THE MUTAROTATION OF α-D-XYLOSE

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The mutarotation reaction is acquiring ever greater importance in the chemistry of the carbohydrates; it greatly extends our ideas of the structure of the molecules of the monosaccharides in solutions and also permits the quantitative amounts of their various anomers to be established [1]. This reaction has been considered in numerous papers. Thus, for example, in a monograph [2], there are more than 700 references on this subject.

The mutarotation of glucose and fructose has been studied to the greatest extent. Xylose, and some other monosaccharides, have attracted less attention even though they are fairly widely distributed in nature.

We have investigated the influence of temperature on the equilibrium and the initial specific angle of rotation of aqueous solutions of α-D-xylose at temperatures of 10-50°C and the kinetics of the mutarotation of these solutions.

Experimental procedure. A 5 g sample of crystalline α-D-xylose was dissolved in 100 ml of distilled water in a measuring flask at the predetermined temperature. The solution was placed in a polarimetric tube 2 dm long having a special jacket for thermostating. The specific rotations were measured on a "SOK-1" instrument. The variation of the temperature did not exceed ±0. 1°C. In all experiments, the concentration of α-D-xylose was the same (5 g in 100 ml of water). Figure 1 gives the mean values (from five parallel experiments) of the equilibrium (final) rotation of aqueous solutions of α-D-xylose as a function of the temperature in comparison with literature data [3, 4].

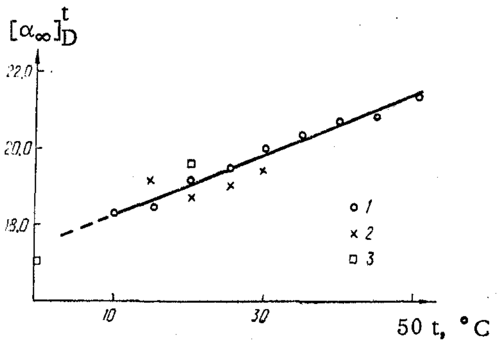

Fig. 1. Specific equilibrium rotation $[\alpha_\infty]_D^t$ (in degrees) as a function of the temperature: 1) points obtained experimentally; 2) from the data of Schulze and Tollens [3]; 3) from the data of Los and Wiesner [4].

As can be seen from Fig. 1, the equilibrium rotations of aqueous solutions of α-D-xylose increase with rising temperature. Mathematical treatment of these data led to the following empirical formula

$$\left[\alpha_0\right]_D^t = 17.58745 + 0.07941\ t, \qquad (1)$$

where $[\alpha_0]_D^t$ is the equilibrium rotation at t°C for the D line of sodium light.

Formula (1) is valid for the range of temperatures from 10 to 50°C. The experimental points are located fairly closely along the regression line obtained from Formula (1). We have studied the kinetics of the mutarotation of aqueous solutions of α-D-xylose for the same temperatures by the method described above. As is well known, according to modern ideas the mutarotation of monosaccharides in solutions takes place in accordance with the following scheme [5]

$$A \underset{K_2}{\overset{K_1}{\rightleftarrows}} B \underset{K_4}{\overset{K_3}{\leftrightarrows}} C.$$

Here, A is the amount of α anomer (closed form), B is the amount of the open aldehyde form (γ form), C is the amount of β anomer (closed form), and K_1, K_2, K_3, and K_4 are the velocity constants of the transformation of one form to another in each case.

Analysis of the differential equations obtained in accordance with the scheme shown above led to the conclusion that the kinetics of the mutarotation of aqueous solutions of α-D-xylose can be described completely satisfactorily by the formula for a first-order reaction:

$$\left[\alpha_t\right]_D^t = \left[\alpha_\infty\right]_D^t + \tilde{\alpha}_1\, exp\,(-x_1 t) + \tilde{\alpha}_2\, exp\,(-x_2 t). \qquad (2)$$

However, for α-D-xylose $\tilde{\alpha}_1$ exp $(-x_2 t)$ is practically zero. Consequently,

$$\left[\alpha_t\right]_D^t = \left[\alpha_\infty\right]_D^t + \alpha_2\, exp\,(-x_2 t). \qquad (3)$$

Denoting $[\alpha_t]_D^t - [\alpha_\infty]_D^t$ by Δ, we obtain

$$\Delta = \tilde{\alpha}_2 \exp(-x_2 t), \tag{4}$$

where Δ is the difference between the rotation at time t and the equilibrium rotation; $\tilde{\alpha}_2$ is a coefficient; x_2 is the mutarotation velocity constant, depending on K_1, K_2, K_3, and K_4; and t is the time from the moment of dissolution in minutes. By taking logarithms of formula (4) we may write the equation

$$\lg \Delta = \lg \tilde{\alpha}_2 - x_2 \cdot t \tag{5}$$

On the basis of the experimental results (Δ and t), we have determined $\tilde{\alpha}_2$ and x_2 by the method of least squares. Figure 2 shows, by means of a graph, the influence of temperature (on the Kelvin scale) on the velocity of mutarotation of aqueous solutions of α-D-xylose.

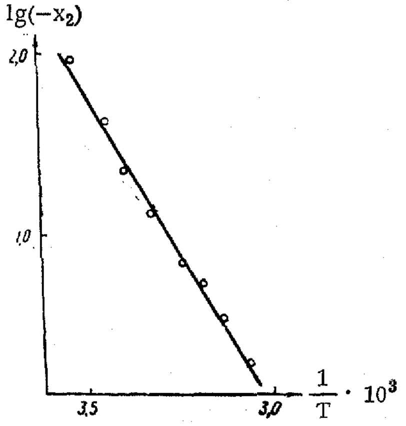

Fig. 2. Velocity constants (x_2) (in $\min^{-1}$) as a function of the reciprocal temperature.

It follows from Fig. 2 that the absolute magnitude of the velocity of mutarotation of aqueous solutions of α-D-xylose increases with rising temperature and is a linear function of the reciprocal of the temperature (in degrees Kelvin). The empirical formula for this function that we have obtained has the form

$$\lg(-x_2) = 10.07 - \frac{3330}{T}.$$

The initial specific rotation of aqueous solutions of α-D-xylose is determined from Formula (5) at t = 0, i. e.,

$$[\alpha_0]_D^t = \tilde{\alpha}_2 + [\alpha_\infty]_D^t,$$

where $[\alpha_0]_D^t$ is the initial rotation; and $\tilde{\alpha}_2$ is a magnitude that can be calculated when the mutarotation velocity constant has been determined.

In this way, the initial specific rotations of aqueous solutions of α-D-xylose have been calculated for various temperatures from the experimental data (Fig. 3). Within the temperature range studied, the corresponding relationship is expressed by the formula

$$[\alpha_0]_D^t = 77.1213 + 0.7135\, t;$$

here $[\alpha_0]_D^t$ is the initial rotation; and t is the temperature, °C.

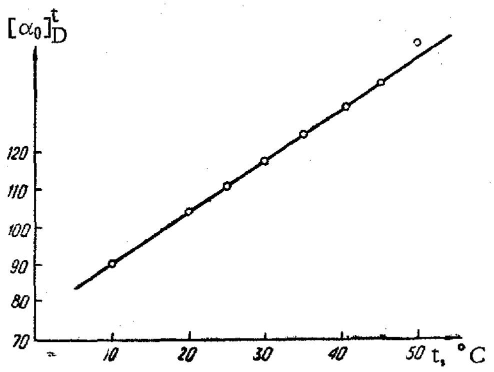

Fig. 3. Initial angle of rotation $[\alpha_0]_D^t$ (in degrees) as a function of the temperature.

Summary

1. The specific equilibrium rotation of aqueous solutions of α-D-xylose in the temperature range from 10-50°C varies proportionally to the temperature and is expressed by a linear relation.

2. The mutarotation velocity constant of aqueous solutions of α-D-xylose increases (in absolute magnitude) with a rise in the temperature and may be represented by a linear function of the reciprocal temperatures (on the Kelvin scale).

3. The dependence of the initial rotations of aqueous solutions of α-D-xylose on the temperature has been established for the first time.

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