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Abstract

Full Text

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Study of the Kinetics of Mutarotation of Aqueous Solutions of Monosaccharides

The questions of the kinetics of mutarotation of monosaccharides, despite the fact that numerous works have been devoted to them [1-10], have still not been resolved.

The process of mutarotation may include 6 components (1, 2, 10) (2 anomers of the pyranose form, 2 anomers of the furanose form, and 2 open forms—the hydrate and the oxo form), not counting conformations.

At present, for calculating the kinetics of mutarotation of monosaccharides, two schemes are used, including only 2 and 3 components: scheme (I) for one series of monosaccharides (*d*-glucose, *d*-xylose, *d*-lyxose, etc.), and scheme (II) for another series of monosaccharides (*d*-galactose, *l*-arabinose, *l*-ribose, etc.).

Scheme (II) differs from scheme (I) only by the presence of an open form. But, as is evident from the data of (9) (Table 1), the amount of the open form cannot characterize membership in one or another series of monosaccharides.

Table 1

Relative content of the open—aldehyde—form in aqueous solutions of monosaccharides at 20°C (mole fractions)

d-glucose	*d*-galactose	*d*-xylose	*l*-arabinose	*d*-lyxose	*l*-ribose
0.00024	0.00082	0.00170	0.00280	0.00400	0.08500

Studying the kinetics of mutarotation of aqueous solutions of *d*-xylose, *d*-galactose, and *l*-arabinose by the polarimetric method, we obtained results that do not differ from the literature data.

For *d*-xylose we did not find significant deviations from the requirements of the scheme

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} C \tag{I}$$

and the formula

$$[\alpha_t]^{20}_D - [\alpha_\infty]^{20}_D = \tilde{\alpha}_0 \exp(-k_0 t), \tag{1}$$

where $[\alpha_t]^{20}_D$ and $[\alpha_\infty]^{20}_D$ are the specific rotations, respectively, after time t and at equilibrium (when $t = \infty$); $\tilde{\alpha}_0$ is a coefficient depending on the nature of the monosaccharide; $k_0 = k_1 + k_2$; k_1 and k_2 are the rate constants of first-order reactions; A and C are the specific contents, respectively, of the α- and β-anomers of the pyranose form in solution.

In contrast to *d*-xylose, the changes in the angles for *d*-galactose and *l*-arabinose in the first 10–15 min proceed faster, slowing down subsequently. At the same time, the entire course of the process satisfactorily agrees with the scheme

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \underset{k_4}{\overset{k_3}{\rightleftarrows}} C \tag{II}$$

and by the formula

$$[\alpha_t]^{20}_D [\alpha_\infty]^{20}_D = \tilde{\alpha}_1 \exp(-x_1 t) = \tilde{\alpha}_2 \exp(-x_2 t), \tag{2}$$

where B is the relative amount of the open form of the monosaccharide in solution, and x_1 and x_2 are the roots of the characteristic equation:

$$x^2 - sx + P = 0; \tag{2a}$$

$$s = \sum_{n=1}^{4} k_n; \qquad P = k_1 k_3 + k_1 k_4 + k_2 k_3.$$

Part of the data we obtained is given in Table 2.

Table 2

Parameters of the mutarotation process in aqueous solutions of the monosaccharides studied at 20°

	d-xylose	*d*-galactose	*l*-arabinose		*d*-xylose	*d*-galactose	*l*-arabinose
A_∞, fractions	0.3518	0.2769	0.2004	x_1, min^{-1}	–	0.2075	0.3178
C_∞, fractions	0.6465	0.7223	0.7968	x_2, min^{-1}	–	0.02049	0.06908

	d-xylose	*d*-galactose	*l*-arabinose		*d*-xylose	*d*-galactose	*l*-arabinose
k_0, min^{-1}	0.04322	–	–	$\Phi_{12} = x_1/x_2$	–	10.12	4.600

Note. A_∞ and C_∞ are the relative amounts of the α- and β-anomers in the equilibrium monosaccharide solution.

Our calculations of the relationships between the content of the individual components of the monosaccharide in solution and the process parameters according to scheme (II) led to the ratios

$$\frac{k_1}{k_2} = \frac{B_\infty}{A_\infty} = \delta_1; \qquad \frac{k_3}{k_4} = \frac{B_\infty}{C_\infty} = \delta_2. \tag{3}$$

Assuming that $A_\infty + B_\infty + C_\infty = 1$, with B_∞, and consequently δ_1 and δ_2, being several orders of magnitude less than unity, we obtain the approximate relations:

$$\begin{gathered} s \simeq k_2 + k_4, \qquad P \simeq \frac{B_\infty}{A_\infty C_\infty} k_2 k_4; \\ x_1 \simeq s; \qquad x_2 \simeq \frac{P}{s} \simeq \frac{B_\infty k_2 k_4}{A_\infty C_\infty (k_2 + k_4)}; \\ \Phi_{12} = \frac{x_1}{x_2} \simeq \frac{A_\infty C_\infty (k_2 + k_4)^2}{B_\infty k_2 k_4}. \end{gathered} \tag{4}$$

The ratio Φ_{12} has its smallest value when $k_2 = k_4$; consequently:

$$\Phi_{12} B_\infty \not> 4 A_\infty C_\infty. \tag{5}$$

Substituting the corresponding values from Table 2 into formula (5), we obtain: for *d*-galactose $B_\infty \not> 0.07906$, and for *l*-arabinose: $B_\infty \not> 0.1389$. These values are greater than the analogous values in Table 1 by factors of 100 and 50, respectively. Consequently, the three-component scheme (II) is insufficient for describing all the details of the mutarotation process of monosaccharides of the *d*-galactose and *l*-arabinose type. For this purpose we adopted the scheme

$$\begin{gathered} A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \underset{k_4}{\overset{k_3}{\rightleftarrows}} C, \\ B \underset{k_5}{\overset{k_6}{\rightleftarrows}} D \end{gathered} \tag{III}$$

with the formula

$$[\alpha_t]_D^{20} - [\alpha_\infty]_D^{20} = \tilde{\alpha}_1 \exp(-x_1 t) + \tilde{\alpha}_2 \exp(-x_2 t) + \tilde{\alpha}_3 \exp(-x_3 t), \tag{6}$$

where B and D are, respectively, the hydrate open form and the oxo form; x_1, x_2, and x_3 are the roots of the characteristic equation

$$x^3 - sx^2 + Px - Q = 0; \tag{6a}$$

$$s = \sum_{m=1}^{6} k_m; \qquad P = k_1 \sum_{m=3}^{6} k_m + k_2(k_3 + k_5) + k_3(k_5 + k_6) + k_4 k_5;$$

$$Q = k_1 k_3 k_5 + k_1 k_3 k_4 + k_1 k_4 k_5 + k_2 k_3 k_5.$$

The relation between the various parameters of the process is expressed by the ratios

$$\frac{k_1}{k_2} = \frac{B_\infty}{A_\infty} = \delta_1; \qquad \frac{k_3}{k_4} = \frac{B_\infty}{C_\infty} = \delta_2; \qquad \frac{k_5}{k_6} = \frac{B_\infty}{D_\infty} = \delta_3;$$

$$\frac{k_4}{k_2} = \delta_4; \qquad \frac{k_6}{k_2} = \delta_5; \qquad \frac{x_1}{x_2} = \Phi_{12}; \qquad \frac{x_2}{x_3} = \Phi_{23}. \tag{7}$$

In the mathematical treatment of the experimental data it was established that Φ_{12} is several orders of magnitude greater than unity (if $\delta_3 \leq 1$). The value of Φ_{23} depends mainly on the value of δ_5, exceeding it by less than 50 times. Therefore, according to formula (6), the influence of the first exponential, owing to the relatively large value of Φ_{12}, will be so small that the process is completely described by formula (2). In this case, the condition must be fulfilled under which the value of δ_5 ensures a value of Φ_{23} within the limits $4 \div 10$ (the case of *l*-arabinose and *d*-galactose). If, however, the values of δ_5 and, correspondingly, Φ_{23} prove to be considerably larger, then at the initial moments of the process the influence of the second exponential will disappear, and the process will be completely described by formula (1) (the case of *d*-xylose). Thus, according to scheme (III), all features of the mutarotation kinetics of monosaccharides of the type we have investigated are entirely determined by the kinetics of the transition of the hydrate form of the monosaccharide into its oxo form.

Scheme (III) may change in the case of the presence in solution of furanose rings and conformations, the consequence of which will be a change in the number of terms on the right-hand side of formula (6) and in the degree of the characteristic equation. The principle of the calculation will not change in this case.

The scheme is chosen depending on the experimentally reliably established number of components in solution. The latter depends on the expansion of experimental possibilities, which, however, proceeds slowly.

The considerations set forth open new paths for kinetic studies of the transformations of monosaccharides in solutions.

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Note: Figure translations are in progress. See original paper for figures.

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