Mechanochemical Transformations of the Crystalline Anomers of *D*-Glucose

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Abstract

The transformations that proceed during mechanochemical treatment of the crystalline anomers of *D*-glucose have been studied. It is established that a solid organic acid or solid inorganic ampholyte ($NaHCO_3$) are efficient catalysts of the solid-phase anomerization of *D*-glucose. It is demonstrated that mechanical activation in the presence of a solid organic acid gives rise to the products of *D*-glucose dimerization. β-*D*-glucose shows the highest reactivity in reactions of solid-phase anomerization and dimerization. The difference in reactivity between the two crystalline anomers arises from the efficient mechanism of proton transfer inherent in the β-anomer. Unlike α-*D*-glucose, the β-anomer shows electrical conduction, which is most likely to be due to proton transfer for this class of substances. Conduction of crystalline β-*D*-glucose depends on the defectness and correlates with the reaction rate of mechanochemical anomerization.

INTRODUCTION

Great attention has recently been paid to research into chemical processes that take place during mechanical treatment of carbohydrates. The majority of works deal with processing of polysaccharides, which have found wide use in technology [1–5]. The potential application as chelating agents for carbohydrates gave an impetus to the creation and study of systems in which complex carbohydrates perform the function of carriers for biologically active compounds [6–8]. For example, cyclodextrins are useful in the production of effective pharmaceutical substances [9, 10]. Data are also available on the possibility of using disaccharides (*e. g.*, lactose) as efficient carriers of medicinal substances [11].

Simple carbohydrates, for example, saccharose and glucose, may be used for mechanochemical activation of extraction of biologically active compounds from vegetative raw materials, and also for mechanochemical preparation of drugs with pronounced physiological activity. In the latter case, mechanochemical treatment in the presence of simple carbohydrates makes it possible to obtain compositions in which biologically active compounds, for example, phytosterols and phytoecdisteroids, are present in a water-soluble form [12, 13].

Transformations of polysaccharides and oligosaccharides that take place during mechanochemical treatment have been studied much more thoroughly than the transformations of simple carbohydrates (mono- and disaccharides). With lactose as an example, it has been demonstrated (using polarimetry) that mechanical treatment may be accompanied by isomerization of carbohydrates, namely, by conversion of one anomer into another [14].

Despite great progress in the field of organic mechanochemistry, a detailed research of mechanochemical transformations of simple carbohydrates using the system of contemporary physical and chemical methods has yet to be performed. The purpose of the present work is the study of the chemical transformations of the crystalline anomers of *D*-glucose under mechanical activation

conditions. An attempt has been made to systematically study the products by chemical analysis, polarimetry, IR spectroscopy, chromatography, mass spectrometry, differential scanning calorimetry, and electric conductivity measurements. Mechanisms of physical and chemical processes, occurring during mechanical activation of *D*-glucose, are suggested.

EXPERIMENTAL

Reagents of chemically pure or analytical grade were used. The solvents were refined by the standard procedures [15].

Crystalline α-*D*-glucose was obtained by the procedure of [16]. IR spectrum, cm^{-1}: 3330 (νO–H), 2945, 2916, 2894 (νC–H), 917 (*as* of the ring), 841 (atomic group at C-1), 775 (breathing rings) [17]. According to X-ray phase analysis (XRPA), the product was the crystalline orthorhombic phase of α-*D*-glucose [18]. Crystalline β-*D*-glucose was obtained by recrystallization from pyridine. IR spectrum, cm^{-1}: 3330 (νO–H), 2940, 2890 (νC–H), 900 (atomic group at C-1) [17]. According to XRPA, the product consisted of the crystalline orthorhombic phase of β-*D*-glucose [19].

Mechanical treatment was carried out in an AGO-2 planetary centrifugal mill (Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk) with water cooling and in a Spex Mill 8000 (USA) vibrating mill. Conditions of mechanical treatment in AGO-2: rotating speed of steel reactors 630 min^{-1}, weight ratio between the milling bodies and reagent sample 20 : 1. Conditions of mechanical treatment in Spex Mill 8000: agate reactor and milling bodies, ratio between the weights of the milling bodies and reagent samples 10 : 1.

Quantitative analysis of hydroxyl groups in the products of mechanical treatment was performed by the modified method of Ogg, Porter, and Willits [20]. A 15 : 10 : 5 : 1 mixture of pyridine, Ac_2O, EtOAc, and 1-methylimidazole was used as acetylating agent. The free acid was determined by potentiometric titration on an "Anion-4100" ionometer-conductometer equipped with a combined glass electrode ESK-1060/7.

Complete acetylation was conducted in pyridine using 1-methylimidazole as a catalyst. The mechanically activated sample (400 mg) was dissolved in warm pyridine (2.0 ml), and 1-methylimidazole (0.16 ml) and cool Ac_2O (1.6 ml) were added. The reaction mixture was shaken for 40 min. The products of acetylatation were extracted with Et_2O after cold water had been added (10 ml). The extract was washed with a saturated NaCl solution and then analyzed by MS-HPLC. Acetylation, in the version used here, proceeds with a loss of configuration at C-1 and gives the α-anomer [21].

Trimethylsilation of the products of mechanochemical treatment was performed by a procedure that allowed the reaction to be conducted quantitatively with retention of configuration at the C-1 atom of glucose [22]. The contents of the glucose anomers in the obtained samples were analyzed by GLC and MS-GLC.

MS-HPLC analysis [23] was carried out on a liquid chromatograph with a mass-selective detector (Agilent 1100 Series LC/MSD). Chromatography conditions: column Zorbax XDB-C8 4.6×150 mm, particle size 5 μm, mobile phase H_2O–CH_3OH, linear gradient 40–90 % CH_3OH, flow rate 1.00 ml/min. Positive scan after chemical ionization at atmospheric pressure (APCI) was carried out using a mass-selective detector with a quadrupole analyzer (G1946C model), the scan range corresponded to the ratio $m/z = 100–1000$. The eluent was distilled off in a spray chamber using a gas-drier stream (N_2) 7 l/min; sprayer temperature 340 °C, pressure on the sprayer 4.42 atm, and evaporator temperature 350 °C.

Gas chromatographic analysis of the trimethylsilation products was carried out on a Hewlett-Packard 5890A chromatograph with a quadrupole mass-analyzer (electron impact ionization, 70 eV) and on a «Model 3700» chromatograph equipped with a flame ionization detector. The components were separated in a programmed heating mode (250–280 °C, 10 °C/min) on 25 m quartz capillary columns (internal diameter 0.2 mm, thickness of the SE-30 ILP layer 0.32 μm).

Diffractograms were obtained on a DRON-4 diffractometer (CuK_α radiation); the angles of optical rotation of the samples were measured

TABLE 1

Specific rotation for aqueous solutions of the starting anomers of glucose and for samples mechanically activated in an AGO-2 planetary-centrifugal mill for 5 min

Sample	$[\alpha]_D^{25}$, deg
Starting β-*D*-glucose	19.6
β-*D*-glucose mechanically activated without additives	19.8
The same with *p*-$ClC_6H_4SO_3H$	42.2
The same with $NaHCO_3$	39.0
Starting α-*D*-glucose	110
α-*D*-glucose mechanically activated without additives	109
The same with *p*-$ClC_6H_4SO_3H$	78.8

on a Polamat A device (Carl Zeiss Jena) at 578 nm. IR spectra were taken on a VEKTOR 22 (Bruker) spectrometer for KBr pellets.

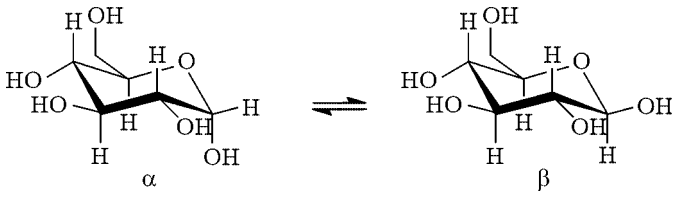
The specific surface of the samples was determined from thermal desorption of argon with an internal standard [24]. Prior to measurement, the samples were warmed in a flow of Ar and He at 80 °C for 0.5 h.

Electric conductivity measurements were performed for pellets obtained by pressing at 200 MPa with pressed-in powder copper electrodes; forevacuum $1.3\ 10^{-4}$ atm, temperature 25–120 °C, LCR Hewlett-Packard HP-4184A high-precision analyzer.

RESULTS AND DISCUSSION

Mechanochemical isomerization of the crystalline anomers of glucose

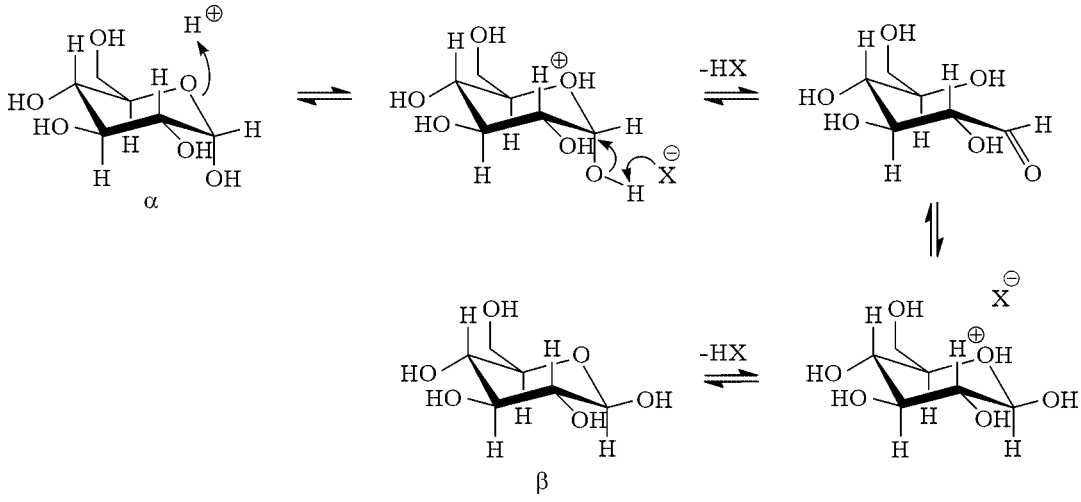
Table 1 shows how specific rotation changes in mechanically activated crystalline anomers of *D*-glucose. It was found that mechanical activation of *D*-glucose anomers with an addition of a solid acid (*p*-$ClC_6H_4SO_3H$) or solid ampholyte ($NaHCO_3$) (2 mass %) leads to interconversion of the anomer modifications (Scheme 1). The formation of anomers is confirmed by IR spectroscopy and MS-GLC. Similar tautomeric transformations are known as ring-chain tautomerism.



Scheme 1.

In protic solvents (water, methanol, *m*-cresol), ring-chain tautomerism (mutarotation) proceeds by the mechanism presented in Scheme 2. The rate-determining stage of mutarotation is the intermediate formation of an open form, occurring via protonation of the ring oxygen and deprotonation of the hydroxyl group at the C-1 atom of the anomer [25]. The mutarotation is considerably accelerated by acids and bases. As the reaction rate is limited by deprotonation of hydroxyl at C-1, the effect of bases is stronger [26]. The key stage of mutarotation requires an acid to donate a proton to ring oxygen and a base to accept a proton from the hydroxyl at C-1. Therefore, mixtures of acid and base, for example, phenol and pyridine, as well as ampholytes, for example, 2-oxypyridine, produce a stronger catalytic effect than the acid or base alone [27].

The mechanism of anomerization in the solid phase probably has much in common with mutarotation observable in aqueous solutions. Solid-phase anomerization proceeds with an appreciable rate only when a substance able to act as a proton donor has been added to the system. *p*-Chlorosulfonic acid and $NaHCO_3$ were equally strong catalysts of the mutual transformation of anomers, while Na_2CO_3 failed to cause any appreciable change. Hence, solid-phase anomerization is most likely to proceed through protonation of the pyranose ring.



Scheme 2.

Conceivably, glucose molecules or crystalline structure defects (for example, glucosate ion) located on the surface or in the near-surface layer might be proton acceptors taking the proton from the C-1 hydroxyl. In this case, the catalyst (proton) transfer may be realized not only on the surface, but also in the bulk of crystal.

Comparative kinetic experiments using a Spex Mill low-intensity activator established that solid-phase anomerization of α-*D*-glucose in the presence of a solid acid occurs after a prolonged induction period (Fig. 1). The divergent behavior of *D*-glucose anomers in relation to solid-phase anomerization is testimony in favor of the fact that one of them, namely, the β-anomer has a more efficient mechanism of proton transfer, which is essential to the key stage of anomerization. If the mechanisms that ensure both proton emergence in the system and its mobility are actually realizable, then *D*-glucose anomers are expected to exhibit conduction, and its value will correlate with the reactivity of the anomer.

It was established that β-*D*-glucose, as distinguished from the α-anomer, shows appreciable electric conductivity whose value is comparable to the value for ionic conductors. Protons are the most probable charge carriers in the given class of substances. Factors responsible for the appearance of mobile protons are either dissociation of water molecules adsorbed on the surface or bulk molecules or intrinsic dissociation of glucose followed by the transfer of a proton or proton hole over the system of hydrogen bonds:

$$2G{-}OH \rightarrow G{-}O^- + G{-}OH_2^+$$

$$G{-}OH^+ + G{-}OH \rightarrow G{-}OH + G{-}OH^+$$

$$G{-}O^- + G{-}OH \rightarrow G{-}OH + G{-}O^-$$

The difference in the conductivity of the anomers may stem from the differences in their specific surface, dissociation energy, or mobility of the above-mentioned proton defects due to peculiarities of crystal lattice or surface structure.

The results of measurements of the temperature dependence of conductivity are presented in Fig. 2 for pellets pressed from crystalline β-*D*-glucose and for mechanically activated samples. The conductivity abruptly de-

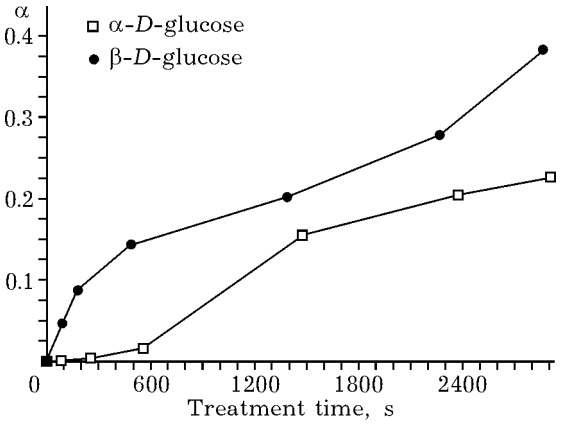


Fig. 1. Fractional conversion α of the crystalline anomers of *D*-glucose in the course of mechanical activation in the presence of *p*-$ClC_6H_4SO_3H$ (2 mass %).

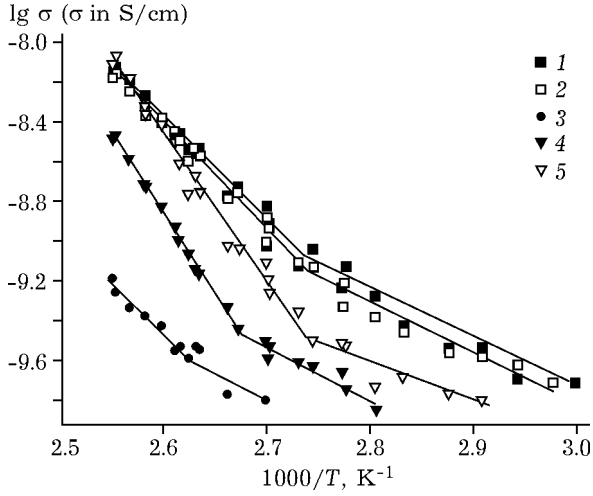


Fig. 2. Change in electric conductivity of β-*D*-glucose as a function of mechanical activation time, s: 0 (*1*), 600 (*2*), 1200 (*3*), 1800 (*4*), 2400 (*5*).

creases in the course of mechanical activation and then rises. The specific surface does not change. The decreased rate of solid-phase anomerization of β-*D*-glucose (treatment time 1200 s) correlates with the decreased conductivity for mechanically activated samples of β-*D*-glucose (Fig. 3), *i. e.* with the decreased quantity of protons most likely to be charge carriers.

The initial drop in conductivity and its subsequent growth correlate with the change in the melting heat of β-*D*-glucose (Fig. 4). Based on DSC data, the maximum level of stored energy (+10 % of the heat of melting) was registered for the sample with the least conductivity (β-*D*-glucose activated for 1200 s); the

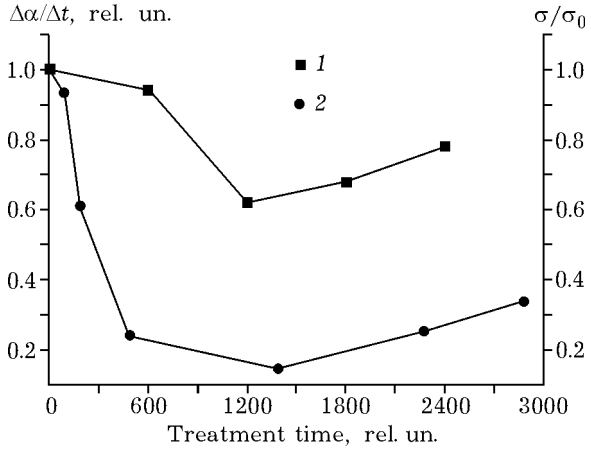


Fig. 3. Change in electric conductivity of β-*D*-glucose *(1)* and anomerization rate *(2)* during mechanical activation. The ratio σ/σ_0 is given for the ambient temperature.

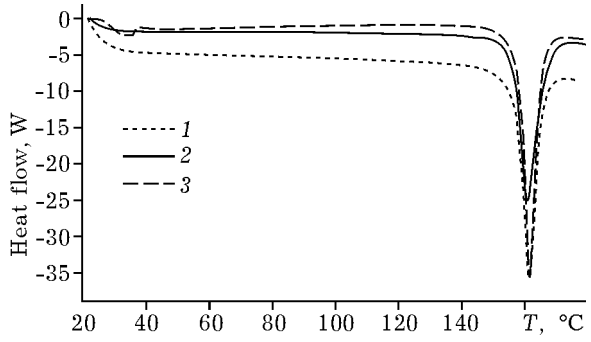


Fig. 4. Variation of the melting heat of β-*D*-glucose during mechanical activation:

Curve No.	Treatment time, s	Melting heat, J/g
1	0	188.3
2	1200	174.9
3	2600	195.6

minimum level was reported for the final sample. Due to mechanical activation, the level of defectiveness of the crystalline phase of β-*D*-glucose at first increases (for treatment time of less than 1200 s). The resulting defects (dislocations, shifts of layers, disturbances in the hydrogen bonds system, *etc.*) probably decrease the mobility of the charge carriers. After 1200 s of activation, the melting heat of β-*D*-glucose increases. The decrease in the level of defectiveness of the crystalline phase is accompanied by an increase in electric conductivity.

Mechanical activation alters the diffraction pattern of crystalline β-*D*-glucose insignificantly (Fig. 5). The diffraction intensities are redistributed in the region $2\theta = 15-20°$. Most probably, the observed effects of disordering mainly relate to the hydrogen bond subsystem.

Based on the results obtained it may be deduced that the reactivity of *D*-glucose anomers in solid-phase anomerization is controlled by the mechanism of the catalyst (proton) transfer. Unlike the α-anomer, β-*D*-glucose offers a more efficient mechanism of proton transfer, which is supported by a comparison of the kinetic and conductivity data.

Mechanochemical dimerization of glucose anomers

Variation of the specific rotation of the samples subjected to short mechanical activa-

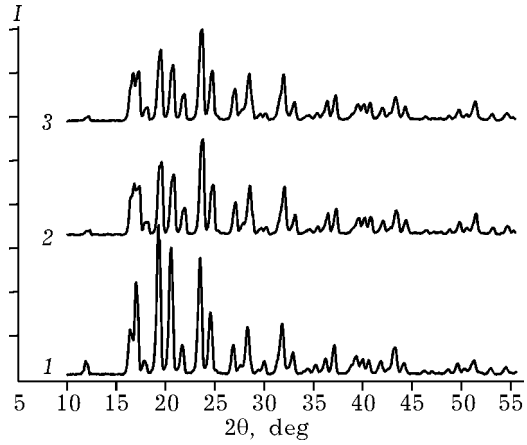


Fig. 5. Variation of the diffraction pattern of β-*D*-glucose during mechanical treatment. Treatment time, s: 0 (*1*), 1200 (*2*), 2400 (*3*).

tion is mainly caused by ring-chain tautomerism. Figure 6 shows the IR spectra of the starting glucose anomers and the products of their mechanical activation in AGO-2 for 5 min. For β-*D*-glucose samples mechanically activated with an acid, the IR spectra exhibit a band at 920 cm^{-1}, which corresponds to the asymmetric vibrations of the pyranose ring of the α-anomer. The spectra also show the vibration band of the atomic group at C-1 (840 cm^{-1}) characteristic of the α-anomer. A similar pattern is also observed when sodium hydrocarbonate is used as a catalyst for anomerization.

For samples subjected to prolonged mechanical activation in AGO-2 (more than 10 min) in the presence of a solid acid, the IR spectra exhibit more substantial changes. Quantitative analysis of the hydroxyl groups demonstrated that some hydroxyl groups of glucose are modified during mechanical treatment in the presence of a solid acid. Compared to the initial samples, the lack of hydroxyl groups was 7.2 % for α-*D*-glucose and 11 % for the β-anomer. This means that every second glucose molecule changed its functional features during mechanical treatment.

As is well known, simple carbohydrates easily enter reactions catalyzed by acids and bases. Under the action of acids and bases the functional nature of monosaccharides experiences radical changes [28]. Thus, reversion of monosaccharides (a reaction reverse to hydrolysis of oligosaccharides) is observed in the presence of inorganic acids [29].

To study the products of mechanochemical transformations of *D*-glucose we used the MS-GLC method. The chromatographic analysis of the products was carried out after synthesis of their trimethylsilyl ethers. Along with α- and β-glucose anomers identified by comparison with authentic samples, high-molecular compounds have been detected in the products of mechanochemical treatment, which corresponded in their relative retention times and character of fragmentation in mass spectra to trimethylsilyl ethers of disaccharides [22, 30]. Mass spectra of these substances contained fragments typical for saccharide trimethylsilyl ethers: $[C_3H_9Si]^+$ (m/z = 73), $[C_4H_{11}OSi]^+$ (m/z = 103), $[C_6H_{13}OSi]^+$ (m/z = 129), $[C_5H_{11}O_3Si]^+$ (m/z = 147), $[C_7H_{17}O_2Si_2+H]^+$ (m/z = 190), $[C_8H_{20}O_2Si_2]^+$ (m/z = 204), $[C_9H_{21}O_2Si_2]^+$ (m/z = 217), $[C_{15}H_{34}O_4Si-H]^+$ (m/z = 361). The greatest contribution to the total ionic current was made by the $[C_8H_{20}O_2Si_2]^+$ fragment with m/z = 204, which

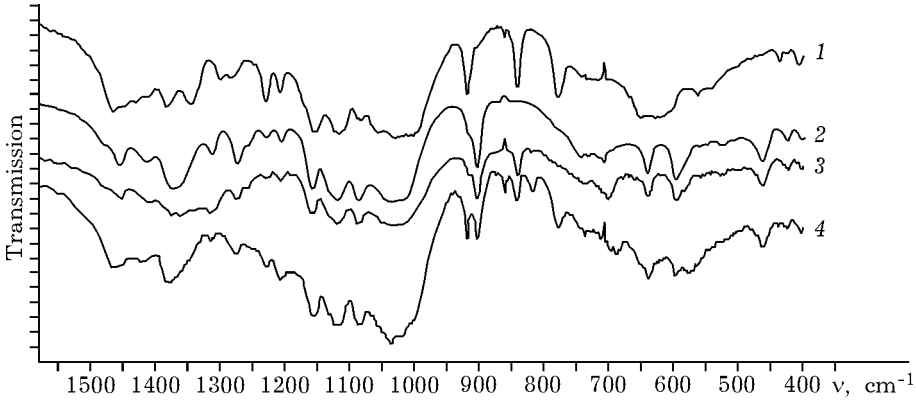


Fig. 6. IR spectra of α-*D*-glucose (*1*), β-*D*-glucose (*2*), products of mechanical activation of β-*D*-glucose for 5 min in the presence of $NaHCO_3$ in AGO-2 (*3*) and in the presence of *p*-$ClC_6H_4SO_3H$ (*4*).

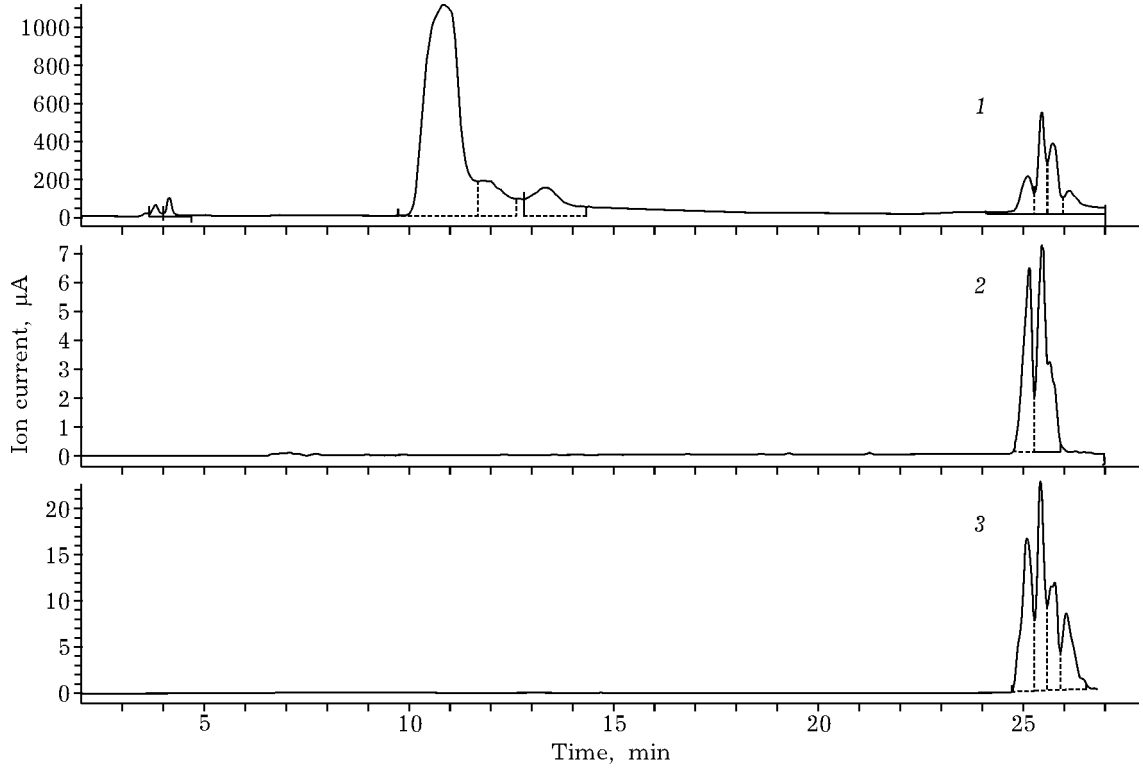


Fig. 7. Results of the analysis of acetylated products of the mechanical treatment of α-*D*-glucose in AGO-2 in the presence of *p*-$ClC_6H_4SO_3H$ (10 mass %) by MS-HPLC (chemical ionization): *1* – chromatogram for the total ionic current; *2* – extracted chromatogram for the $[M + CH_2O]^+$ pseudomolecular ion with m/z = 708, *3* – the same for the $[M\text{-}C_2H_3O_2]^+$ fragment with m/z = 619.

is typical for trimethylsilyl ethers of carbohydrates constructed from six-membered (hexapyranose) rings [31]. Hence, the substances found are the products of glucose reversion.

The MS-HPLC method, combining liquid chromatography with mass spectrometry, also proved the presence of reversion products in the samples obtained by mechanical treatment of α-*D*-glucose and β-*D*-glucose in the presence of a solid acid. On the chromatogram of the total ion current (Fig. 7), the peaks with retention times of 10–15 min correspond to compounds with a molecular weight of 390.3, *i. e.*, to hexose pentaacetates. Probably, acetylation under the given conditions was accompanied by interconversion of anomers and partial transformation of al forms into oxo forms. This transformation occurs readily enough in the presence of bases, in particular, pyridine [32]. Probably for this reason, three pentaacetates instead of two were eluted from the mixture. Between the 24th and 27th min, octaacetates with a molecular weight of 678.6 are eluted (pseudo-molecular ion $[M + CH_2O]^+$ with m/z = 708). The character of fragmentation in mass spectra is similar for pentaacetate and octaacetate. In all cases, fragments corresponding to metastable ions with m/z = 109, 127, 169, 211, 229, 331 are observed. The presence of these ions is typical for mass spectra of acetylated sugars and fits in the fragmentation scheme suggested in [33].

According to chromatographic analysis, the yield of dimers amounts to approximately 15–20 %. Taking into consideration the conversion (50 %) estimated from the results of quantitative determination of hydroxyl groups, one can conclude that the reversion products are not limited to disaccharides. Mechanical treatment of glucose with a solid acid addition is most likely to be accompanied by more profound transformations and to result in oligomerization products.

CONCLUSIONS

The physical and chemical consequences of mechanochemical treatment of the crystalline

anomers of *D*-glucose have been studied. It is established that solid organic acids or solid inorganic ampholytes ($NaHCO_3$) are effective catalysts of solid-phase anomerization of *D*-glucose.

It has been demonstrated that mechanical activation in the presence of a solid organic acid results in *D*-glucose dimerization products. β-*D*-Glucose shows the highest reactivity in reactions of solid-phase anomerization and dimerization. The divergent reactivity of the two crystalline anomers is due to the efficient mechanism of proton transfer available in one of them (β-anomer), which catalyzes the transformations above.

Unlike α-*D*-glucose, the β-anomer shows electrical conduction, which is most likely to result from the proton transfer for this class of substances.

The magnitude of conduction in crystalline β-*D*-glucose depends on the structure defectiveness and correlates with the reaction rate of mechanochemical anomerization.

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