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Peculiarities of glucose molecules destruction under irradiation at the M-30 microtron (12.5 MeV): mass spectrometric studies

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Abstract

The method of mass spectrometric studies was used to study the fragmentation of bioorganic molecule glucose in the gas phase upon collision with low-energy electrons (20-70 eV) before and after irradiation at the M-30 microtron (12.5 MeV) with doses of 14 and 164 kGy. The dose dependence of the transformation of glucose mass spectra was established. The results indicate the dominance in mass spectra of symmetric fission channels of the molecule itself and its fragments formed under the action of M-30 microtron radiation. Studies of the energy dependence of the mass spectra's individual fragment yields indicate the non-equilibrium state of the array of molecular fragments formed after the action of high-energy radiation. The interpretation of the obtained results was carried out within the framework of the method of structural combinations, which allows for analyzing the stability of possible sets of molecular structures formed from glucose after irradiation. The dominant channels of fragmentizing the glucose molecule without considering its radiation treatment are explained. The theoretical method allows one to calculate both the configurational entropy and the information capacity of a bioorganic molecule.

Keywords: glucose, radiation, mass spectra, energy dependences, structural transformations, fragmentation channels, information

1 Introduction

There is a well-known interest in studying the nature of the synthesis and transformations of monosaccharides and polyatomic alcohols under the influence of physicochemical and biological factors and their role in the formation of the structure and metabolic processes of biota [1, 2]. They are a subclass of simple carbohydrates containing only three chemical elements, H, C, and O, and they make up 98% of the human body. Their distributions are not limited to the territory of the Earth; there are data on the discovery of such molecules in interstellar space and the atmospheres of other planets [3]. Glucose, $C_6H_{12}O_6$, is the most common monosaccharide in nature, the oxidation of which is the source of energy for muscle contractions and the work of the human nervous system. It also performs the function of detoxification of the body. In particular, it participates in the detoxification of toxic metabolites and xenobiotics. The important biochemical properties of glucose are realized at various stages of the fragmentation of the molecule during chemical transformations: in metabolic processes, the phosphorylation and dephosphorylation of more than 13,000 human proteins, and the formation of the cell's framework. These facts explain the value of practice of monosaccharides for the food and pharmaceutical industries; for example, the world production of dry glucose exceeds 20 million tons. Despite the long history of the use and study of monosaccharides, new facts due to the understanding of the role of terrestrial radiation in the life of biota, the consequences of nuclear disasters, and the development of nuclear medicine caused the need for radiation studies of these substances. First of all, this is connected with the realization that the biota's functioning occurs under the terrestrial radiation's action. Therefore, it is essential to study the impact of radiation on the processes of metabolism and physiology of biota, which in turn are determined by the nature of the destruction of bioorganic molecules. Such studies are especially important for understanding the phenomena that occur during radiation damage to biological systems [4–6], for which it is a problem to study the direct mechanism of the destruction of a living cell under the influence of radiation [7]. The current level of knowledge in this direction is based on the data of correlation dependences "biochemical indicator - radiation dose," as a study of metabolic shifts from oxidative phosphorylation to aerobic glycolysis at the cellular level [8, 9] during biota irradiation. This requires differentiating the effects caused by the action of radiation on the organisms themselves and on important biochemical components, such as monosaccharides, that are used in this process. Therefore, there is an urgent interest in studying the elementary processes of fragmentation of organic molecules under the influence of radiation; however, this is available to a limited number of experimental methods. Using molecular beam technology for such tasks opens up new opportunities for studying the nature of excitation and fragmentation of bioorganic molecules in situ. Such data are obtained by studying the interaction of molecules with a monoenergetic electron beam in the range of 0-100 eV and establishing the mass spectra of their fission products. Recently, a number of similar studies have been carried out on amino acid molecule beams, without and with their prior radiation treatment, which made it possible to establish the nature of their fragmentation and ways of molecular modification [10–12]. Equally important are such studies for monosaccharides and polyhydric alcohols, which are the initial components of the synthesis of proteins,

DNA, and factors of energy and metabolic processes of bioorganisms. Interest in the fragmentation of monosaccharides when interacting with electrons is due to the presence of two channels - direct impact and dissociative when the destruction occurs under the action of secondary low-energy electrons. In the latter case, electron resonances, so-called transient anions, play a dominant role in the region of threshold energies of 0-15 eV. The process of dissociation of this anion inside DNA can occur by direct attachment of electrons at the point of molecular bond break or by transfer of an electron from another subunit [13]. Such studies are particularly important for understanding the processes occurring during radiation damage to DNA [11, 14] and biological systems [15–17], where the sugar fragment is the main building block. It follows that the study of the interaction of electrons with the monosaccharide molecule itself and all its components that affect the formation of DNA is very relevant. Many works [18–24] have been devoted to the theoretical and experimental study of the ionization of complex organic compounds, including monosaccharides, under the action of a beam of low-energy electrons. Still, their primary attention is to determining the parent molecule’s ionization potential and the energy of appearance fragment ions arising from dissociative ionization. However, such data for monosaccharide molecules, before and after the action of ionizing radiation, are practically absent. One should be emphasized that mass spectrometry methods are widely used in clinical medicine [25–27]. Special attention is paid to determining glucose concentration using isotope dilution mass spectrometry [28]. This paper presents the results of mass spectrometric studies of D-glucose samples before and after irradiation with a beam of nuclear particles - accelerated electrons of the M-30 microtron with an energy of 12.5 MeV. To study the stages of radiation fragmentation of glucose, two radiation doses, 14 and 164 kGy, were selected, and the results of its dissociation as a result of interaction in a vacuum with low-energy (0-70 eV) electrons are presented. The energy dependences of the yields of the main fragments of glucose division have been established. It is shown that the proposed structures of models of radiation transformations make it possible to estimate the information capacity of biomolecules.

2 Structural modeling of radiation transformations of the glucose molecule

The structural 2D and 3D schemes of glucose are well known and are presented in Fig. 1. As you can see, glucose contains five hydroxyls (-OH) and one aldehyde group (-COH). The location of the fifth and fourth carbon atoms facilitates the interaction with the aldehyde group, which causes the presence of two forms: cyclic and linear. The spatial isomers of glucose have a five-membered (furanose) cycle, which is formed due to the addition of hydrogen from the hydroxyl group of the fourth carbon atom to the oxygen of the carbonyl group (see Fig. 1a). As shown in Fig. 1b, there are four asymmetric chiral carbon atoms centers (marked with *), each associated with substituents - a hydrogen atom and OH. Fig. 1c shows the linear formulas of glucose, built according to E. Fischer’s formula, which can explain most of the physical and chemical properties visually. The channels of glucose molecule destruction, including under the influence of radiation, have been studied much less. Their theoretical simulation

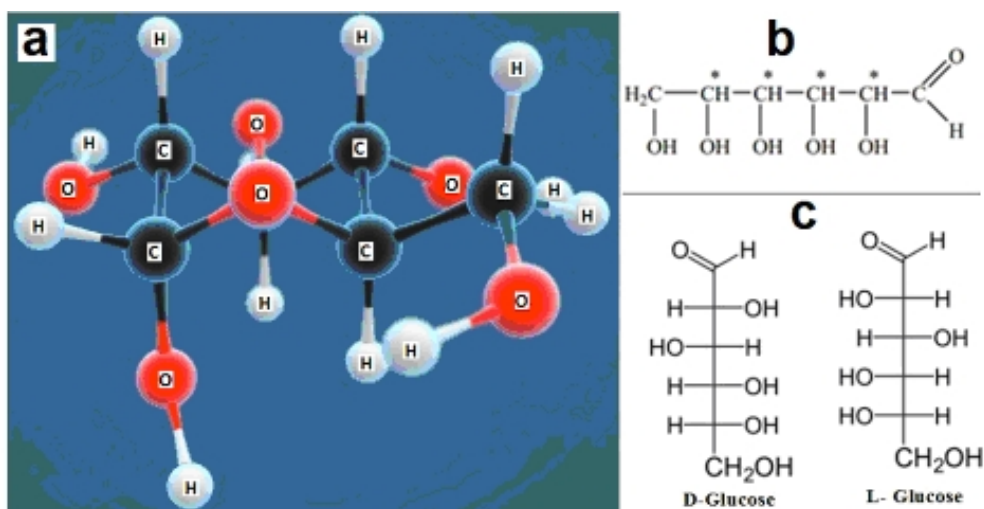


Fig. 1 The structure of the glucose molecule: a – spatial 3D shape, b – scheme of chemical centers, and c – linear formulas for different isomers.

is conveniently carried out within the framework of the Ball-and-Stick model, as a part of click chemistry theory [29], which allows analyzing the structural and energy parameters of molecules and possible molecular structures when chemical bonds are switched. It is known that the molecules of simple monosaccharides and polyatomic alcohols are built by a combination of C, H, and O atoms, which have different values of their valences, electronegativities, homo- and hetero bonds breaking energies. For organic polymers, the specific bond energy is not additive over the number of atoms. Instead, their arrangement is described by color statistics [30] when atoms with different ratios of homo- and hetero bonds are considered statistically non-equivalent. The binding energy of an atom in such a model is equal to the sum of the breaking energies of its chemical bonds. Using the empirical database [31], you can obtain the following hierarchy of energies of single chemical bonds for glucose (in parentheses is the share of their breaking energy to O-H):

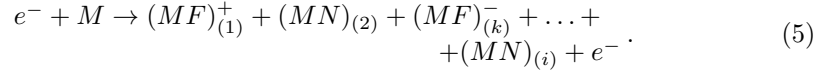
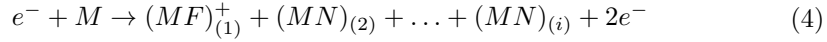
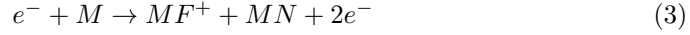
$$E_{O-H}(1) > E_{C-H}(.93) > E_{C-C}(.8) > E_{C-O}(.73) \quad (1)$$

The analysis of formula (1) allows estimating the ways of fragmentation of such molecules under radiation. The method of structural combinations as the click chemistry theory can be used to study the set of structural complexes that formed during the radiation destruction of a glucose molecule. Enter the value of the number of C-C, C-O, and C-H bonds, respectively, as $x_1 - x_3$; O-H as y_1 , the number of broken C-bonds will be denoted by x_{11} , and y_{22} for O-. The structural features of this molecule when switching homo- and heterobonds and the presence of broken bonds are determined by color sets (CS) containing atoms with different bond energies in the molecule. First, we will introduce the following rule for the designation of CS atoms: they are denoted by capital letters C, H, O, and subscripts c, h, and o represent their chemical

bonds with neighboring atoms. Then, for a glucose molecule with $M = 24$ atoms, the formula $C_{0.25}H_{0.5}O_{0.25}$ can be used to set the following CS, $\{Ccoh, 4Ccoch, Cc2oh, 5Och, O2c, 7Hc, 5Ho\}$, here, for example, $Cc2oh$, $O2c$ denote atoms having a double bond, respectively, with oxygen and carbon. You can write down the following system of equations, which determines all possible structural combinations during the fragmentation of glucose:

$$\begin{aligned}
2x1 + x2 + x3 + x11 &= 24 \\
x2 + y1 + y11 &= 12 \\
x3 + y1 &= 6 \\
x1 &= 1/2(Ccoh + 2Ccoch + Cc2oh) \\
x2 &= Ccoh + Ccoch + 2Cc2oh \\
x1 &= Och + 2O2c \\
x3 &= 2Ccoh + Ccoch + Cc2oh \\
x3 &= Hc \\
y1 &= Och \\
y1 &= Ho
\end{aligned} \tag{2}$$

The result of the interaction of electrons beam with molecules M in a vacuum is the destruction of an individual molecule from forming its singly charged and neutral fragments. These reactions can be written as follows:



Here, $(MF)_{(i)}^\pm$ the ionic and $(MN)_{(i)}$ neutral fragments, equations (4), (5) describe the multi-fragment processes of the destruction of the molecule, and $i=1, n$. The specific channel of the breakdown of a molecule as a result of a collision with electrons is determined by the values of the breaking energy of its chemical bonds, formula (1), and the ionization thresholds of its fragments. Thus, the reaction according to the scheme (3) indicates the formation of a positive parent ion of the original molecule M . Scheme (4) corresponds to the process of multi-fragment dissociation of the macrosegment of the molecule $A_{(i)}$, $A_{(i)} = \{(MF)_{(1)}^+ + (MN)_{(i)}\}$, which can occur under the condition:

$$E(A_i^+) - E((MF)_{(i)}^+) > D_0(\{(MF)_{(1)}^+ + (MN)_{(i)}^+\}) \tag{6}$$

where $E(A_i^+)$, $E(MF_i^+)$ are the ionization energy or potential of the appearance of the macrosegment, respectively, and D_0 is the dissociation energy of the macrosegment. And finally, scheme (5) is realized if one of the fragments formed in the process of dissociative ionization captures a slow electron and becomes a negative ion, leading to the formation of an ion pair. In this case, the ionization energy of the parent molecule must be higher than the energy of the appearance of the fragment ion, which is related to the electron affinity energy of the negative ion fragment. Formula (1) establishes the hierarchy of destruction of a glucose molecule: C–O bonds are the least resistant to breaking so the first step can be the loss of a hydroxyl group during interaction with electron beams. As a result, both a set of O–H hydroxide ions and neutral water molecules are formed. At the same time, the result of the "healing" of the structure can be the formation of C=C double bonds, the breaking energy of which is higher than the sum of two C–C bonds. Another destruction stage is associated with breaking C–C bonds, which can lead to the fragmentation of the structural framework of the glucose molecule. The mass spectrometric method is the most informative for studying these processes on glucose samples, without and during irradiation with high-energy nuclear particles. Studies conducted under the same experimental conditions allow us to obtain information about complete and dissociative ionization processes and estimate the relative contribution of each dissociated fragment of glucose.

3 Experimental setup and apparatus

The experiment was performed using a mass-spectrometric setup with an oil-free pumping unit described earlier [32–34]. An MX-7304A type monopole mass spectrometer was used as an analytical instrument. The range of the recorded masses is 0–180 Da, with a mass resolution not worse than $\Delta M = 1$ Da. The following modes of operation of the electron source are possible:

- Measurement of mass spectra data in a fixed energy mode in the range of 10–70 eV.
- Measurement of energy dependences of exit of fragment ion formation with a smooth energy variation within 5–30 eV for specific cation mass.

The electron current in our experiment varied within the range of 0.05–0.5 mA. At the same time, the minimum energy spread $\Delta E = 250$ meV, where ΔE is the full width at half maximum (FWHM) of the electron energy distribution. The energy distribution of electrons was determined by differentiating the initial part of the current-voltage characteristic of the electron beam. The ions of molecular fragments, formed from interaction with electrons, are mass-separated, detected, and recorded by a measuring system with a digital indication of the particle mass number and intensity, with manual, cyclic, or programmed variation of the mass spectrum and the impact electron energy. A beam of neutral molecules is created by a channel source of effusive type, which provides the concentration of molecules in the area of interaction with the electron beam in the range of $5 \cdot 10^{10} - 10^{11} \text{ cm}^{-3}$. A special controller with feedback provided a highly stable heating temperature in the 300–600 K° range. The ion source temperature was 20–30 C° higher than the ampoule with the substance, which prevented the condensation of the substance under study on the electrodes of

the ion-optical system of the mass spectrometer. The mass scale was calibrated using Ar and Xe beams, and the control mass spectra were measured for freon, sulfur hexafluoride, and krypton. The energy scale was calibrated using the initial part of the ionization cross section for the Kr, Ar, Xe atoms and nitrogen, freon, and sulfur hexafluoride molecules injected into the ionization chamber from a separate source. This procedure enabled the electron energy to be determined with an accuracy not worse than ± 0.08 eV. Measurements of the mass spectra of the molecules (Sigma–Aldrich) were carried out at different energies of the ionizing electrons. The experiment was performed in two stages: at the first stage, the mass spectra of non-irradiated glucose in the range of 0–160 Da were thoroughly measured at the ionization energies E_i of 20, 30, 40, 50, 60 and 70 eV. Irradiation was carried out on an electron accelerator M-30 microtron of the Institute of Electron Physics, certified for radiation dosimetry research. The advantage of the M-30 microtron is high monoenergetic power in the range of 1–25 MeV and the ability to generate intense electron, gamma, and neutron beams for fundamental and applied nuclear physics research [35]. Conditions for nuclear irradiation of glucose samples in powder form were as follows: irradiation was carried out in the air, at room temperature; two doses were provided 14 kGy with electron flux density $2.8 \cdot 10^{10}$ el·cm⁻²·s⁻¹ and 164 kGy, respectively, $1.4 \cdot 10^{11}$ el·cm⁻²·s⁻¹. The irradiated conditions did not lead to heating of the glucose samples; irradiation field homogeneity was more than 90%; the contribution of associated photoneutrons and bremsstrahlung gamma radiation was monitored and did not exceed 5%. Furthermore, the energy of the 12.5 MeV particles provided the same irradiation conditions for the entire glucose sample, as the shadow effects were virtually absent.

4 Results and discussion

Mass spectrometry is one of the important physicochemical analysis methods, allowing one to conclude about the molecular mass of a compound, its composition, and its structure. Such data can be obtained by analyzing the mass spectra of ions formed during the interaction of molecular beams with electrons in a vacuum. When analyzing a substance’s mass spectra, one should consider that they are preceded by two stages of destruction of the substance. In the first of them, the destruction may occur during the heating of the effusion cell during the formation of the molecular beam. Detailed studies of these processes for glucose [19, 34, 36] showed that an increase in temperature leads to a decrease in the yield of larger, $m/z > 60$ fragments and an increase in the yield of small ($m/z < 43$) fragments. Another destruction stage is realized when a molecular beam interacts with electrons with an energy of 10–100 eV. This energy is higher than the bond energy of the molecule’s atoms. Therefore, in addition to the ionization of molecules or their molecular segments, electrons can stimulate their fragmentation through an impact mechanism or dissociative ionization when condition (6) is satisfied. At a constant temperature of the evaporator, the structure of the molecular beam will be determined by the state of the substance, in particular, before or after its radiation treatment.

Figure 2 presents the mass spectra data of glucose samples obtained without (a) and irradiated on the M-30 microtron with doses of 14 (b) and 164 (c) kGy. The

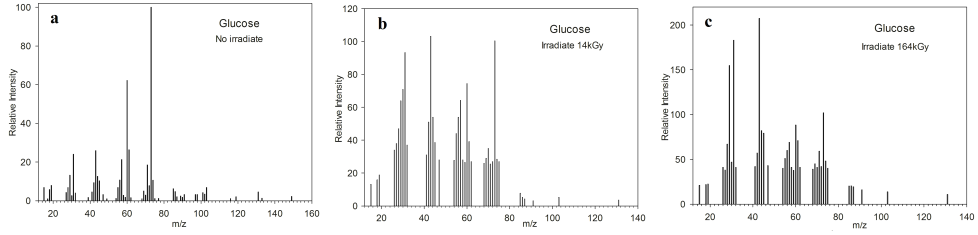
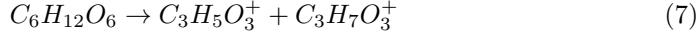


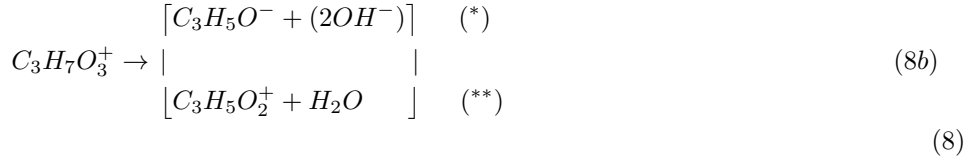
Fig. 2 Mass spectra data of the glucose molecule:
a – before irradiation, b, c irradiated with a dose of 14 and 164 kGy, respectively.

temperature of the effusion source was kept constant and equal to 430 K^o, and the energy of ionizing electrons was standard 70 eV. As can be seen from fig. 2, the general characteristic of mass spectra is a high fragmentation depth, a large number of accompanying peaks of fragment ions, and the absence of a peak of the parent molecular ion of glucose $C_6H_{12}O_8^+$ ($m/z = 180$). Mass spectra of irradiated and unirradiated glucose samples, Fig. 2, allow one to study the ways of its fragmentation during all possible ways of transformations: chemical, thermal, and kinetic. Thus, the mass spectrum of unirradiated glucose, Fig. 2a, contains five groups of fragments, which are grouped near values of (m/z) = 15-20; 30; 45; 50-60, and 73. Moreover, the latter is dominant in the spectrum and is close to the fragments of the symmetric fission of the parent glucose molecule. As can be seen in fig. 2b and 2c, the mentioned groups of fragment yields in irradiated glucose are preserved. Still, their intensities are significantly redistributed: at a dose of 14 Gy, the share of ions with ($m/z = 32$), 45 increases almost 3.7 times, and at 164 Gy, respectively, 7.6 times. At the same time, the yields of ($m/z = 15$) fragments remain almost unchanged. It is important to analyze the yields of fission fragments depending on the energy of electrons interacting with glucose molecular beams in a vacuum (Fig. 3). As can be seen, such products of unirradiated glucose practically do not change for electron beam energies above 40 eV, Fig. 3a. The picture of the energy dependences of the yields of molecule fragments of irradiated glucose is different. There is a monotonous increase in the yields of their fragments in almost the entire range of electron beam energies. An increase in the radiation dose reduces the relative yield of the ($m/z = 73$) molecule fragment compared with the unirradiated one by approximately 1.8 times. There is also a tendency to increase the yields of light fragments ($m/z = 31$) and 43 with an increase in the irradiation dose. The interpretation of the obtained results should take into account the structure of the glucose molecule, Fig. 1 and the differences in the strength of its chemical bonds (1), which gives the advantage of the loss of the hydroxyl group (OH-) and the destruction of the carbon skeleton of the molecule during interaction with an electron and the formation of a fragment ion. In addition, it is necessary to consider the fission schemes of glucose into two molecule fragments that are similar in mass (symmetric mode) and when the fragments differ significantly in mass (asymmetric mode). The energy of the scanning beam electrons is sufficient for dissociative ionization (6), and single ionization processes should be considered the dominant process over multiple ones. When analyzing the schemes of the destruction of a molecule along with (1), one should take into account the schemes of their "switching," according to

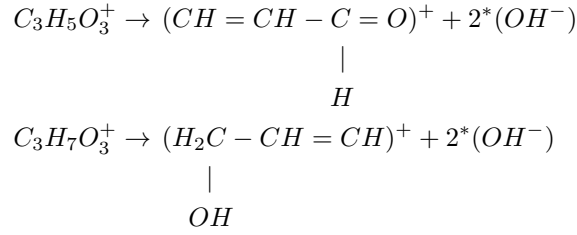
(2). In the case of symmetric mode fission:



and taking into account their further fragmentation with the formation of a hydroxyl group (*), or the release of a water molecule (**), the following final states of molecular fragment ions are possible:



Moreover, in both cases, their realization requires the formation of double bonds C=C:



One must note that variant (**) of formula (8) with forming a water molecule is possible when a 30% stronger C-H bond is broken. The symmetrical version of the destruction of the glucose molecule (8) leads to the formation of heavy positively charged ions in the case of (8a) with $m/z=55$ and 71 , and for (8b) $m/z=57$ and 73 , which are recorded in the mass spectrometric experiment, Fig. 2a). The same analysis can be carried out for the possible case of the asymmetric fission mode of the glucose molecule: $C_6H_{12}O_6 \rightarrow C_2H_5O_2^+ + C_4H_7O_4^+$. A calculation similar to (8) leads to two fragment fragments of the molecule having m/z values: (27, 85) and (43, 101). For another asymmetric scheme $C_6H_{12}O_6 \rightarrow C_2H_3O_2^+ + C_4H_9O_4^+$, there are the following sets of m/z : (42, 104) and (41, 89). It should be noted that the experiment, Fig. 2, a) indicates insignificant yields of molecular fragments with m/z values greater than 75, so the asymmetric channel of glucose destruction cannot be considered dominant.

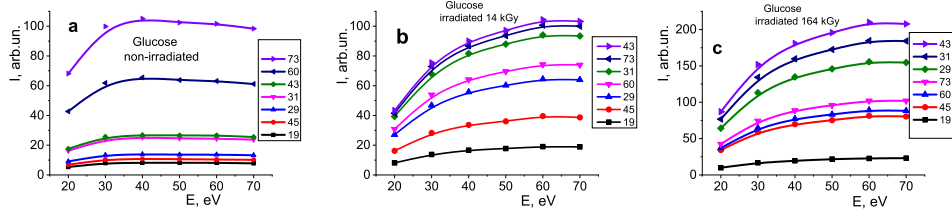
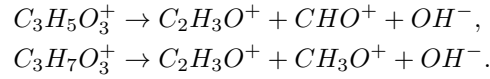


Fig. 3 Energy dependences of the molecule glucose fragments yields: a) before irradiation, b),c) irradiated with a dose of 14 and 164 kGy, respectively, Numbers on the right side of the pictures are the m/z values from Fig.2, curves are the B-spines of experimental points.

Furthermore, since the energy of the electron beam is 70 eV, the contribution to the mass spectra from processes with the formation of three or more molecular fragments is also insignificant. Therefore, the spectra and Fig. 2 a) can be explained as a result of the symmetric fission of the molecule during interaction with electrons. Mass spectra of glucose samples previously irradiated on the M-30 microtron with different doses demonstrate the preservation of the main groups of glucose fragment ion yields and a significant redistribution of their intensities. Furthermore, an interesting regularity is observed when, with a decrease in the intensity of yields in the vicinity of $m/z = 73$, there is an increase in the yields in the area of $m/z - 27; 45$, corresponding to the following symmetric fission of segments of the glucose molecule, (7).



(9)

Fission schemes (9) lead to a decrease in the intensity of the symmetric fission fragments yield, Fig. 2 a) and amplification of lines in the vicinity of $m/z - 31; 43$, which is observed in Fig. 2 c) and e).

The argument for the formation of mass spectra of irradiated glucose samples as the second step destruction of its parts through the channels (9) is the increase in yields of light fragments with an increase in the dose of irradiation of the original samples.

And finally, it is convenient to use the method of structural combinations and the system of equations (2) to study the possible structural fragments during the dissociation of a glucose molecule under the switching of its homo-, hetero bonds and the regularity of fragmentation. By considering the importance of glucose for biota, it is necessary to investigate the nature of its stability, information capacity, and characteristics accompanying the processes of its fragmentation in biological processes.

The configurational entropy of the molecule S can be determined by the term:

$$S = \ln \left(\sum_{\{k_i\}} \left(\frac{M!}{\prod_{i=1}^n k_i!} \right) \right), \quad \sum_{i=1}^n k_i = M, \quad (10)$$

where, according to Fig. 1, $M=20$, and the set $\{k_i\}$ corresponds to the color sets Ccohh, 4Ccohh, Cc2oh, 5Och, O2c, 7Hc, 5Ho, $n=7$. Equations (10) gives the following value

for $S=33.76$, which can be used to determine the value of the information capacity (in bits) as $I = S/\ln(2)$. Thus, $I=48.7$ bits of information, the relative value of which is only 30% less than for amino acids. In other words, glucose is an essential supplier of structural components of biological objects to ensure their physiological and informational functioning. Thus, the analysis of molecular structures for this composition of glucose atoms using (2) shows the total number of possible combinations for forming a molecule with the formula $C_{0.25}H_{0.5}O_{0.25}$, including 1D, 2D, and 3D complexes is 12. In the explanation of the processes of fragmentation of the molecule through channels (7),(8) and (9), it is necessary to find the solution of system (2), assuming breaks in C-O and C-C bonds. The calculation shows that the number of structural combinations to realize structural fragments formed when the C-O single bond is broken is 11, double - 10. The same picture occurs when C-C bonds are broken. This fact corresponds to the hierarchy of bond strength (1) and confirms the proposed fragmentation channels of the glucose molecule in mass spectrometric experiments.

5 Conclusions

Thus, the results of mass spectrometric studies of irradiated and non-irradiated samples make it possible to establish the fragmentation channels of glucose' molecules, in particular, when interacting with low-energy electron beams. One may assume that the same ways of fragmentation of glucose will be under chemical, thermal, and biological processes. Furthermore, a high level of fragmentation of glucose under the influence of external factors is shown, which confirms its main function of providing structural components for the functioning of biomolecules. For the first time, the database of dose dependence of the mass spectra of glucose samples under high-energy radiation was obtained, and the features of the fission fragment yields depending on the energy of the scanning electron beam were established. The obtained data are important for establishing the nature of monosaccharides' stability and studying their fragmentation during various types of transformations. In particular, arguments are presented in favor of the dominance of the symmetric fission channel of both the molecule itself and its fragments formed under the action of radiation. Studies of the energy dependence of mass spectrum fragment yields testify to the non-equilibrium state of the array of molecular fragments formed after the action of high-energy radiation. Using the method of the structural combination allows us to investigate possible structural combinations of glucose atoms initiated by radiation to evaluate possible clustering schemes of molecular structures in irradiated samples after the relaxation of radiation damage. Probable structural formulas for the molecular segments of the fission fragments of unirradiated and irradiated glucose observed in the mass spectra are proposed. Furthermore, by introducing the concept of colored sets of glucose atoms, its information capacity can be estimated and compared with the same characteristic for amino acids.

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