ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 4, pp. 550–555. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © A.N. Simonov, L.G. Matvienko, O.P. Pestunova, V.N. Parmon, N.A. Komandrova, V.A. Denisenko, V.E. Vas'kovskii, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 4, pp. 586–592.

MECHANISMS OF CATALYTIC REACTIONS

Selective Synthesis of Erythrulose and 3-Pentulose from Formaldehyde and Dihydroxyacetone Catalyzed by Phosphates in a Neutral Aqueous Medium

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Received September 26, 2006

Abstract—The aldol condensation of formaldehyde and the lower carbohydrate dihydroxyacetone in a neutral aqueous medium is effectively catalyzed by solid compounds (hydroxylapatite and calcium phosphate and carbonate), natural minerals (apatite and vivianite), and soluble phosphates. In excess formaldehyde, the decrease in the concentration of the lower carbohydrate is described by a first-order rate law with respect to dihydroxyacetone. The major products of the reaction between formaldehyde and dihydroxyacetone in the presence of the above catalysts are erythrulose (45–50% selectivity) and 3-pentulose (35–40% selectivity). Branched pentulose and hexulose are also identified among the reaction products.

DOI: 10.1134/S0023158407040118

INTRODUCTION

The simplest method for the synthesis of higher monosaccharides from simple compounds is the formose reaction [1], which is the autocatalytic oligomerization of formaldehyde in an aqueous alkaline medium in the presence of a base. Due to intensive studies of the mechanism of the formose reaction [2, 3], it became clear that the overall process is almost uncontrollable because of many parallel aldol condensation, retroaldol cleavage, and isomerization reactions catalyzed by hydroxide ions. Indeed, the formose reaction yields more than ten carbohydrates, and it is hardly possible to enhance the selectivity of the process in a strongly alkaline medium. To enhance the selectivity of the process, it is necessary to rule out the retroaldol cleavage reactions, which are responsible for the autocatalytic character of the formose reaction, and to retard the aldol condensation of formaldehyde with carbohydrates in order to prevent the uncontrollable growth of the carbohydrate chain. Based on these ideas, we studied the possibility of selective synthesis of monosaccharides from formaldehyde and the lower carbohydrates in a neutral medium in the absence of dissolved calcium ions, under conditions excluding the retroaldol cleavage of the synthesized carbohydrates. A number of heterogeneous and homogeneous phosphates were chosen as catalysts.

There have been several works aimed at increasing the selectivity of the formose reaction using heterogeneous catalysts in neutral media. The earliest and, unfortunately, somewhat unreliable results [4] refer to the selective oligomerization of formaldehyde into ribulose catalyzed by calcium carbonate. It is also known that synthetic corundum at pH 7.4 [5] and carbonate apatite [6] catalyze nonselective formaldehyde aldolization yielding a mixture of carbohydrates. Hexoses can be obtained by the aldolization of glyceraldehyde on an iron oxide catalyst [7]. There were reports concerning the selective synthesis of erythrulose, 3-pentulose, and branched hexulose (2-hydroxymethyl-pentulose) from formaldehyde in nonaqueous solvents, such as DMF and DMSO, in the presence of organic compounds (2-dimethylaminoethanol and thiamine hydrochloride) as catalysts [8–11].

In the present work, we describe, for the first time, the aldol condensation of formaldehyde and the C_3 carbohydrate dihydroxyacetone (DHA) in an aqueous medium at pH 7.3 in the presence of heterogeneous catalysts, namely, hydroxylapatite, calcium phosphate and carbonate, and the natural minerals apatite and vivianite, as well as homogeneous phosphates. It is demonstrated that aldol condensation results in the preferential formation of erythrulose and 3-pentulose with a selectivity higher than 40%.

EXPERIMENTAL

Solutions and chemicals. H_2SO_4 (special purity grade), Na_2HPO_4 (analytical grade), KH_2PO_4 (analytical grade), $Ca_3(PO_4)_2$ (analytical grade), NaOH (analytical grade), HCl (analytical grade), chromotropic acid disodium salt (analytical grade), acetonitrile (special purity grade, sort 1), paraform (high-purity grade), dihydroxyacetone (>98%, Acros Organics), cation-exchange resin KU-2-8, and anion-exchange resin AV-17-8 were used as received.

Natural apatite, $Ca_5(OH, F, Cl)(PO_4)_3$, was received from the Slyudyanka deposit (Irkutskaya oblast, Russia); natural vivianite, $Fe_3(PO_4)_2$, from the Kerch Peninsula (Crimea, Ukraine). The composition and the 98% purity of the minerals were checked by X-ray spectral analysis. Hydroxylapatite, $Ca_5(OH)(PO_4)_3$, was synthesized according to a standard procedure [12].

A formaldehyde solution was prepared by the dissolution of paraform in water on a boiling water bath. 2,4-Dinitrophenylhydrazine (high-purity grade) was recrystallized from ethanol. Water purified with a Milli-Q system (Millipore, United States) was used in all experiments.

Experimental procedure. The experiments involving the heterogeneous catalysts were carried out as follows. A 0.1 M solution of formaldehyde (100 ml) was placed into a deaerated reactor thermostated at 40°C using a KRIO-VT-01 thermostat (Russia). DHA (45 mg) was dissolved in the formaldehyde solution, and 1 g of a heterogeneous catalyst (particle size <0.25 mm) was added. The initial concentration of DHA was 5 mmol/l, and that of the catalyst was 10 mg/ml. In the experiments involving a homogeneous catalyst, a 0.1 M formaldehyde solution in a phosphate (Na_2HPO_4 + KH_2PO_4) buffer was prepared, and no other catalyst was added. The runs in the homogeneous medium were carried out at 40 and 60°C.

The pH of the reaction mixture was measured with an Anion-4101 pH/ion meter (Infaspak-Analit, Russia). The UV–vis spectra of the reaction mixture were recorded on a UVIKON 923 spectrophotometer (Kontron, Italy).

Reaction mixture samples to be analyzed were cooled, centrifuged (in the case of a heterogeneous catalyst), and acidified with sulfuric acid. The acidified samples were analyzed for formaldehyde and carbohydrates.

Analytical methods. The formaldehyde concentration was determined spectrophotometrically [13]. The Ca^{2+} concentration was determined by titration with EDTA [14].

Dihydroxyacetone and reaction products were analyzed by HPLC using precolumn derivatization with 2,4-dinitrophenylhydrazine [15, 16] on a Milikhrom A-02 chromatograph (Ekonova, Russia) equipped with a ProntoSIL-120-5-C18 AQ column (75 × 2 mm) and a UV detector.

Identification of reaction products. The structures of the formaldehyde–DHA condensation products were determined in the reaction mixture obtained at an elevated concentration of the starting carbohydrate. The experimental conditions were as follows: DHA (675 mg) was dissolved in a 0.1 M solution of formaldehyde (150 ml) in a 0.5 M phosphate buffer (Na_2HPO_4 + KH_2PO_4, pH 7.3). The temperature of the resulting mixture was maintained at 60°C for 4 h in an argon atmosphere. Next, the mixture was cooled down and the inorganic salts were removed from the solution using ion-exchange resins (cation-exchange resin KU-2-8 in proton form and anion-exchange resin AB-17-8 in carbonate form).

The HPLC analysis and preparative separation of the mixture were carried out in the isocratic regime (eluant 75% CH_3CN) on a Agilent HPLC 1100 chromatograph (United States) equipped with a ZORBAX Carbohydrate column (4.6 × 250 mm) and a refractometric detector. Carbohydrates in polyol acetate form [17] were analyzed on an Agilent 6850 GL chromatograph (USA) equipped with an HP-5MS capillary column with 5% phenylmethylsiloxane (30 m × 250 μm), using the temperature gradient 150–230°C and a heating rate of 3 K/min. The GLC–MS analysis of the polyol acetates of carbohydrates was carried out on a Hewlett-Packard 5890 chromatograph (United States) coupled to a Hewlett-Packard 5973 mass spectrometer (United States) using the same column and the same conditions as in the case of GLC.

The ^1H and ^{13}C NMR spectra of solutions in D_2O at 20°C (methanol as the internal standard, $\delta_H = 3.30$ ppm, $\delta_C = 50.15$ ppm) were obtained on a Bruker DRX-500 spectrometer (Germany).

RESULTS AND DISCUSSION

Reaction in the Presence of the Heterogeneous Catalysts

The natural minerals apatite and vivianite, synthetic hydroxylapatite, and calcium phosphate and carbonate were used as the heterogeneous catalysts for the condensation of formaldehyde and DHA.

The kinetics of the decrease in the DHA concentration in the presence of different catalysts is shown in Fig. 1. The change in the formaldehyde concentration in all runs was insignificant and was approximately equal to the decrease in the DHA concentration. In all cases, the DHA concentration curves are linearizable in the coordinates of a first-order reaction with respect to DHA (Fig. 1a). Although DHA is among the most active initiators of the formose reaction in an alkaline medium [2, 3], none of the runs resulted in an *S*-shaped formaldehyde consumption curve typical of autocatalytic reactions. Therefore, the reaction between formaldehyde and DHA in the system examined is stoichiometric.

A slight decrease in pH (from 7.3 to 7.0) was observed in 100 h in the reaction involving synthesized hydroxylapatite. Erythrulose, branched hexulose, and a considerable amount of an unknown carbohydrate were identified in the mixture by HPLC using the precolumn derivatization of the carbohydrates with 2,4-dinitrophenylhydrazine. Additional analytical studies (see below)

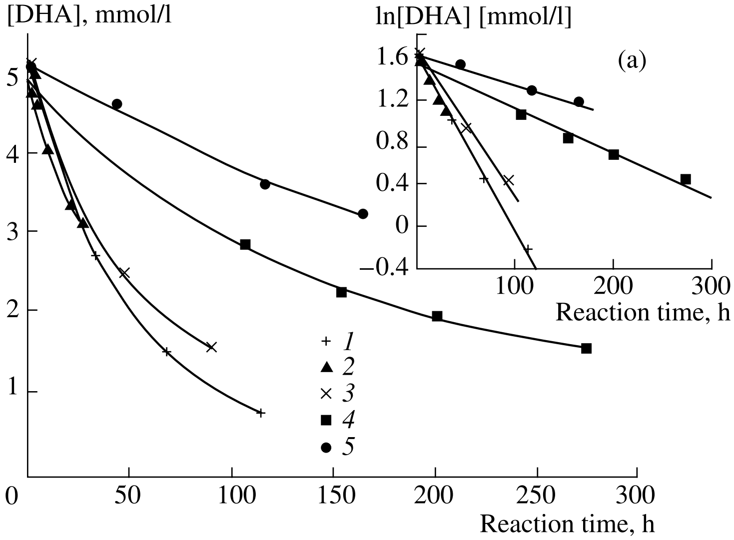

Fig. 1. Time variation of the DHA concentration in the reaction between DHA and formaldehyde in the presence of (*1*) the homogeneous 0.02 M phosphate buffer and (*2–5*) heterogeneous catalysts (Cat): (*2*) natural apatite, (*3*) natural vivianite, (*4*) hydroxylapatite, and (*5*) $Ca_3(PO_4)_2$, $CaCO_3$. $[CH_2O]_0 = 0.1$ mol/l, $[DHA]_0 = 5$ mmol/l, $[Cat]_0 = 10$ mg/ml, and $T = 40$°C. (a) The same data in semilogarithmic coordinates.

showed that the unknown carbohydrate was 3-pentulose, whose concentration in the mixture was close to the erythrulose concentration. The erythrulose selectivity was equal to 45–50%, and the 3-pentulose selectivity was 35–40%. The 3-pentulose concentration was ~1 mmol/l in 100 h. After that the concentration of 3-pentulose remained unchanged, whereas the DHA concentration decreased at the initial rate and the concentration of branched hexulose increased. A decrease in pH was then observed, which was most likely due to the disproportionation of the residual formaldehyde or the rearrangement of carbohydrates, including 3-pentulose, whose concentration decreased in 200 h.

In the presence of $Ca_3(PO_4)_2$, the pH of the reaction mixture was 6.6; for this reason, at the beginning of the reaction, the solution was alkalified with 0.1 M NaOH to pH 7.3, which remained constant during the reaction. The rate of the reaction catalyzed by calcium phosphate was lower than the rate of the reaction catalyzed by hydroxylapatite. Nevertheless, the same products resulted from these reactions. It can be assumed that the decrease in the reaction rate is due to the solubility of $Ca_3(PO_4)_2$ (1.2×10^{-3}%) being lower than the solubility of hydroxylapatite (1.6×10^{-3}%). The solubilities were estimated from the concentration of Ca^{2+} ions in the reaction mixture. The reaction in the presence of $CaCO_3$ proceeded similarly to the reaction catalyzed by $Ca_3(PO_4)_2$.

The addition of natural apatite to a solution of formaldehyde and DHA increased the pH to 8.4. For this reason, the reaction mixture was acidified with 0.1 M HCl to pH 7.3 at intervals. In the presence of natural apatite and hydroxylapatite, the reaction products were the same but the reaction rate in the case of the natural mineral was noticeably higher.

In the presence of natural vivianite, the pH value of the initial solution decreased to 6.3 and, for this reason, the mixture was alkalified with 0.1 M NaOH at intervals. Under these conditions, the DHA concentration decreased considerably (to 1.6 mmol/l) in 90 h. However, only traces of 3-petulose, branched hexulose, and erythrulose were identified in the mixture. Probably, DHA was mainly consumed in the disproportionation reaction rather than in condensation with formaldehyde.

A special-purpose experiment was carried out to answer the question of whether the catalytic effect of the phosphates is heterogeneous or homogeneous. The reaction was performed in the presence of natural apatite, and 24 h after the beginning of the reaction the catalyst was removed from the reaction mixture by filtration through filter paper (blue tape). pH 7.3 was maintained. The removal of the solid apatite particles decreased the reaction rate by a factor greater than 10 (Fig. 2), but the reaction did not stop. The fact that the reaction is not completely terminated can be a consequence of both the catalytic effect of the phosphate and hydrogen phosphate ions that have passed into the solution and the incomplete removal of the heterogeneous catalysts, since micron-sized particles can pass through the filter. Nevertheless, this experiment indicated that the poorly soluble phosphates are involved in the reaction as heterogeneous catalysts.

Reaction in the Presence of the Homogeneous Catalyst

Since we found that the condensation of formaldehyde and DHA can occur in the absence of a heterogeneous catalyst, we carried out several experiments in a homogeneous solution of the phosphate (Na_2HPO_4 +

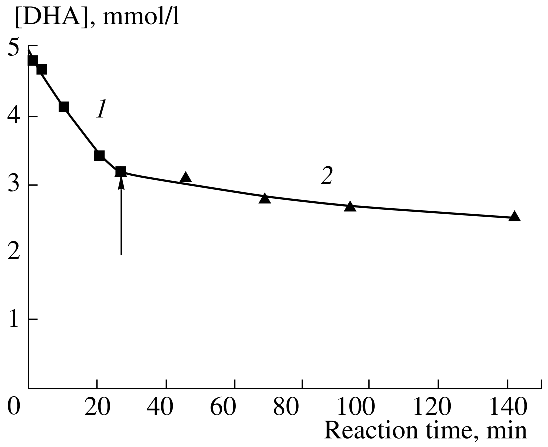

Fig. 2. Time variation of the dihydroxyacetone concentration (*1*) in the presence of natural apatite and (*2*) after the solid phase is removed from the reaction mixture (shown by the arrow). $[CH_2O]_0$ = 0.1 mol/l, $[DHA]_0$ = 5 mmol/l, $[Cat]_0$ = 10 mg/ml, and T = 40°C.

KH_2PO_4) buffer, which was used to maintain the pH of the reaction mixture and as a catalyst.

The reaction rate in the 0.02 M phosphate buffer solution at pH 7.3 and T = 40°C turned out to be higher than the reaction rate in the presence of a heterogeneous catalyst (hydroxylapatite or natural apatite) (Fig. 1). In this case, after a 110-h-long reaction, the DHA concentration decreased to 0.8 mmol/l and the concentration of 3-pentulose was ~1.3 mmol/l.

To elucidate the effect of the concentration of homogeneous phosphate ions on the reaction rate, we carried out experiments at 60°C and different buffer concentrations of 0.5, 0.2, 0.05, and 0.01 mol/l (Fig. 3). It turned out that the reaction order with respect to the phosphate buffer was approximately 0.3. Perhaps such a weak effect of the phosphate concentration on the reaction rate is due to the considerable excess of the buffer over the initial DHA concentration.

We recorded the UV–vis spectra of the reaction mixture in the presence of both the heterogeneous and homogeneous catalysts to obtain additional information about the reaction mechanism. In all experiments, we observed a single absorption band peaking at 290 nm. According to earlier data [18, 19], this band indicates the formation of the enediol form of a carbohydrate. It is well known that the enediol rearrangement of hydroxycarbonyl compounds having a hydroxyl group and a hydrogen atom at the α-carbon atom occurs under base catalysis conditions, like the keto–enol rearrangement in carbonyl compounds. The base catalyst abstracts a proton from the α-carbon atom, electron density redistribution then occurs, the proton adds to the oxygen atom of the carbonyl group, and the base catalyst returns to the initial state. Therefore, the hydrogen phosphate ion acts as a base catalyst and the condensation of DHA with formaldehyde occurs via the addition of a formaldehyde molecule to the deprotonated α-carbon atom of DHA, as in the case of aldol condensation in an alkaline medium. The general reaction scheme that we suggest for homogeneous catalysis is presented in Fig. 4. In the presence of a heterogeneous catalyst, the first step, which is deprotonation, is most likely due to the interaction of a DHA molecule with a phosphate group on the surface of a solid catalyst particle.

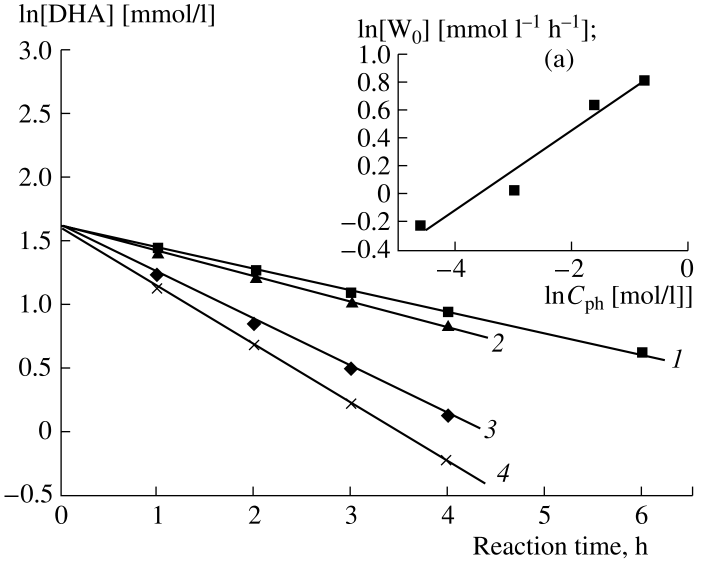

Fig. 3. Time variation of the dihydroxyacetone concentration in the presence of the homogeneous phosphate buffer with a phosphate concentration of C_{ph} = (*1*) 0.01, (*2*) 0.05, (*3*) 0.2, and (*4*) 0.5 mol/l. $[CH_2O]_0$ = 0.1 mol/l, $[DHA]_0$ = 5 mmol/l, and T = 60°C. (a) Dependence of the initial reaction rate on the phosphate buffer concentration in logarithmic coordinates.

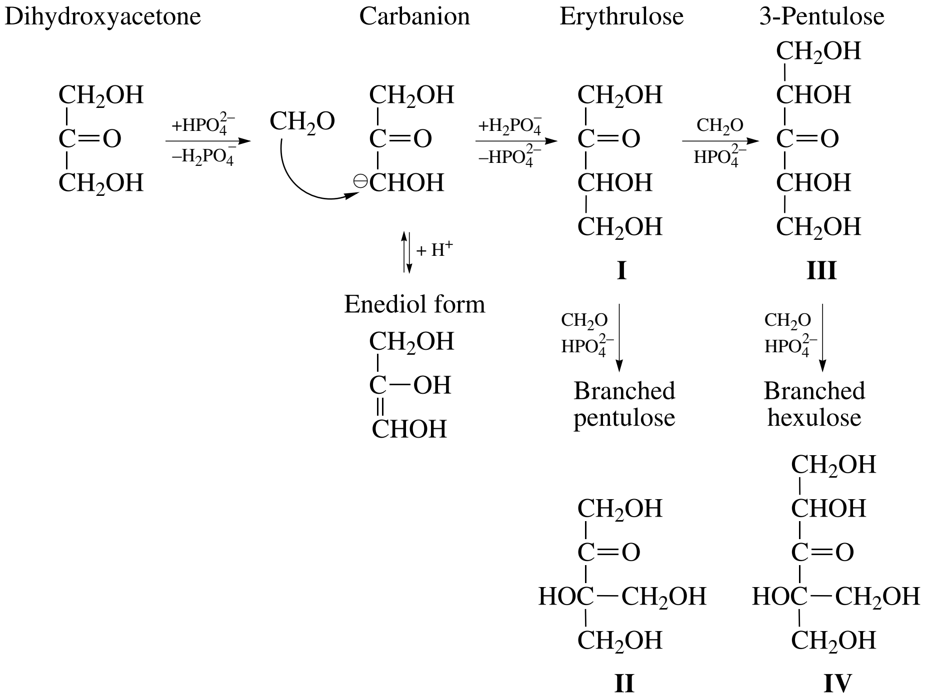

Fig. 4. Condensation of formaldehyde and dihydroxyacetone in the presence of phosphates.

Identification of Reaction Products

An analysis of the reaction products by microcolumn HPLC using precolumn derivatization with 2,4-dinitrophenylhydrazine identified four monosaccharides in the reaction products. Two of them were identified as erythrulose and branched hexulose according to their retention times. We were unable to identify the other products by this method because no standard substances were available. A detailed analytical study was performed to determine the exact composition of the products of the reaction between formaldehyde and DHA in the presence of the phosphate catalysts. In the presence of any of the catalysts, the reaction of formaldehyde and DHA yielded the same products. For this reason, we studied the products of the reaction between 0.05 M DHA and 0.1 M formaldehyde in the presence of the 0.5 M phosphate buffer. Formaldehyde and DHA react stoichiometrically, and the product composition is the same as in the case of an excess of formaldehyde over DHA.

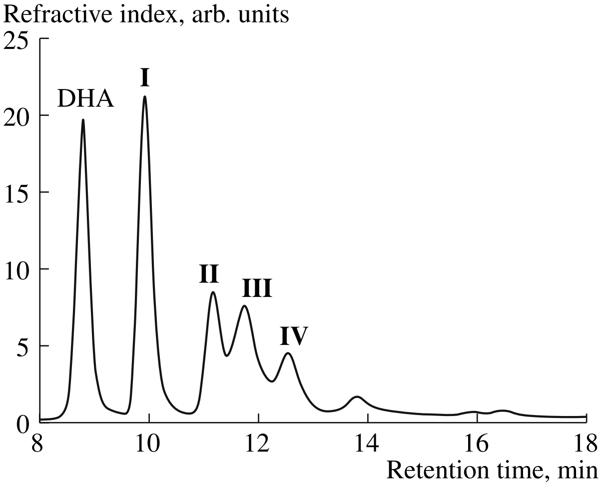

Fig. 5. Analysis of the reaction mixture by HPLC (refractometric detector). The initial composition of the mixture: $[CH_2O]_0 = 0.1$ mol/l, $[DHA]_0 = 5$ mmol/l, 0.5 M phosphate buffer. $T = 60$°C. Before the analysis, the inorganic catalyst was removed by ion-exchange chromatography.

A direct HPLC analysis of the reaction mixture using a ZORBAX Carbohydrate column (Fig. 5) showed that the solution contained DHA and four reaction products. To identify the four unknown products, their fractions were isolated by micropreparative HPLC. The purity of each fraction was checked by HPLC under the same conditions. The amounts of the isolated fractions, which are designated **I**, **II**, **III**, and **IV**, were 10, 2, 9, and 3 mg, respectively. All isolated substances were characterized by GLC, GLC–MS, and ^{1}H and ^{13}C NMR spectroscopy.

The ^{13}C NMR spectrum of substance **I** contained signals from a carbonyl group at 212.7 ppm (1C, C2), hydroxymethyl groups at 66.2 (1C, C1) and 63.2 ppm (1C, C4), and a hydroxymethylene group at 76.2 ppm (1C, C3). The ^{1}H NMR spectrum exhibited the following signals: $\delta_H = 4.47$ (1H, d, $J_{HH} = 19.5$ Hz, C(1)H), 4.41 (1H, d, $J_{HH} = 19.5$ Hz, C(1)H), 4.33 (1H, t, $J_{HH} = 4.2$ Hz, C(3)H), 3.75 (1H, dd, $J_{HH} = 4.2$ Hz, $J_{HH} = 12.2$ Hz, C(4)H), and 3.73 (1H, dd, $J_{HH} = 4.2$ Hz, $J_{HH} = 12.2$ Hz, C(4)H). The only carbohydrate having this set of functional groups is erythrulose. Indeed, GLC and GLC–MS analyses of **I** as polyol acetates showed that the reduction of **I** yields treitol and erythritol, which are the products of erythrulose reduction (Fig. 4, **I**).

The ^{13}C NMR spectrum of fraction **II** contained signals from a carbonyl group at 214.5 ppm (1C, C2), a quaternary carbon atom at 83.9 ppm (1C, C3), and hydroxymethyl groups at 67.0 (1C, C1) and 64.5 ppm (2C, C4, and C5). The presence of a quaternary atom in the structure indicates that substance **II** is a branched carbohydrate. The ^{1}H NMR spectrum of fraction **II** contained the following signals: δ_H = 4.52 (2H, s, C(1)H), 3.70 (2H, d, J_{HH} = 11.7 Hz, C(5)H), and 3.49 (2H, d, J_{HH} = 11.7 Hz, C(4)H). In addition, pentaacetates of two branched polyols were identified by GLC and GLC–MS in the acetylation products of reduced fraction **II**. For this reason, this monosaccharide was identified as branched pentulose, namely, 2-(hydroxymethyl)erythrulose (Fig. 4, **II**).

GLC and GLC–MS analyses of fraction **III** as polyol acetates showed that the reduction of this substance yields polyols corresponding to ribose, arabinose, lyxose, and xylose. The only monosaccharide whose reduction can yield these products is 3-pentulose (Fig. 4, **III**). Its structure was additionally confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum contained signals from a carbonyl group at 212.0 ppm (1C, C3), hydroxymethyl groups at 63.1 ppm (2C, C1, and C5), and hydroxymethylene groups at 76.1 ppm (2C, C2, and C4). The signals in the ^{1}H NMR spectra were as follows: δ_H = 4.56 (2H, t, J_{HH} = 4.2 Hz, C(2)H, and C(4)H); 3.79 (4H, d, J_{HH} = 4.2 Hz, C(1)H, C(1)H, C(5)H, and C(5)H).

The GLC–MS and NMR data obtained for substance **IV** are contradictory. Nevertheless, it can be assumed that this carbohydrate is branched hexulose resulting from the aldol condensation of formaldehyde and 3-pentulose (Fig. 4, **IV**).

CONCLUSIONS

The reaction examined is the condensation of formaldehyde with dihydroxyacetone, a lower carbohydrate. It is one of the numerous parallel reactions that occur in the formose system. The reaction preferentially yields erythrulose and 3-pentulose. The process is catalyzed by heterogeneous phosphate-containing catalysts, such as natural apatite and synthetic hydroxylapatite, and by homogeneous hydrogen phosphate anions. The elongation of the monosaccharide chain proceeds via an aldol condensation mechanism in which the phosphates act as base catalysts. The finding that the reaction rate decreases by a factor larger than 10 upon the removal of the heterogeneous apatite from the system is unquestionable evidence of the substantial catalytic activity of the surface phosphate groups of the heterogeneous catalyst. Due to its rather high selectivity, the catalytic system is promising for the preparative synthesis of rare and expensive monosaccharides from simpler ones.

ACKNOWLEDGMENTS

The authors are grateful to O.P. Moiseenko for help in GLC–MS analysis.

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-32862), the Presidium of the Russian Academy of Sciences (program “Origin and Evolution of Biosphere”), the Ministry of Education of the Russian Federation (grant no. RNP.2.1.1.1969), and the program “Scientific Schools of Russia” (grant no. NSh 6526.2006.3).

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