Determination of kinetic data for the hydrolysis of enol ether of the ester of uronic acid

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The hydrolysis of methyl (methyl-4-deoxy-2,3-di-O-methyl-β-L-*threo*-
-hex-4-enopyranosid)uronate in 25% acetic acid was studied kinetically.
A calculating procedure using the iteration method was proposed for proces-
sing the kinetic data and determining the rate constants and theoretical
reaction course. The results are compared with the results obtained by
evaluating the measurements by the method of least squares or linear regres-
sion.

Кинетически был изучен гидролиз метил(метил-4-дезокси-2,3-ди-O-ме-
тил-β-L-*трео*-гекс-4-энопиранозид)уроната в 25%-ной уксусной кислоте.
Для обработки кинетических данных, определения констант скорости
и теоретического хода реакции был предложен численный способ
итерации. Результаты сравниваются с данными, полученными методами
наименьших квадратов и линейной регрессии.

Lindberg et al. [1] have found by studying the selective degradation of
polysaccharides containing rests of uronic acid that the unsaturated uronate
including the enol-etheric group is instable in acids and if the hydrolysis is carried
out with weak acids so that the glycosidic bond remains preserved, it gives
4-deoxy-hex-5-ulosuronate which, however, reacts further and probably yields
a derivative of furfural. It is a system of consecutive reactions manifesting
themselves in modifications of alkaline degradation methods [2] which is important
from the view-point of determination of the structures of polysaccharides.

The aim of this study is to investigate the stability of enol ether of the ester of
uronic acid in the medium of weak acid during the hydrolytic degradation of
polysaccharides and describe it quantitatively, to elaborate a method of rate
constant determination for a simple system of irreversible consecutive first-order
reactions without any complicated computing technique, to connect this calculation
with the determination of theoretical course, and to compare the results thus

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obtained with the results obtained by processing the measured data using the method of least squares or linear regression.

Determination of rate constants

The solution of consecutive first-order reactions and the description of determination of rate constants as well as pratical applications are given in [3—7]. If we write $[A_1]_0$, t, $[A_1]$, $[A_2]$, and $[A_3]$ for the initial concentration of original substance, time, the concentration of original substance, the concentration of intermediate, and the concentration of reaction product, respectively, a simple system

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3$$
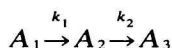
obeys the following equations

$$[A_1] = [A_1]_0 \, e^{-k_1 t} \tag{1}$$

$$[A_2] = [A_1]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{2}$$

$$[A_3] = [A_1]_0 \frac{k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})}{k_2 - k_1} \tag{3}$$

where k_1 and k_2 are the rate constants. Eqn (1) is valid for the first-order reactions and serves for determining k_1 from the relation $[A_1] = f_1(t)$. Provided $k_1 \gg k_2$ or $k_2 \gg k_1$, the whole reaction system is governed by this equation. In the first case, k_2 may be analogously determined.

If we are able to find out the function $[A_2] = f_2(t)$ analytically and to determine the time t_{max} in which the concentration of intermediate reaches the maximum, then we can use eqn (2) for deriving the subsequent equation from the condition of maximum $d[A_2]/dt = 0$

$$k_2 = D + \frac{1}{t_{max}} \ln k_2 \tag{4}$$

where

$$D = k_1 - \frac{1}{t_{max}} \ln k_1$$

This equation enables us to calculate k_2.

If we cannot determine t_{max}, we may use the relation $[A_3] = f_3(t)$ for determining k_2. By substituting and rearranging eqn (3), we obtain

$$k_2 = B + C\, e^{-k_2 t} \tag{5}$$

where $A = [A_3] - [A_1]_0 + [A_1]_0\, e^{-k_1 t}$; $B = \dfrac{k_1([A_3] - [A_1]_0)}{A}$, and $C = \dfrac{k_1[A_1]_0}{A}$.

Eqns (4) and (5) allowing to calculate the rate constant k_2 are transcendental equations. We have solved them by the iteration method. The concentration change of two reaction components at least must be followed analytically. The concentration of the third component is complementary.

The constants k_1 and k_2 were also determined by fitting the functions $[A_1] = f_1(t)$ and $[A_3] = f_3(t)$ by the method of least squares for eqns (1) and (3). The constant k_1 was determined by linear regression from the logarithmic form of eqn (1), too.

Experimental

A 0.01 M solution of methyl (methyl-4-deoxy-2,3-di-O-methyl-β-L-*threo*-hex-4-eno-pyranosid)uronate (synthesized by *P. Kováč, J. Hirsch*, and *V. Kováčik* [8]) in 25% acetic acid (Merck, Darmstadt) was hydrolyzed at 90°C and pH 2.15. The temperature was held constant accurate to ± 0.1°C by means of a thermostat TB 75 (Prüfgeräte Medingen, Dresden). The reaction was stopped at particular time intervals by a rapid cooling of the sample to 20°C. The reaction product $[A_3]$ and the intermediate $[A_2]$ were determined polarographically by direct method on the basis of separated cathodic waves ($E_{1/2} = -1.15$ and -1.55 V *vs.* SMSE) in 0.5 M-K_2HPO_4 (Lachema, Brno) at 20°C and pH 8.55. The concentration of original uronate was 5×10^{-4} M. The reaction order was determined by the half-life method and the value of $[A_1]$ was found by calculation. The polarographic measurements were performed on a polarograph OH 102 (Radelkis, Budapest).

The rate constants and theoretical concentrations of the reaction components were calculated by means of a programming calculator of the type TI-59 connected with a printer of the type PC-100 B (Texas Instruments, Dallas). The algorithm of the calculation is represented in Fig. 1.* The same programming calculator was used for computing both constants by the method of least squares [9] and the constant k_1 by linear regression [10].

Results and discussion

The concentration changes of the reaction components measured in the hydro-lysis of methyl (methyl-4-deoxy-2,3-di-O-methyl-β-L-*threo*-hex-4-enopyra-nosid)uronate by the method described in Experimental are presented as a function of time in Fig. 2 in the form of circles whereas the calculated values (theoretical course) are given as full lines.

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*The authors are disposed to supply the programme of calculation in AOS as well as the directions for use on request.

The values of the rate constants k_1 and k_2 determined by the iteration method which correspond to the measured values $[A_1]$, $[A_2]$, and $[A_3]$ at particular time moments are listed in Table 1. Their mean values are $k_1 = 1.59 \times 10^{-2} \, h^{-1}$ and $k_2 = 2.21 \times 10^{-1} \, h^{-1}$ The mean errors of k_1 and k_2 determinations are $\pm 12.7\%$ and 10.9%, respectively. These values are relatively high. If we omit the first two values of k_1 and k_2 determined after 1 h and 3 h when the accuracy of determination of the concentration change of reaction components is the lowest, and exclude the
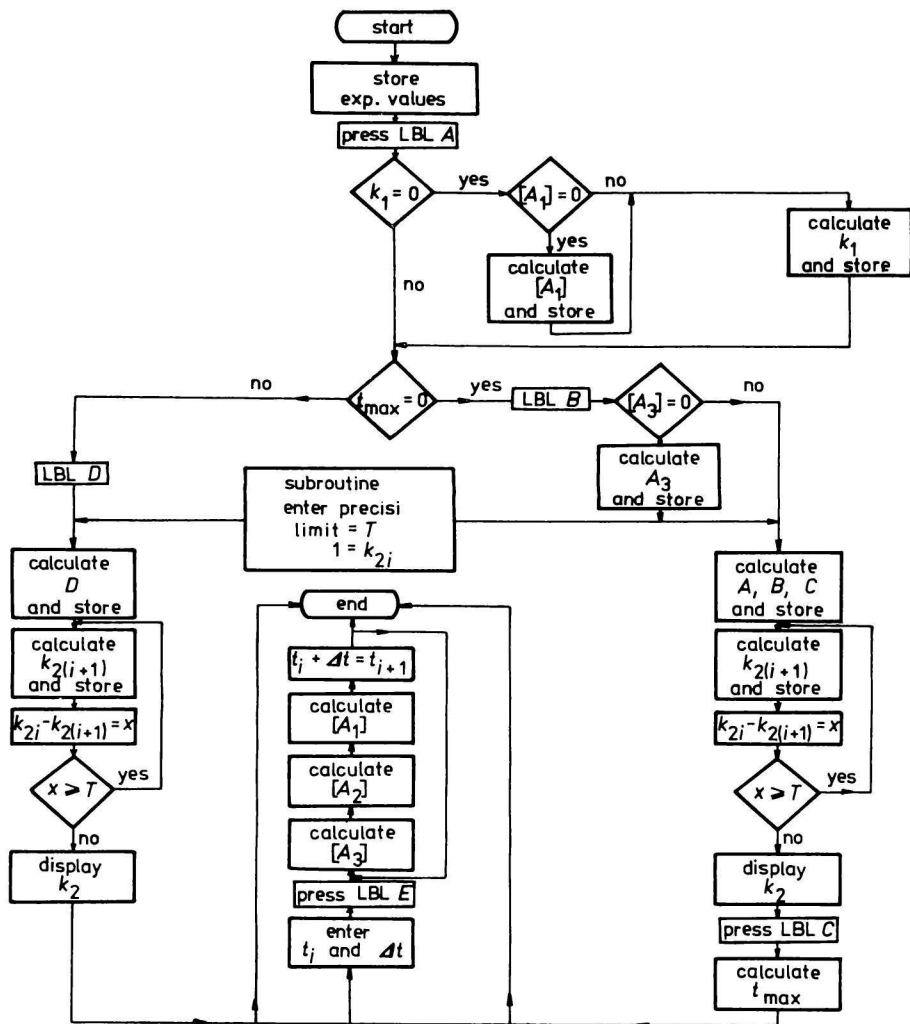

Fig. 1. Algorithm of the calculation of the k_1 and k_2 rate constants and theoretical course of two irreversible consecutive first-order reactions.
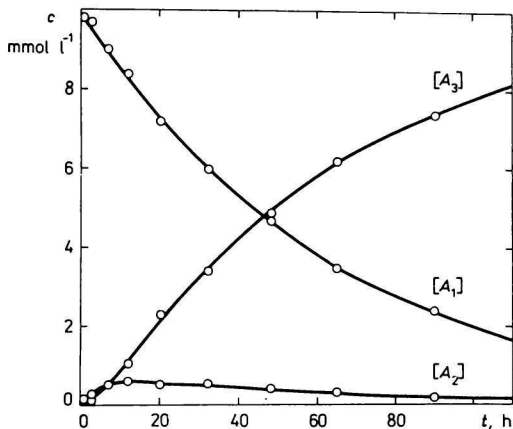
Fig. 2. Hydrolysis of methyl (methyl-4-deoxy-2,3-di-O-methyl-β-L-*threo*-hex-4-enopyranosid)uronate in 25% acetic acid at 90°C and pH 2.15.
Initial concentration of uronate 0.01 M.
Full lines: calculated concentration changes of the reaction components; theoretical course of hydrolysis.
Circles: measured values of the concentration of the original substance $[A_1]$, intermediate $[A_2]$, and reaction product $[A_3]$.

Table 1

Rate constants k_1 and k_2 of the hydrolysis of methyl (methyl-4-deoxy-2,3-di-O-methyl--β-L-*threo*-hex-4-enopyranosid)uronate in 25% acetic acid at 90°C and pH 2.15. Initial concentration of uronate 0.01 M

t h	$k_1 \cdot 10^2$ h^{-1}	$k_2 \cdot 10$ h^{-1}
1	2.02	2.14
3	1.02	3.0
7	1.51	2.23
12	1.45	2.17
20	1.64	2.51
32	2.0	1.75
48	1.49	1.97
65	1.62	2.05
90	1.59	2.06

inaccurate values corresponding to 32 h, we obtain the average values calculated by iterations $k_1 = 1.55 \times 10^{-2}$ h^{-1} and $k_2 = 2.17 \times 10^{-1}$ h^{-1} while the relative mean errors are $\pm 4.3\%$ and $\pm 6.2\%$, respectively. The average values of the rate constants thus determined may be regarded as more correct. For the acid catalysis

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of the hydrolysis by the H_3O^+ ions studied at pH 2.15 the values of catalytic constants are $K_1 = 2.19$ l mol^{-1} h^{-1} and $K_2 = 30.7$ l mol^{-1} h^{-1}

The values of the rate constants determined by fitting the measured time relationships $[A_1] = f_1(t)$ and $[A_3] = f_3(t)$ are $k_1 = 1.57 \times 10^{-2}$ h^{-1} and $k_2 = 2.18 \times 10^{-1}$ h^{-1} The linear regression has given $k_1 = 1.59 \times 10^{-2}$ h^{-1}, the intercept and regression coefficient being $q = 0.007362$ and $R = 0.999205$, respectively.

As evident from the algorithm in Fig. 1, this calculating procedure may be employed complete or divided into fragments for the determination of k_1, k_2 (from t_{max} or $[A_3]$) and theoretical course of the reaction and is to be used according to capacity of the programming calculator.

The determination of the rate constants of hydrolysis of the investigated enol ether of uronic acid has shown that this substance is in the medium of weak acid more stable than it was assumed [1]. The formation of furfural derivative as a reaction product has not been confirmed [11]. Its $E_{1/2}$ is more positive by 100 mV.

References

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