

Determination of kinetic data for the transformation of methylglyoxal

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The transformations of methylglyoxal, namely oxidation-reduction disproportionation into lactic acid and aldolization reactions, were investigated in alkaline medium (Na_2CO_3 , NaOH) as a system of parallel reactions of the first and second order. The rate and catalytic constants were determined by a numerical calculation involving the method of least squares from polarographic and potentiometric investigations of the course of the transformation reactions.

Были изучены превращения метилглиоксала, окислительно-восстановительная диспропорционация в молочную кислоту и реакции альдолиза в щелочной среде (Na_2CO_3 , NaOH) в качестве системы побочных реакций I и II порядка. Константы скорости и катализа были определены числительным методом на основании полярографического и потенциометрического исследования хода превращений при помощи метода наименьших квадратов.

Methylglyoxal which frequently appears as a product of alkaline degradation of sugars, is subject to further transformations [1]. It is relatively stable in acid medium. However, it undergoes mainly two transformations in alkaline medium, i.e. oxidation-reduction disproportionation into lactic acid and aldolization reactions.

The qualitative characteristics of these transformations [2, 3] were quantitatively kinetically ascertained [4, 5] for two parallel reactions of the first and second order. An intramolecular mechanism of the formation of lactic acid was confirmed by measurements in D_2O . Besides the reaction order and character of catalysis, we have found that the primary product of aldolization enters into further consecutive reactions. The enol character of the methylglyoxal anion or subsequent products of aldolization has not been confirmed (mass, u.v. methods).

The determination of the ratio of rate constants based on the solution of the above system of parallel reactions by the manual method of slope in the origin [6] did not give any satisfactory results. Therefore the ratio of constants was determined from the boundary concentration conditions for which only one type of reactions was preferred [5]. As that was an approximative solution, we decided to study this problem again by using the numerical methods based on the application of the method of least squares. The measurements were performed in media with constant pH and the reaction components were analytically determined by polarographic and potentiometric methods [5]. The numerical calculations were carried out with a programming calculator.

Determination of rate constants

From the kinetic view-point, the transformations of methylglyoxal A_1 represent a system of parallel reactions, namely oxidation-reduction disproportionation into lactic acid A_2 (a first-order reaction) and aldolization into hexane-4-ol-2,5-dione-1-al A_3 (a second-order reaction). If we neglect the rate of dealdolization of A_3 , we may calculate the ratio of rate constants k_1/k_2 of the parallel reactions of the first and second order from the relationship $[A_2] = f_1([A_1]_0 - [A_1])$ where

$$f_1 = k_1/k_2 \ln \frac{k_1/k_2 + a}{k_1/k_2 + a - x}$$

$[A_1]_0 = a$ is the initial concentration of methylglyoxal, $[A_1] = a - x$ is the concentration of methylglyoxal at the time moment t while $[A_2] = y$ and x stand for the concentration of lactic acid and consumed methylglyoxal, respectively [6].

We shall seek the optimum numerical value $b_{\text{opt}} = k_1/k_2$ which fulfils the condition of least squares. Thus it holds for the residual sum of squares ΔS_1

$$\Delta S_1 = \sum_{i=1}^{n_1} \left(y_i - b_i \ln \frac{b_i + a}{b_i + a - x_i} \right)^2 = \min$$

where n_1 is the number of selected measurements.

The rate constant of the first reaction order k_1 was calculated from the temporal relationship $[A_1]_0 - [A_1] = x = f_2(t)$ which was governed by the following equation

$$t = \frac{1}{k_1} \left(\ln \frac{a}{a - x} - \ln \frac{k_1/k_2 + a}{k_1/k_2 + a - x} \right)$$

If we insert $b_{\text{opt}} = k_1/k_2$, we obtain for the residual sum of squares ΔS_2

$$\Delta S_2 = \sum_{i=1}^{n_2} \left[t_i - \frac{1}{k_{1\text{opt}}} \left(\ln \frac{a}{a - x_i} - \ln \frac{b_{\text{opt}} + a}{b_{\text{opt}} + a - x_i} \right) \right]^2 \quad (1)$$

where n_2 is the number of selected measurements. On squaring and rearrangement, we obtain

$$\Delta S_2 = A - \frac{2B}{k_{1\text{opt}}} + \frac{C}{k_{1\text{opt}}^2} \quad (2)$$

where

$$A = \sum_{i=1}^{n_2} t_i^2$$

$$B = \sum_{i=1}^{n_2} t_i \left(\ln \frac{a}{a - x_i} - \ln \frac{b_{\text{opt}} + a}{b_{\text{opt}} + a - x_i} \right)$$

$$C = \sum_{i=1}^{n_2} \left(\ln \frac{a}{a - x_i} - \ln \frac{b_{\text{opt}} + a}{b_{\text{opt}} + a - x_i} \right)^2$$

If we put $\frac{1}{k_{1\text{opt}}} = Z$, eqn (2) assumes the form

$$\Delta S_2 = A - 2BZ + CZ^2 \quad (3)$$

According to the theory of least squares $\Delta S_2 = \min$, because it holds $d\Delta S_2/dZ = 0$. It results from eqns (2) and (3) that $Z = B/C$, i.e. $k_{1\text{opt}} = C/B$. The value of k_2 is to be calculated from $k_{1\text{opt}}$ and the optimum ratio of the constants k_1/k_2 .

Experimental

Instruments

The transformation reactions were carried out in a universal titration vessel EA 880 equipped with a glass electrode EA 109 H and calomel electrode EA 404 (Metrohm, Herisau). This equipment was connected with an automatic titrator of the type TTT2 serving for pH control (Radiometer, Copenhagen). A burette controlled through a magnetic valve by the titrator was used for potentiometric determinations. The polarographic analyses were performed with a polarograph of the type Polariter PO4 (Radiometer, Copenhagen). The temperature of the polarographic and titration vessel was held constant accurate to $\pm 0.02^\circ\text{C}$ with a thermostat U10 (Prüfgeräte Medingen, Dresden). The kinetic parameters were calculated by means of a programmable calculator TI-59 equipped with a printer PC-100 B (Texas Instruments, Dallas).

Chemicals

Methylglyoxal, a 30—35% solution in H_2O , of technical purity (Fluka, Buchs) was adapted to nominal concentration on the basis of polarographic determination.

Isobutylamine purum employed for preparation of the isobutylamine buffer and 1,2-phenylenediamine purissimum (Fluka) were redistilled before use. Sodium hydroxide, sodium carbonate, and hydrochloric acid used for adjusting alkalinity of the reaction medium and potentiometric determinations were prepared from standard solutions "Titrisol" (Merck, Darmstadt). The ionic strength was adjusted by adding KCl of anal. grade purity (Lachema, Brno).

Procedures

The kinetic measurements were performed in a pH- and temperature-controlled reaction vessel in nitrogen atmosphere by using the instrumental technique and procedure described in the preceding paper [5]. The preparation of carbonate-free solutions of sodium hydroxide was described in [5]. The concentration of methylglyoxal was polarographically determined as 2-methylquinoxaline in the isobutylamine buffer after condensation with 1,2-phenylenediamine [7]. Lactic acid was determined by potentiometric titration carried out directly in the reaction vessel by reading the values of the carbonate-free NaOH consumed for pH-statting. Except the temperature dependences, the kinetic measurements were performed at 25°C while the analytical polarographic determinations were made at 20°C. The ionic strength was held constant and was 0.3 in sodium carbonate and 0.1 in sodium hydroxide.

The methods of calculation for determining the optimum values of the ratio of the rate constants of both transformation reactions and the rate constant of disproportionation are represented by algorithms in Fig. 1.*

Results and discussion

The values of the rate and catalytic constants determined for the catalysis of the transformation reactions of methylglyoxal by the OH^- ions measured at constant ionic strength $I=0.3$ and constant concentration of methylglyoxal ($0.001 \text{ mol dm}^{-3}$) in the Na_2CO_3 concentration interval $0.001\text{--}0.1 \text{ mol dm}^{-3}$ at 25°C are given in Table 1. The values of the constants found under equal basic conditions at the constant $0.001 \text{ mol dm}^{-3}$ concentration of Na_2CO_3 and varying concentration of methylglyoxal in the interval $0.001\text{--}0.1 \text{ mol dm}^{-3}$ are presented in the lower part of this table.

The values of analogous constants ascertained for disproportionation and aldolization of methylglyoxal at 25°C for constant ionic strength $I=0.1$, 0.01 mol dm^{-3} NaOH, and $0.005 \text{ mol dm}^{-3}$ methylglyoxal as well as 0.01 mol dm^{-3} methylglyoxal and 0.002 and $0.001 \text{ mol dm}^{-3}$ NaOH are given in

* The authors supply the program of calculation in AOS and directions for use on request.

Table 2.

In both tables, there are also the optimum values of the ratio of the rate constants of disproportionation and aldolization serving for calculating the optimum values of the rate constants of the oxidation-reduction disproportionation of methylglyoxal the importance of which considerably increased by introducing the numerical methods of calculation. The pH values are quoted because they significantly influence the determination of the catalytic constants. A fluctuation of the determined kinetic data is observable in the first part of Table 1 because the pH-statting in the initial stage of reaction makes inconvenience at low concentrations of Na_2CO_3 .

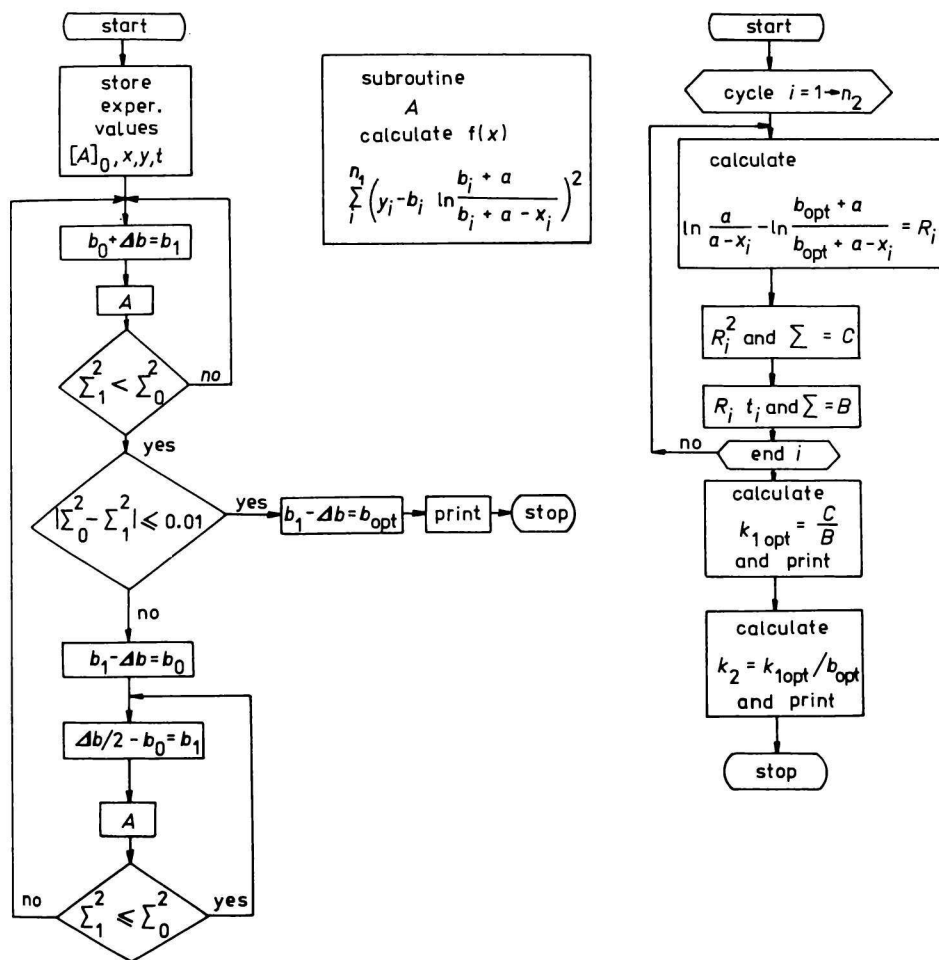


Fig. 1. Algorithms for the calculation of the optimum values $b_{\text{opt}} = (k_1/k_2)_{\text{opt}}$ and the values of the rate constants of parallel reactions of the first ($k_{1\text{opt}}$) and second (k_2) order.

Table 1

Rate constants k_1 , k_2 and catalytic constants $k_1^{\text{OH}^-}$, $k_2^{\text{OH}^-}$ for the oxidation-reduction disproportionation and aldolization of methylglyoxal catalyzed by the OH^- ions in Na_2CO_3 solutions at $I = 0.3$ and 25°C

Na_2CO_3 resp. $\text{CH}_3\text{COCOCH}_3$ mol dm^{-3}	pH	$k_1 \cdot 10^5$ s^{-1}	$k_2 \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	k_2/k_1 $\text{dm}^3 \text{mol}^{-1}$	$k_1^{\text{OH}^-} \cdot 10$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_2^{\text{OH}^-}$ $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
0.1	11.0	10.7	5.7	542	1.07	57.9
0.05	11.1	12.9	8.03	619.8	1.03	64.2
0.01	10.35	2.06	1.2	592.6	0.92	54.5
0.002	10.7	4.9	3.2	640	0.99	63.4
0.001	10.5	3.2	1.9	627.4	1.00	62
0.001 mol dm^{-3} Na_2CO_3						
0.1	10.72	5.51	3.24	588.5	1.05	61.7
0.05	10.5	3.46	1.97	568	1.09	62.3
0.01	10.72	5.6	3.3	592.6	1.07	63.3
0.002	10.86	8.4	4.6	551.7	1.16	64
0.001	10.88	8.8	4.86	551.7	1.13	62.6

Table 2

Rate constants k_1 , k_2 and catalytic constants $k_1^{\text{OH}^-}$, $k_2^{\text{OH}^-}$ for the oxidation-reduction disproportionation and aldolization of methylglyoxal catalyzed by the OH^- ions in NaOH solutions at $I=0.1$ and 25°C

CH_3COCOH resp. NaOH mol dm^{-3}	pH	$k_1 \cdot 10^4$ s^{-1}	$k_2 \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	k_2/k_1 $\text{dm}^3 \text{mol}^{-1}$	$k_1^{\text{OH}^-} \cdot 10$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_2^{\text{OH}^-}$ $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
0.005	11.5	2.9	5.7	596	1.03	60.2
0.01 mol dm^{-3} CH_3COCOH						
0.002	10.9	8.3	4.7	571	1.05	60.2
0.001	10.87	7.3	4.2	581	0.98	57.2

The mean values of the catalytic constants determined for both transformations catalyzed by the OH^- ions under given reaction conditions are $k_1^{\text{OH}^-} = 0.104 \pm 11.1\% \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the oxidation-reduction disproportionation and $k_2^{\text{OH}^-} = 61.1 \pm 6.4\% \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for the aldolization of methylglyoxal. The percents express the corresponding mean relative errors. The values of activation energies determined from the temperature dependences in the temperature interval 15—35°C divided into sections of 5°C for the reactions of 0.01 mol dm^{-3} methylglyoxal in the medium of $0.01 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ at $I=0.3$ are $E_{A1} = 56.6 \text{ kJ mol}^{-1}$ for the oxidation-reduction disproportionation and $E_{A2} = 117.7 \text{ kJ mol}^{-1}$ for the aldolization of methylglyoxal.

A comparison of the data numerically determined by the use of the method of least squares with those obtained by the approximate method shows that the kinetic data obtained by both methods are consistent for disproportionation but the data obtained by the first method for aldolization are higher. This fact may be caused just by the approximative determination of the value of the ratio of rate constants in the preceding study [5]. The determined constant of aldolization is lower because even a higher concentration of methylglyoxal starts to decrease during the reaction and the disproportionation proceeds to get the upper hand. If we use the numerical method for determination of k_1/k_2 , we avoid approximation and both transformation reactions continue to be weighed. The identification of products of the consecutive aldolization reactions is the topic of further study.

The procedure of numerical calculations based on the method of least squares [8] may be divided into two fragment determinations, *i.e.* $(k_1/k_2)_{\text{opt}}$ and $k_{1\text{opt}}$ determination, and used according to the extent of usable memory of the programmable calculator. In general, it is suited to analogous use for kinetic systems of parallel reactions of the first and second order.

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