [the approximate determination of the parameter D_0 (7.5 kGrad and 10 kGrad for sulphite cellulose and cotton linter respectively) in Eqn.(6), and the arbitrary choice of the value of K in Eqn.(4)]; moreover, the treatment in Ref.92 was based on the fundamentally unjustified assumption that the yield of the cellulose degradation process remains constant and independent of the absorbed dose. In Ref.92 it was pointed out that the determination of the degradation

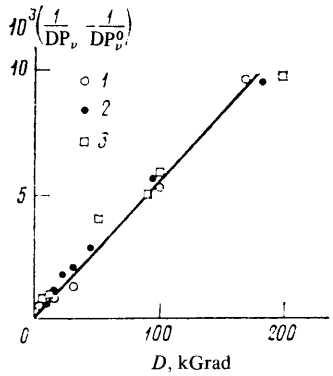
† According to Ref.58, the calculation of the yield in Ref.92 is erroneous, and the corrected value is only half the published value, that is 5.

yield has a low accuracy, because of a number of listed approximations in the calculation procedure.[3]

Later work[58] also used the approach proposed in Ref.92 and established that for cotton cellulose, $A = 4.0$, $\alpha = 0.78$, and $D_0 = 5$ kGrad. Taking from Ref.104 the value 1.71×10^{-4},[104] the value obtained[58] for the cellulose degradation yield was 4.5 ± 0.3.

There is apparently more justification for estimating the cellulose degradation yield using Eqns.(3) and (5), which are obtained from a statistical examination of the processes taking place. The degree of polymerisation in this case is determined from Eqn.(3), which relates it to the viscosity characteristics of the polymer solution. A solution of cellulose in Cd-oxene (a solution of the ethylenediamine complex of cadmium) is the most suitable for the measurement of the viscosity characteristics; this method has been widely used in recent years. According to Ref.105, the values of α and K in Eqn.(4) for this system are 0.94 and 7.1×10^{-3} respectively.

The dependence of $\overline{DP}_v$ for cellulose on the absorbed dose, constructed on the coordinates of Eqn.(3) (using data from Refs.53, 102, and 106), is shown in the Figure. It can be seen that Eqn.(3) is satisfied up to an absorbed dose of ~200 kGrad. In Ref.102, the characteristic viscosity was measured in a solution of the ethylenediamine complex of copper; the values of K and α were taken as 1.33×10^{-4} and 0.905 respectively.[107] In Refs.53 and 106, the characteristic viscosity was measured in Cd-oxene solutions. Since for the values of α used in the works cited[53,102,106] the number-average and viscosity-average degrees of polymerisation are related by the expression $\overline{DP}_v = (1.90–1.96)\overline{DP}_n$,[3] the radiation cellulose degradation yield, determined from the data given in the Figure, is 7.2 ± 0.2. The applicability of Eqn. (3) indicates that the radiation degradation of cellulose does in fact take place according to a random law.



Plot of $1/\overline{DP}_v - 1/\overline{DP}^0_v$ against the absorbed dose (*1*—Ref.53, *2*—Ref.102, *3*—Ref.106).

Eqns.(1) and (3) are applicable for the most probable distribution of the molecular weights of the polymer. For real specimens, which have a broad original degree of polymerisation distribution, some deviation from the linear relationship between $(\overline{DP}_v)^{-1}$ and the absorbed dose can be expected in the initial stages of the irradiation, as far as a certain dose D_0 corresponding to the attainment of the most probable distribution. It can be seen from the Figure, however, that if this deviation does take place for the data being considered at doses up to ~30 kGrad, it is very slight. At absorbed doses ≥ 200 kGrad, deviations from Eqn.(3) are observed, and the experimental data up to fairly large doses (~1000 kGrad) can be described effectively by the following empirical relationship

$$1/\overline{DP}_n - 1/\overline{DP}^0_n = KD^m \ . \qquad (7)$$

According to Refs.53 and 102, the value of m in Eqn.(7) is 0.83; Ref.98 gives the value 0.73 (the dose D is expressed in kGrad).

The deviation of the experimental data at high absorbed doses from the relationship (3) predicted on the basis of simple statistical considerations is apparently due to the fact that irradiation is accompanied not simply by depolymerisation of the cellulose, and the rupture of the bonds in the macromolecules is accompanied by the formation and accumulation of radicals which are stable at room temperature, and also new functional groups. The latter are apparently formed at the points where the cellulose polymer chains are ruptured. The presence of these polar groups influences, firstly, the values of the effective characteristic viscosity of the solutions of the irradiated cellulose, used to determine the average molecular mass. Secondly, the C=O groups, like the free radicals, act as effective acceptors of electrons and excited states, formed during the irradiation of various substances. Thus their accumulation during radiolysis leads to a decrease in the rate of the subsequent degradation of the cellulose. This is indicated by the results of a study[57] which established a significant decrease in the rate of the degradation of cellulose specimens containing carboxyl groups (monocarboxycellulose).

The radiation degradation of cellulose is accompanied by a decrease in the width of the molecular mass distribution, and with increase in the absorbed dose, a monodisperse distribution is approached. A decrease in the polydisperse character of technical celluloses at high absorbed doses (500–1000 kGrad) has been noted.[70,108] It has also been established[109] that a change in the molecular mass distribution of cellulose takes place even at low doses. Thus the non-uniformity coefficient decreases from 1.3 for the original cellulose to ~0.4 for irradiated cellulose (for an absorbed dose of 3.2 kGrad). A similar picture is observed for the radiolysis of native dextran, consisting of D-glucose units, joined by a 1,6-glucoside bond.[110] The ratio of the average molecular masses $M_z : M_w : M_n$ is 3.5 : 2.0 : 2.0, whereas for the degradation of the macromolecules according to a randam law, this ratio should have been 3 : 2 : 1.[1,3] This difference is apparently due to the characteristic features of the molecular mass distribution on fractionation, where no account is taken of the final values of the molecular masses and their distribution in the separate factors.

V. CHEMICAL TRANSFORMATIONS IN IRRADIATED CELLULOSE

1. Gas Liberation During the Irradiation of Cellulose

The action of ionising radiation leads to extensive chemical transformations in cellulose. When cellulose is irradiated, gaseous products are liberated: hydrogen, carbon monoxide, carbon dioxide[39,51,111] and small quantities of methane.[111] In the initial stages of irradiation (up to ~200 kGrad), the accumulation of the products is proportional to the absorbed dose (in a vacuum). The radiation-chemical yields of H_2, CO, and CO_2 for an absorbed dose of ~500 kGrad are respectively 1.3, 0.8, and 1.6 in a vacuum, and 1.2, 1.7, and 3.3 in an oxygen atmosphere.[39,51] A similar percentage ratio of the yields of the gases in the dose range 50–2500 kGrad is given in Ref.111.

2. Redox Transformations of Cellulose

An important role in the radiation-chemical transformation of cellulose is played by processes of redox degradation. The copper number (c.n.), which characterises the reducing power, increases considerably with increase in the absorbed dose.[102,106] Analysis has shown that carbonyl and carboxyl groups are formed in irradiated cellulose[39,51,102] (Table 3).

Table 3. Chemical analysis of cellulose γ-irradiated at room temperature.[102]

Dose, kGrad	$10^{-19}N_1, g^{-1}$	$10^{-19}N_2, g^{-1}$	P.p.m.
0	0.32	1.90	1.3
8.8	0.71	1.97	1.9
20.6	0.90	2.01	2.8
45.2	0.94	2.11	3.8
94.6	1.48	2.23	6.2
183.0	2.20	2.36	11.2
406.0	2.99	2.59	24.6
908.0	4.11	2.78	46.5
1880.0	4.84	3.04	70.2

Notes. N_1 and N_2 are the numbers of carbonyl and carboxyl groups respectively in one gram of cellulose.

The radiation-chemical yield of carbonyl and carboxyl groups is slightly lower for irradiation in a vacuum or in a nitrogen atmosphere than for irradiation in an oxygen atmosphere.[39,51,98] The yields of carbonyl groups are higher than the yields of carboxyl groups.[102] Thus for a specimen of dry cellulose γ-irradiated at room temperature in a closed volume for an absorbed dose of 8.8 kGrad, the yields of carbonyl and carboxyl groups were 7.6 and 1.3 respectively.[102] For irradiation by accelerated electrons (dose 3.7 kGrad), the yields of these groups are 7.8 and 3.1.[102] Other workers[39,51,93] give appreciably higher values for the yields: 58 (for the CO groups) and 3.5 (for the COOH groups). A yield of 3.6 for the carboxyl groups was also obtained in Ref.19.

It can apparently be assumed with sufficient accuracy that the yield of carboxyl groups in the radiolysis of cellulose is 3 ± 1. The values of the yields of the carbonyl groups given in Refs.102, 39, 51, and 93 differ considerably, but the most reliable value is apparently ~7–8.[102] The unusually high value obtained in Refs.39, 51, and 93 is probably due to the conditions of the analysis (this involved the hydrolysis of the oligosaccharides extracted by aqueous solution from the irradiated cellulose). An equally high yield (~50) can be obtained from the data given in Table 3 if it is assumed that the copper number provides a quantitative characteristic of the concentration of carbonyl groups in irradiated cellulose. Their accumulation at high absorbed doses takes place according to the same law as the degradation of the macromolecules [Eqn.(3)]. The data in Ref.102 gave the following relationship

$$c = BD^m$$

where c is the concentration of carbonyl or carboxyl groups, and B is a coefficient equal to 6.8×10^{-7} mole g^{-1} or 1.8×10^{-7} mole g^{-1} for the carbonyl and carboxyl groups respectively. The value of n for the radiation accumulation of carbonyl and carboxyl groups was the same and equal to ~0.5. In Ref.98, in an interpretation of published data[93] on the accumulation of COOH groups, the exponent m was found to be 0.69.

Because of the high molecular weight of cellulose and other polysaccharides, the use of the methods of chemical analysis, in particular chromatography and mass spectrometry, to determine the final radiolysis products is practically impossible. It was previously noted[97,112,113] that irradiated cellulose contains water-soluble and water-insoluble fractions. From the water-soluble fraction it was possible to isolate components soluble in ethanol, among which cellobiose, glucose, 2-ketogluconic acid, arabinose, glyoxal, and a number of other complex acids were detected.[97] The hydrolysis of the water-soluble fraction of radiolysed cellulose gives xyloses, arabinoses, glucuronic acid, formic acid, and malonic dialdehyde.[21] The following values were obtained for the radiation-chemical yields for the formation of some of these compounds: 48.7 ± 2.4 for glucose, 10.1 ± 2 for xylose, 0.016 for malonic dialdehyde, and 2.3 ± 0.2 for formic acid. The formation of pentosans has been reported.[102]

3. The Radiation-chemical Transformations of Various Model Carbohydrates

To establish the principal routes in the radiation-chemical transformations of cellulose and other polysaccharides, it is appropriate to use simpler carbohydrates, whose transformations, on the one hand, can model the chemical reactions taking place in polysaccharides, and on the other hand, can be studied by modern methods of chemical analysis.

These carbohydrates include cellobiose, which contains two glucose residues connected by a glucoside bond. This disaccharide can be regarded as a fragment of cellulose. In aqueous media, the greater part of the final radiolysis products of this carbohydrate (~98%) consists of glucose, gluconic acid, 5-ketoglucose, 4-deoxyglucose, 2- and 5-deoxygluconic acid, deoxyketoglucose, arabinose, dihydroxyacetone, ribose, erythrose, and various other compounds.[114,115] The mechanism of their formation involves the hydrolysis of radicals obtained by the rupture of the C–H bonds in positions 1 and 4 and partly 5.

The cellobiose decomposition yields depend on the nature of the gas saturating the aqueous solution. Thus in a nitrogen atmosphere, the radiation yield is 3.1, and increases to 6.5 when the solution is saturated with nitrous oxide.[116] Since in the last case the hydrated electrons formed are converted into OH radicals:

$$N_2O + e(aq) + H_2O \rightarrow N_2 + OH^- + OH \cdot$$

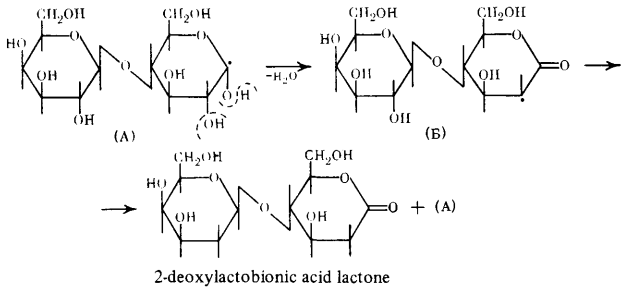
The observed doubling of the disaccharide decomposition yield most probably indicates that OH radicals play a decisive role in their radiation-chemical transformation. The role of the OH radicals most probably reduces to the removal of an H atom from the C(1) or C(4) atoms with the subsequent hydrolytic splitting of the radical at the glucoside bond.

According to Ref.117, the yield for the breakdown of the glucoside bond in cellobiose decreases by a factor of about 2.5 in the presence of oxygen. This is apparently due to the addition of an O_2 molecule to the C(1) or C(4) atoms with the formation of a peroxide radical and other transformation paths different from the rupture of the glucoside bond. Thus the radiolysis of aqueous solutions of cellobiose, as in the case of many other disaccharides (see the published monograph[118]), involves the rupture of glucoside bonds, oxidation, redox degradation, and the formation of deoxy- and deoxyketo-compounds.

A number of carbohydrates show appreciable radiation-chemical instability in the polycrystalline state. In this case the radiolysis is accompanied by the formation of a limited number of products. For example, the radiation-chemical

transformations of α-lactose monohydrate take place with a yield of 40–60 [119] according to three main schemes.[120]

Scheme 1

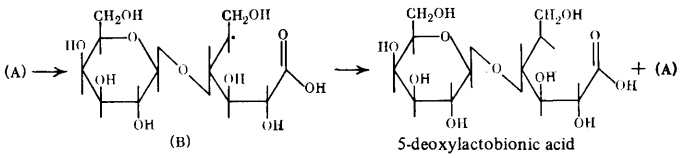


2-deoxylactobionic acid lactone

The radical (A) formed on γ-irradiation loses water as a result of dehydration; this gives the radical (B), which removes an H atom from the C(1) atom of a neighbouring lactose molecule. This gives 2-deoxylactobionic acid lactone, and also a new radical (A). Thus a chain process is initiated, in which the yield of lactone is 20.

The reaction involving the radical (A) can also take place by another mechanism to give the radical (C). The radical (C) removes an H atom from a neighbouring molecule, and as a result of a chain mechanism gives the final product 5-deoxylactobionic acid with a yield $G = 40$.[120]

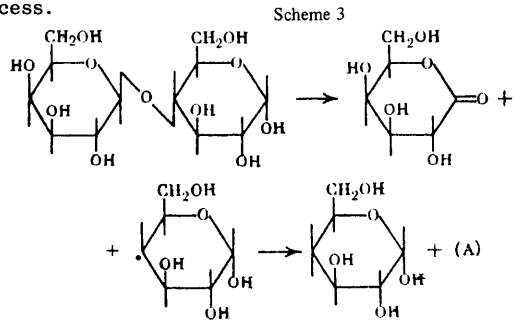
Scheme 2



5-deoxylactobionic acid

The rupture of the glucoside bond apparently takes place according to scheme 3 with the participation of a radical in which the electron is localised on the C(4) atom to give galactonic acid lactone ($G = 4.5$) and 4-deoxy-*D*-glucose ($G = 4.5$).[120] This process is not a chain reaction, unlike the two previous ones. The radical (A) is also generated in this process.

Scheme 3



Similar reactions take place in other systems. For example, the radiation-chemical transformations of 2-deoxy-*D*-ribose give 2,5-dideoxyerythropentonic acid with yield $G \geq 650$.[121] Crystalline *D*-fructose also decomposes under the influence of radiation, with a yield of 40–60.[122]

These examples show that for a number of carbohydrates, radiation-chemical decomposition takes place by a chain process. It is important to emphasise, however, that the yield of products associated with the rupture of the glucoside bond is low, and corresponds to the usual yields of the decomposition of substances by a non-chain mechanism. Thus 4-deoxy-*D*-glucose and galactonic acid lactone are formed by the rupture of the glucoside bond of α-lactose monohydrate by a non-chain mechanism with a yield of 4.5. This is an extremely important feature, since the yield for the degradation of cellulose (~7) indicates that a non-chain mechanism is most probable for the rupture of the glucoside bonds. Because of the contradictory nature, noted above, of the data relating to the yield of carbonyl groups (~7.6 [102] and ~58 [39,51,94]), however, a chain process in the radiation-chemical decomposition of cellulose by reactions analogous to those just examined cannot be finally excluded.

It has also been suggested that cyclic oligosaccharides—cycloamyloses—be used as model compounds imitating the radiation-chemical transformations of cellulose and other biological polysaccharides.[123,124] These compounds also do not have free reducing groups, that is aldehyde and keto-groups, whose presence in simple carbohydrates is responsible for the chemical properties which they exhibit.

It has been reported[125] that the γ-irradiation of cyclohepta-amyloses to an absorbed dose of 15 kGrad gives maltohexaoses. Subsequent studies[123,124] of cyclohepta- and cyclohexa-amyloses showed that the presence of water influences the efficiency of their radiation-chemical decomposition (Table 4). The products did not contain significant concentrations of glucose or maltoheptaose. The chief products were gluconic acid lactone and maltohexaose. Similar transformations were observed in the γ-radiolysis of cyclohexa-amyloses. The products included the same lactone and maltopentaose, but not maltohexaose, which is the chief product of the acid hydrolysis of this compound.

Thus the action of ionising radiation on cycloamyloses leads to cleavage of the cyclic system. The nature of the transformations taking place in the dried substance demonstrates unambiguously the identical yields of the initial radiolysis products maltohexaose and acid on the one hand, and the yield for the decomposition of the amylose on the other. Thus the cleavage of the polysaccharide ring is accompanied by the formation of one molecule of maltohexaose and acid. It can be seen from Table 4 that the presence of water inhibits the decomposition of the polysaccharide. On drying in air at 378 K, a moisture content of about 1.5% is preserved, corresponding to a molar ratio water : substance of 1 : 1. The presence of one water molecule per molecule of the polysaccharide leads to a decrease in the decomposition yield by a factor of almost 2 (see Table 4).

The crystals of the cyclohepta-amyloses isolated from aqueous solution contain ~14.8% water; the same quantity of water is present in amylose which has been kept for a long time in air. In this case there are ten water molecules per molecule of the substance. The cyclohepta-amylose decomposition yield, calculated for the total absorbed energy, is 6.2. If however account is taken only of the energy absorbed by the polysaccharide, the yield is 7.5, as in the previous case.

From this examination it might be concluded that the radiolysis products of water (H atoms and OH radicals) do not take part in reactions with the cyclohepta-amylose; this is undoubtedly not the case, however. Their reaction is apparently not accompanied by the breakdown of the cyclic structure of the polysaccharide. The presence of water also leads to an appreciable decrease in the yield of acid compared with the yield of maltohexaose, apparently due to the participation of water in reactions with intermediate decomposition products of the polysaccharide.

A detailed chemical analysis of the final products of the radiation-chemical transformations of cycloamyloses has been carried out.[126] The data obtained confirm the previously

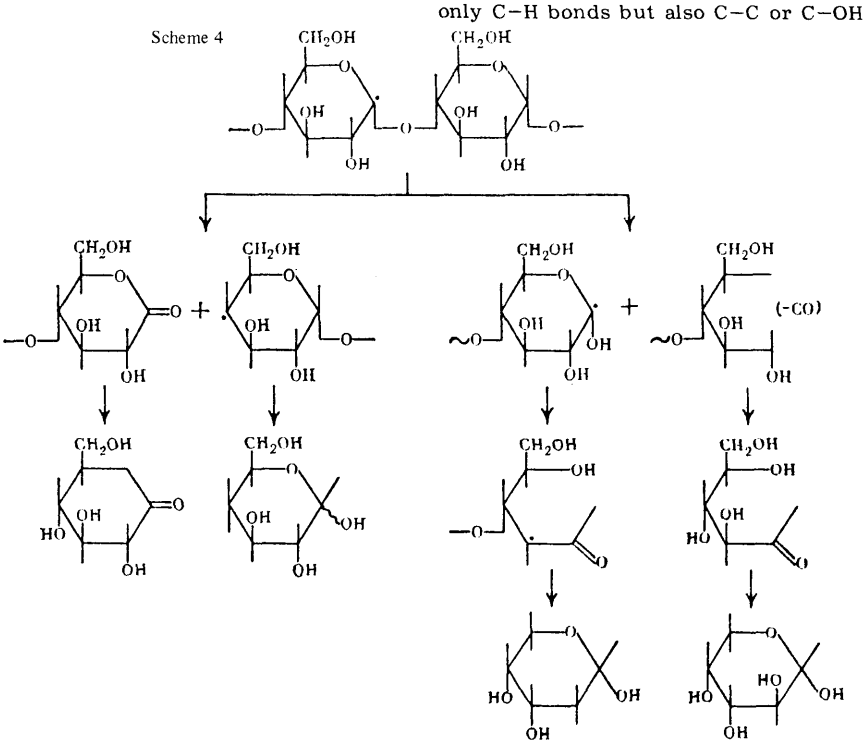
established fact[123–125] that the cleavage of the cyclic structure is the main process in cycloamyloses subjected to the action of radiation. By analogy with earlier studies of the radiolysis of simple carbohydrates,[118] it was suggested that the position of the keto-groups in the *D*-glucose residues produced in the radiolysis of the amyloses coincides with the position of the initial attack, that is with the localisation of the radical centres. These keto-groups are produced in irradiated carbohydrates as a result of the following reactions: a) disproportionation, or possibly the removal of hydrogen atoms from the α-OH group as a result of attack by primary or secondary radicals; b) radical rearrangement; c) removal of a molecule of water, alcohol, or CO; d) hydrolysis of acetal bonds if the radical centre is in an adjacent position; e) the formation of deoxy-groups as groups adjacent to keto-groups in a reaction following the addition of an H atom as a result of disproportionation.

Schemes for the radiation-chemical transformations of amyloses, proposed on the basis of these concepts, are given below.[123,124] It is assumed that the formation of the final radiolysis products is determined by the method by which the radical state is localised in the cycloamylose.

Scheme 4 illustrates chemical transformations involving radicals in which the electron density is localised on the C(1) atom [$R_{C(1)}$ radical]. Here and in subsequent schemes, the last stage corresponds to the hydrolysis of the oligosaccharides in aqueous solution to an identified monosaccharide. According to scheme 4, glucono-1,5-lactone is formed either by the hydrolysis of the glucoside bond closest to the radical centre or (preferentially) by the radical rearrangement C(1) ⇌ C(4). In the last case, electron transfer to the C(4) atom gives 4-deoxy-*D*-xylohexaose. The altered linear chain of the oligosaccharide will thus contain two functional groups at its ends, and the product will be a derivative of maltohexaose or maltoheptaose.

Other reactions involving the removal of CO and OH groups from the $R_{C(1)}$ radical have been proposed[123,124] to explain the formation of arabinose, ribose, and 2-deoxypentaose. The main product obtained according to scheme 5 is apparently *D*-arabinose.

Scheme 4



Scheme 5 shows the chemical changes in cycloamylose when the radical centre is localised on the C(4) atom [$R_{C(4)}$ radical]. The main result of the chemical transformations according to scheme 5 is the formation of 3-deoxyerythro-hexaose-4-ulose.

Table 4. Influence of the presence of water in a specimen of cyclohepta-amylose (CHA) on the yields of its radiation-chemical transformation*.[123]

Specimen	Decomposition of CHA	Formation of acid	Formation of maltohexose
Kept in air**	6.2	2.8	6.6
Kept in air at 378 K	7.4	7.5	7.5
Kept in a vacuum at 77 K	14.6	14.2	14.2
Aqueous 8×10^{-3} M solution	1.4	2.2	1.2

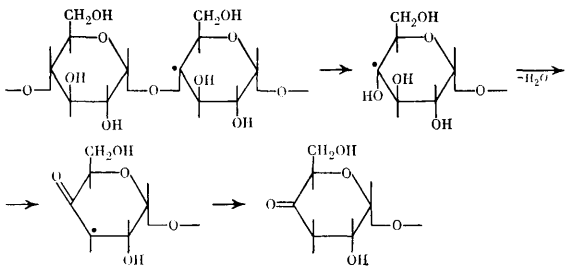
*The γ-irradiation of the specimens was carried out in a vacuum at room temperature. Dose power ~ 2.6×10^{17} eV g^{-1} min^{-1}, $D \sim 2 \times 10^{20}$ eV g^{-1}.
**The yields of H_2, CO_2, and CO were 3.1, 2.2, and 0.9 respectively.

Finally, scheme 6 reflects the possible transformations of amyloses with a reaction centre on the C(5) atom [$R_{C(5)}$ radical].

When the reaction takes place according to scheme 6, the radical rearrangement C(5) → C(1) gives a keto-group on the C(5) atom, and also a 4-deoxy-group.

A number of identified compounds do not appear in the proposed general schemes. Some of them are apparently produced as a result of the transformations of radicals with localisation of the unpaired electron, for example, on the C(6) atom, or by more complex schemes based on the less probable process of radical formation by the rupture of not only C–H bonds but also C–C or C–OH bonds.

Scheme 5

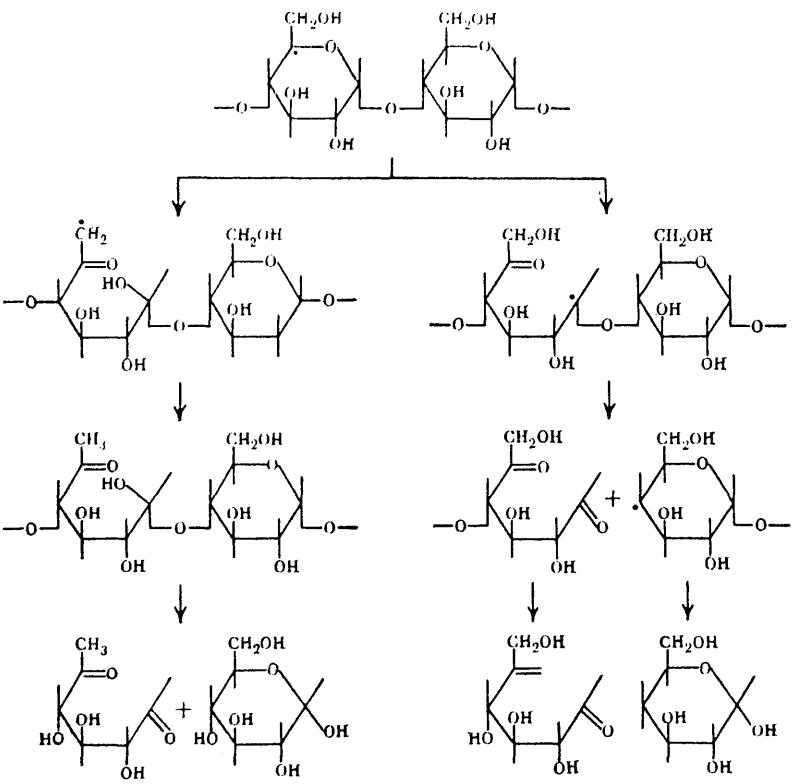


VI. MECHANISM OF THE RADIATION-CHEMICAL TRANSFORMATIONS OF CELLULOSE

The examination of data on the radiation-chemical transformation of cellulose shows that in the initial stages of the interaction with ionising radiation, free radicals are produced in the polymer, with localisation of the electron density mainly on the carbon atoms in positions 1 and 4. The subsequent degradation of the macromolecules and the formation of carbonyl and carboxyl groups and various chemical compounds, are initiated by radical species. A quantitative comparison of the yield of radicals, measured by EPR, after the γ-irradiation of cellulose at 77 K (~3.6 [71]) with the yield of its degradation (7–8, see section IV) and with the yield of carbonyl (7.6 [102]) and carboxyl (3–4 [102,119]) groups after γ-irradiation or irradiation by accelerated electrons at room temperature, shows that all these yields are of the same order of magnitude. When account is taken of the difference in the accuracies of their determination, including chemical side reactions of cellulose during the chemical analyses, and also the influence of the conditions of the irradiation on the efficiency of the radiation-chemical decomposition of cellulose, the possible partial disappearance of radicals even at 77 K, and other factors, it can apparently be concluded that each case of damage to the cellulose macromolecule with the formation of a radical centre is accompanied by subsequent bond rupture and the formation of carbonyl and carboxyl groups at the point of rupture. Allowance must also be made for the fact that it is possible in principle to have chemical transformations of cellulose involving excited states, without the formation of intermediate radical–ion products.

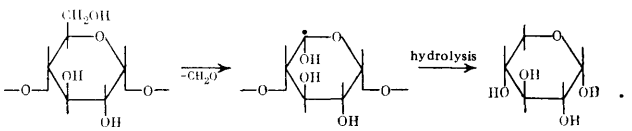
The study of the mechanism of the radiation-chemical degradation of cellulose is extremely difficult, because of the difficulty of the chemical analysis of the functional groups of the macromolecules. Considerable valuable indirect information on the main routes of the chemical transformations of cellulose initiated by reaction of radiation has been obtained by studying the final radiolysis products of model compounds, particularly cycloamyloses. Comparison of the data obtained in the analysis of the products of the acid hydrolysis of aqueous extracts of irradiated cellulose and data on the radiolysis of cycloamyloses shows unambiguously that the radiation-chemical transformations of these compounds take place by the same mechanisms.[127] For example, the final radiolysis products of cellulose, as in the case of cycloamylose, do in fact, in accordance with scheme 4, contain arabinose and 2-ketogluconic acid, and in accordance with schemes 5 and 6, various deoxy- and deoxyketo-compounds are formed.[112,119] There is not only a qualitative correspondence in the chemical reactions but also good quantitative agreement in the efficiencies of the radiation-chemical decompositions. Thus chemical analysis (Table 4) indicates that for cyclohepta-amylose dried in air, the yields for the decomposition and the formation of acid and molecular gases practically coincide with the corresponding yields for cellulose (see section V).

Scheme 6



Mention must be made of the fact, difficult to explain, that the products of the acid hydrolysis of an aqueous extract of irradiated cellulose, in addition to glucose, also contain xylose,[19] and the yields of these monosaccharides are ~49 and ~10 respectively. The formation of glucose in the acid hydrolysis of cellulose is a common phenomenon. The detection of xylose in the hydrolysate in yields comparable with the yield of glucose is extremely unusual, however. Xylose, and also arabinose, have also been detected in irradiated starch.[128]

A mechanism has been proposed for the formation of xylose.[129] It includes the rupture of the C–H bond in position 6 and the removal of formaldehyde, with the subsequent transformation of the resulting radical to give xylose:



According to this mechanism, the radiolysis of cellulose should give formaldehyde with a yield equal to the yield of xylose; it was not detected, however. Formic acid was found, however (yield 2.3).[19] It might be assumed that it is formed from formaldehyde in the acid-containing aqueous solutions during the acid hydrolysis of aqueous extracts of irradiated cellulose. Its yield is appreciably lower than that expected for the above mechanism, however. It has therefore been suggested[19,113] that formic acid appears in the oxidative degradation of glucose. Thus the scheme proposed[129] for the formation of xylose apparently has not been proved.

Malonic dialdehyde has been detected in irradiated cellulose.[19] Its yield for dry cellulose is 0.016, and in neutral and acidic aqueous solutions the yields are approximately the same and equal to $(6–7) \times 10^{-3}$. In alkaline solutions, however, there is a significant increase in the yield, to 0.256. The dependence of the yield of this product on the dose in the last case passes through a maximum at a dose of 2.5 kGrad. The formation of malonic dialdehyde has been established in the radiolysis of simple carbohydrates.[130,131]

Thus in the radiation-chemical degradation of cellulose, carbonyl and carboxyl groups are produced at the ends of the molecular fragments. The subsequent hydrolysis of these low-molecular polysaccharides gives deoxy- and deoxyketo-sugars, complex and simple organic acids, sugars, and other compounds. Dehydrogenation and degradation of the glucopyranose rings take place with the liberation of appreciable quantities of hydrogen, carbon monoxide, and carbon dioxide. Radiation changes can also take place without rupture of the polymer chain, and may be accompanied by the production of new groups (CHO, CO, COOH, etc.) in individual units.

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The analysis of data on the radiolysis of cellulose shows a fairly complex picture of radiation-chemical transformations taking place. At the present time it is possible to put forward only approximate general schemes for the mechanism of the degradation of the macromolecules and the formation of the final compounds, which are polysaccharides with various terminal groups. Subsequent studies of the radiation chemistry of this important natural polymer will make it possible to refine the mechanism of its radiolysis.

The questions which are apparently of greatest interest at present for the successful solution of a number of practical and scientific problems relating to the radiation processing of cellulose-containing materials are related to the search for methods of intensifying the degradation of cellulose and establishing the principal final products. For this purpose it is necessary to study the influence of temperature, moisture content, and various additives on the efficiency of the radiation decomposition of cellulose. The solution of these and other problems will facilitate the introduction of radiation methods into technological processes for the utilisation and processing of cellulose and cellulose-containing materials.

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