Exercise 12

# KINETICS OF SUCROSE HYDROLYSIS

Topics: rate of chemical reactions, integral forms of kinetic equations, Arrhenius equation, reaction mechanisms, examples of reaction mechanisms

The sucrose hydrolysis (inversion) reaction proceeds according to the chemical reaction equation shown in Fig.1. This reaction is characterized by a low rate of reaction, which can be significantly increased by introducing hydrogen ions into the solution, which catalyze the course of the process.

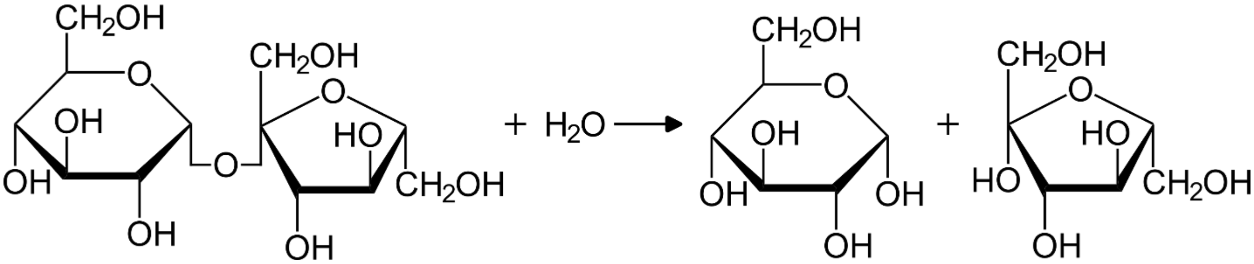

Fig. 1. Sucrose inversion reaction

If the rate of depletion of one of the reactants from the reaction mixture is proportional to its concentration, we say that the process proceeds in accordance with the kinetics of a first-order reaction. The reaction can proceed according to the kinetic equation of the first-order reaction even when the total order of the reaction predicted on the basis of the stoichiometric equation is different from unity. This is possible, for example, if the reaction involves substrates that are either not consumed during the course of the reaction (e.g. H+ ions in sucrose inversion) or are present in such large quantities that their concentrations do not change significantly. As a result of the reaction (e.g. water in the process under consideration). The rate of depletion of sucrose from the reaction mixture can be written using the differential equation (1):

$$k[S] = -\frac{d[S]}{dt} \tag{1}$$

where $[S]$ is the sucrose concentration at time $t$, a $k$ – is the reaction rate constant.

In the case of the considered reaction, these conditions are determined by the temperature and concentration of hydrogen ions, which parameters remain constant during the course of the process. By integrating Equation (1), assuming the initial condition that for t=0 and $[S] = [S]_0$ we get:

$$\ln[S] = -kt + \ln[S]_0 \tag{2}$$

Therefore, if the description of sucrose inversion using the kinetic equation of the primary reaction is correct, then, as follows from equation (2), the dependence of $\ln[S]_0$ on t will be linear, with the slope determined by the value of the rate constant k of the reaction running at a certain temperature and at a certain pH.

Experimental determination of the dependence of $\ln[S]$ on time t requires determination of sucrose concentrations (or quantities proportional to them) at specific moments of the reaction duration. A convenient way to track the sucrose inversion reaction is to observe changes in optical rotation, i.e. changes in the angle of rotation of the plane of light polarized by the reaction mixture. As the inversion reaction proceeds, the rotation of the light changes from positive to negative. This happens when the specific rotation (equation 3) of sucrose at 20 °C for the D line of sodium light (λ=589.6 nm) - $[\alpha]_S^{20,D}$ is 66.5°, while the specific rotation of the post-reaction mixture (an equimolar solution of D-fructose and D-glucose) is the arithmetic mean of the specific rotation of both hexoses and is -20° (the specific rotation of D-fructose $[\alpha]_F^{20,D}$ is -92° and D-glucose $[\alpha]_G^{20,D}$=52°).

$$[\alpha]_A^{T,\lambda} = \frac{\alpha}{l[A]} \tag{3}$$

where, α is the observed angle of twist, l is the thickness of the solution layer through which polarized light passes, [A] is the concentration of substance A. The indices T and λ denote the wavelength and temperature selected for the measurement.

The concentration of sucrose in the reaction mixture at time t is directly proportional to the difference between the angle of rotation of the plane of polarized light measured at time t - $\alpha_t$ and the angle obtained at the end of the reaction, $\alpha_\infty$ (The value of $\alpha_\infty$depends on the temperature, because both glucose and fructose, a temperature-dependent equilibrium is established between the α and β forms, which contribute to varying degrees in the final rotation exhibited by a given solution). Equation (2) can then be written as:

$$\ln(\alpha_t - \alpha_\infty) = -kt + \ln(\alpha_0 - \alpha_\infty) \tag{4}$$

where $\alpha_0$ is the angle of rotation of the polarization plane of the light passing through the sucrose solution at the beginning of the reaction ($t$=0).

The exercise uses the Guggenheim method, based on equation (4), which after transformation gives:

$$\ln\left(\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) = -kt \tag{5}$$

and then:

$$\alpha_t - \alpha_\infty = (\alpha_0 - \alpha_\infty)e^{-kt} \tag{6}$$

for time $t + \Delta t$ equation (6) takes the form:

$$\alpha_{t+\Delta t} - \alpha_\infty = (\alpha_0 - \alpha_\infty)e^{-k(t+\Delta t)} \tag{7}$$

where $\alpha_{t+\Delta t}$ is the angle of rotation of the plane of polarization of light passing through the reaction mixture at time t $t + \Delta t$.

Let us denote the change in the value of the angle of rotation that occurred in time Δt by $\Delta\alpha(t)$, so $\Delta\alpha(t) = \alpha_t + \alpha_{t+\Delta t}$). Subtracting Equation (7) and Equation (6), we get:

$$\Delta\alpha(t) = (\alpha_0 - \alpha_\infty)\left(1 - e^{-k\Delta t}\right)e^{-kt} \tag{8}$$

afer logarithmizing

$$\ln\left(\Delta\alpha(t)\right) = -kt + \ln(\alpha_0 - \alpha_\infty) + \ln\left(1 - e^{-k\Delta t}\right) \tag{9}$$

Note that for a constant value of the time interval $\Delta t$ the dependence of $\ln\left(\Delta\alpha(t)\right)$ on $t$ is a straight line with slope $k$ and intercept $\ln(\alpha_0 - \alpha_\infty) + \ln\left(1 - e^{-k\Delta t}\right)$. Hence, the reaction rate constant can be determined without knowing $\alpha_0$ i $\alpha_\infty$

1. Performing the exercise 1. In a volumetric flask, prepare 50 cm$^3$ of an aqueous solution of sucrose with a concentration of 0.24 g/cm$^3$.

2. We rinse the polarimeter tube with sucrose solution
3. Directly before measuring the angle of rotation of the light polarization plane, prepare the reaction mixture by mixing the prepared sucrose solution and the hydrochloric acid solution in a 1:1 volume ratio.
4. Fill the polarimetric tube with the prepared mixture and measure the torsion angle while noting the measurement time.
5. We make successive measurements of the torsion angle of the tested reaction mixture in 10-minute intervals.
6. We measure the ambient temperature (i.e. reaction temperature)

Calculations

7. We plot the dependence of $\alpha_t$ on $t$
8. Select the time interval Δt, approximately equal to 1/3 of the total experiment time, and read the $\alpha_t$t values for measurement points Δt apart
9. Calculate the differences $\Delta\alpha(t) = \alpha_t - \alpha_{t+\Delta t}$
10. Plot $\ln\left(\Delta\alpha(t)\right)$ against $t$ and use equation (9) to find the value of the sucrose inversion rate constant using linear regression.