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MECHANISM OF THE RADIOLYTIC TRANSFORMATION OF CELLULOSE.
III. FORMATION OF VOLATILE PRODUCTS

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The formation under γ-irradiation of volatile products in cellulose preparations with different degrees of crystallinity has been studied. The volatile products of the radiolysis of cellulose have been found to contain H_2, CH_4, H_2O, *CO, and* CO_2. *According to the results obtained, these products can be divided into two groups, the first of which (*H_2, H_2O, *and CO) is formed as the result of the splitting out of hydrogen atoms and of —OH and —*CH_2OH *groups from the macromolecule, while the second (*CH_4 *and* CO_2*) is the result of radiation-chemical reactions between the components of the volatile products of the first group.*

Several mechanisms for the formation of the volatile products of the radiolysis of cellulose are known [1-5]. It has been established that molecules of hydrogen are formed as the result of the dehydrogenation of O—H bonds by the atomic hydrogen liberated in the radiolytic breakdown of C—H bonds [1]. The formation of water molecules takes place with the cleavage of C—OH and CO—H bonds in neighboring hydroxy groups of the cellulose macromolecule [4]. A mechanism of the formation of CO, CO_2, and CH_4 molecules is given in [5].

In the present paper, on the basis of a mass-spectrometric study of the composition of the volatile products of the γ-radiolysis of cellulose and the use of information on the free radicals of irradiated cellulose obtained by the ESR method, we propose possible radiation-chemical reactions of cellulose leading to the formation of volatile products.

F. L. Dalton et al. [6] have shown that the proportion of hydrogen in the volatile products of the radiolysis of cellulose in vacuum at doses of 0.048-0.96 MGr is not less than 98%. There are statements that on the γ-irradiation of cellulose in vacuum with a dose of only 0.1 MGr the proportion of hydrogen in the mixture of volatile products amounts to 76%, and with an increase in the radiation dose it decreases, reaching 57.7% at a dose of 1 MGr [7]. In [3], the following composition is given for the volatile products from sulfite cellulose irradiated with γ-rays in vacuum at a dose of 0.1 MGr (%): H_2 — 46; CH_4 — 2; CO — 11; and CO_2 — 41. Dalton et al. [6] observe that with an increase in the radiation dose the hydrogen content of the mixture of volatile products falls in view of its consumption in secondary reactions with the cellulose.

In order to describe possible radiation-chemical reactions of cellulose in harmony with the accumulation of the final volatile products of radiolysis, we set ourselves the task of determining the quantitative compositions of the volatile products at such a radiation dose that the secondary reactions of hydrogen with the cellulose would be minimal. To fulfill this task we used cellulose preparations having different degrees of crystallinity (DC). Such a choice of the material for mass-spectrometric analysis was due to the fact that the asymmetric doublet with $\Delta H_p = 13.0$ mTl in the ESR spectrum of cellulose γ-irradiated at 77 K, the intensity of which increases with a rise in the DC, has not been reliably identified [8], and, if this signal actually corresponds to a formyl radical, then with a rise in the DC of the cellulose we should observe a higher level of carbon monoxide in the volatile radiolysis products. The results obtained confirmed this idea. The total amount of CO and CO_2 (CO_2 is formed by the oxidation of part of the CO) in the volatile products of the radiolysis of celluloses with different DCs correlated well with the intensity of the asymmetric doublet in the ESR spectra of these preparations.

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TABLE 1. Levels of the Individual Components in a Mixture of the Volatile Products from the Radiolysis of Cellulose as a Function of the DC of the Preparation (radiation dose 50 kGr)

Component, vol.-%	DC of the cellulose, %			
	40	61	80	83
H_2	97.9	97.2	95.6	92.7
CH_4	0.0	<0.1	0.1	0.2
H_2O	0.1	0.6	0.8	1.1
CO	1.5	1.5	2.3	3.6
CO_2	0.5	0.6	1.2	2.3

According to Dalton et al. [6], on the irradiation of cellulose in vacuum with accelerated electrons up to a dose of 48 kGr only hydrogen appears in the mass spectrum and there are no other volatile products. We therefore decided first to investigate the composition of the volatile products when cellulose was irradiated with a dose of 50 kGr. At this dose, minimal amounts of H_2O, CO, and CO_2 (CH_4 was absent) were obtained in the volatile radiolysis products for one of the cellulose preparations compared with one another — the cellulose with a DC of 40%. There was no point in subsequently decreasing or increasing this dose. Another reason for choosing a radiation dose of 50 kGr was the passage of the intensity of the asymmetric doublet through a maximum at just this dose [8]. At a different dose it would be difficult to compare results obtained by ESR and by mass spectrometry.

The volatile products of the radiolysis of celluloses with different DCs were found to include H_2, CH_4, H_2O, CO, and CO_2 (Table 1). As can be seen from Table 1, the main component of the mixture of volatile products from the radiolysis of cellulose is hydrogen. It is interesting that with a rise in the DC of the cellulose the level of hydrogen in the mixture decreased and the level of the other components increased. In our opinion, this fact may indicate that the formation of CO, CO_2, and, in particular, CH_4, cannot be connected with the opening of the pyanose rings on irradiation, since this would take place more readily in cellulose with a smaller DC.

We also observed a decrease in the total amount of volatile products liberated with a rise in the DC of the preparation, which is due to a fall in the amount of the main component of the volatile products — hydrogen. In the mass spectra of the volatile products from celluloses with DCs of 40, 61, 80, and 83%, the intensities of the *m/z* 2 peaks, measured under the same conditions, were 270, 263, 226, and 224 rel. units, respectively. From these results it may be assumed that with an increase in the DC of the cellulose the number of acts of detachment of a hydrogen atom falls, while the number of acts of detachment of groups leading to an increase in the amount of the other components of the mixture rises. Possible reasons will be discussed below.

In connection with the considerations expressed in [9], on the irradiation of cellulose with γ-rays in vacuum the predominant process is cleavage of C—H bonds in positions 1 and 4 of the basic unit:

$$-\overset{|}{\underset{|}{C}}-H \xrightarrow{\wedge\!\!\vee} -\overset{|}{\underset{|}{C}}^{\bullet} + H$$

It is usual to consider that at the first moment of their appearance H atoms possess high energy [10, p. 80] and can dehydrogenate C—H bonds again in positions 1 and 4:

$$-\overset{|}{\underset{|}{C}}-H + H \longrightarrow -\overset{|}{\underset{|}{C}}^{\bullet} + H_2$$

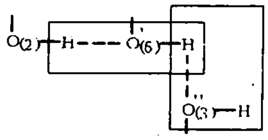
or detach a hydrogen atom from hydroxy groups:

$$-\overset{|}{\underset{|}{C}}-OH + H \longrightarrow -\overset{|}{\underset{|}{C}}-O^{\bullet} + H_2.$$

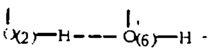
The occurrence of this reaction has been established on the basis of an analysis of the composition of the gas liberated on the radiolysis of partially deuterated cellulose preparations [1].

The formation of water may be connected with the cleavage of C—OH bonds. However, the $\dot{O}H$ radical so formed does not appear in the ESR spectrum because of its relatively low concentration. An adequate number of $\dot{O}H$ radicals was detected in the case of moistened samples of cellulose irradiated with γ-rays at 77 K [11]. On heating to 179 K the $\dot{O}H$ radicals disappeared and the concentration of macroradicals of the same structure as in irradiated dry cellulose increased. This means that $\dot{O}H$ radicals detach hydrogen atoms from those C—H bonds that break down under the direct action of radiation.

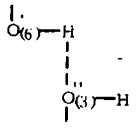
The increase in the amount of water in the mixture of volatile products with a rise in the DC of the preparation can be explained by the fact that in these circumstances the probability of the arrangement of neighboring hydroxy groups in such a way as to favor the elimination of water rises. According to the literature [12, 13], the hydroxy groups in crystalline sections of cellulose, unlike those in amorphous sections, are linked with one another by two hydrogen bonds. Consequently, on the cleavage of C—OH bonds in preparations with a predominating ordered structure the yield of water molecules should be higher.



where, according to [13]



- intramolecular hydrogen bond



- intermolecular hydrogen bond

In principle, water molecules can be formed as the result of a reaction of hydrogen with the oxygen liberated in the radiolysis of CO_2. However, in view of the establishment of a stationary concentration of CO_2 of only a few per cent in the radiolysis of CO_2 under normal conditions [14], it may be considered that a reaction of hydrogen with oxygen is not characteristic for this case.

In our opinion, the formation of CO during the radiolysis of cellulose is connected with a transformation of the $\dot{C}H_2OH$ radical formed on the detachment of a CH_2OH group from the cellulose molecule

$$\dot{C}H_2OH \xrightarrow{T} H_2 + H\dot{C}O$$

The formyl radical $H\dot{C}O$ so formed is unstable and decomposes under the action of visible radiation and heat:

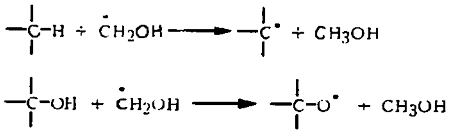
$$HCO \xrightarrow{h\nu T} H + CO.$$

The formation of CO_2 takes place by the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$

which is known under the name of the water-gas reaction [15, p, 476]. The conversion of CO into CO_2 takes place at temperatures above 873 K. The possibility of the occurrence of this reaction under the action of radiation is shown by the figures of Table 1: the proportion of CO_2 in the mixture of volatile products increased with a rise in the CO and H_2O contents. Our results agree with those of [7], in which on the radiolysis of such dry carbohydrates as amylose, amylopectin, cellulose, glucose, and maltose an increase in the CO_2/CO ratio was observed with the presence of water in the volatile radiolysis products.

In the mass spectrum of the volatile products of the radiolysis of cellulose with a DC of 83% (ramie cellulose) we observed additional peaks at *m/z* 29, 31, 32. The strongest was the peak corresponding to *m/z* 31, which reached the intensity of the *m/z* 16 peak. The peaks with *m/z* 29, 31, and 32 were absent from the mass spectra of celluloses with DCs of 40 and 61%, while in the mass spectrum of cellulose with a DC of 80% their intensity was very low. It is possible that these peaks relate to methyl alcohol (*m/z* 32) and to fragments of it (*m/z* 29 and 31). Methyl alcohol can be formed by the detachment of a hydrogen atom from the cellulose molecule by a $\dot{C}H_2OH$ radical in the same way as by a hydrogen atom:



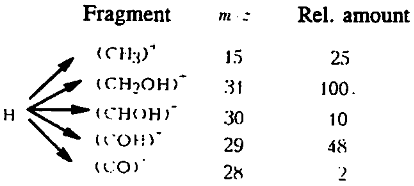
$$-\overset{|}{\underset{|}{C}}-H + \dot{C}H_2OH \longrightarrow -\overset{|}{\underset{|}{C}}^{\bullet} + CH_3OH$$

or

$$-\overset{|}{\underset{|}{C}}-OH + \dot{C}H_2OH \longrightarrow -\overset{|}{\underset{|}{C}}-O^{\bullet} + CH_3OH$$

The probability of the occurrence of these reactions increases with a rise in the number of acts of elimination of CH_2OH groups, which apparently takes place for ramie cellulose.

As is known, in the mass-spectrometric analysis of the volatile products, their molecules are subjected to the action of accelerated electrons, which causes the ionization of the molecules, each molecule losing one of its electrons and subsequently breaking down. According to the results of mass spectrometry [16, p. 75] the fragmentation of methyl alcohol under the action of accelerated electrons may be represented in the following way:



	Fragment	m/z	Rel. amount
CH_3OH	$(CH_3)^+$	15	25
	$(CH_2OH)^+$	31	100.
	$(CHOH)^+$	30	10
	$(COH)^+$	29	48
	$(CO)^+$	28	2

Thus, in the mass spectrum we can detect only CH_3OH molecules and their fragments with masses of 31 and 29, the other fragments not appearing because of their relatively low concentrations. In the mass spectrum that we obtained, the intensity ratio for *m/z* 29, 31, and 32 was 1.0:1.6:1.0, respectively, which agrees well with the figures given in [17] — 64.66, 100.0, and 66.68%, respectively.

We may note that within the framework of the model of the formation of volatile radiolysis products that we are describing it does not appear possible to link the formation of CH_4 with reactions of groups split out under the action of the radiation or with transformations of the radicals so formed. It is most likely that the formation of CH_4 is connected with the reactions

$$CO + 3H_2 \rightsquigarrow CH_4 + H_2O\,,$$

$$CO_2 + 4H_2 \rightsquigarrow CH_4 + 2H_2O\,.$$

The reaction of hydrogen with CO_2 is one of the laboratory methods of obtaining methane and takes place when a mixture of CO and hydrogen is passed over a metallic nickel catalyst at high temperatures [15, p. 472]. The reaction of hydrogen with CO_2 takes place at higher temperatures than the reaction with CO.

The results given in [7] may be a confirmation of the occurrence of these reactions under the action of radiation. According to these results, on the radiolysis of such dry carbohydrates as amylose, amylopectin, cellulose, glucose, maltose, and cellobiose an increased level of CH_4 is observed for those preparations in which the combined amount of CO and CO_2 in the mixture of volatile products is high.

The possibility cannot be excluded of the formation of CH_4 in the radiolysis of CH_3OH:

$$CH_3OH \rightsquigarrow H_2 + CH_4 + CO + CH_2O \text{ etc.}$$

The value of G_{CH_4} for the radiolysis of CH_3OH in the liquid phase is 0.2 [18, p. 84]. However, this reaction is not determinative for the formation of CH_4 on the irradiation of cellulose.

Let us turn to a consideration of changes in the quantitative composition of the volatile products of the radiolysis of the cellulose preparations investigated. At first glance, an increase in the levels of CO, CO_2, and CH_4 in the mixture of volatile products with a rise in the DC of the cellulose appears unlikely. But, at the same time, the decrease in the absolute amount of hydrogen in the mixture is natural, since under otherwise the same conditions the detachment of a hydrogen atom by the action of radiation takes place with greater difficulty for preparations with a high DC than for those with a low DC. This is favored by the increase in the packing density of the macromolecules with a rise in the DC of the preparation.

The densification of the structure of the preparations leads, in its turn, to a still more rigid fixation of the pyranose rings in the chain of the cellulose macromolecule. At the same time, the CH_2OH groups may remain fairly mobile, as is shown by investigations of molecular motions in cellulose by the NMR method [19] and of the structure of cellulose by IR spectrometry [20, 21]. We explain the increase in the amount of components other than H_2 and H_2O in the mixture of volatile products of the radiolysis of cellulose by just this circumstance.

According to the results obtained, the volatile products of the radiolysis of cellulose can be divided into two groups, the first of which (H_2, H_2O, and CO) is formed as the result of the detachment of hydrogen atoms and OH and CH_2OH groups from the macromolecule, and the second (CH_4 and CO_2) as the result of radiation-chemical reactions between the components of the volatile products of the first group.

On the basis of the results of mass and ESR spectrometries it is possible to determine the relative amounts of radicals formed at 77 K as a result of the cleavage of C—H, O—H, C—OH, and C—CH_2OH bonds without taking the yield of captured electrons into account. Here, it must be borne in mind that one molecule of hydrogen arises from two radicals and be assumed that each molecule of H_2O and CO (CO_2 must be recalculated to CO and H_2O) arises from one radical. Calculations for the cellulose preparations investigated showed that the amount of radicals formed with the detachment of hydrogen was 94-98%, of them 25-30% being due to the splitting out of hydroxylic hydrogen. Other radicals (2-6%) are due to the proportion of detachment of OH and CH_2OH groups.

EXPERIMENTAL

We investigated ramie and cotton celluloses and two amorphous samples of cotton cellulose having, according to the results of x-ray diffractometry, degrees of crystallinity of 83, 80, 61, and 40%, respectively. Sample of cellulose with an initial mass in the air-dry state of 1.0 g that had been carefully degassed in a vacuum apparatus were irradiated with a dose of 50 kGr at 300 K with a Co^{60} γ-source at a radiation dose rate of 2 Gr/sec. The analysis of the compositions of the volatile cellulose radiolysis products was carried out on a mass spectrometer of the MKh-1304 type.

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