

# DIHYDROXYFUMARIC ACID TRANSFORMATION

Secara Natalia

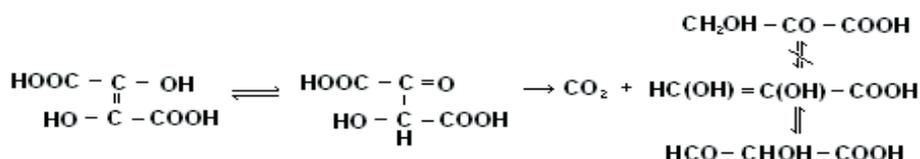
Institute of Chemistry, 3, Academy st., Chisinau, Republic of Moldova  
Email: natalia\_secara@yahoo.com, Phone: (+373 22) 72 97 61

**Abstract:** This short communication presents several preliminary results obtained during kinetic investigation of dihydroxyfumaric acid decarboxylation. The reaction order towards the hydrogen ions concentration has been established, the correlation between the decarboxylation velocity and temperature has been found, the Arrhenius equation for the decarboxylation constant has been drawn.

**Keywords:** dihydroxyfumaric acid, decarboxylation, activation energy

## Introduction

The papers [1, 2] have demonstrated that in solid form, the dihydroxyfumaric acid (DFH<sub>4</sub>) has the structure of the tautomeric ketonic form. Researches conducted by *Souchay et al.* [3] have shown that in solution this equilibrium is greatly influenced by the pH value of the medium, i.e., the equilibrium is totally shifted towards the ketonic form at pH < 0,5 and at pH > 12 – towards the enolic form. *Fleury* [4] has shown that dihydroxyfumaric acid decarboxylation can only take place through the formation of the ketonic form – oxaloglycolic acid, transparent for spectrometric measurements ( $\lambda > 200$  nm). The mechanism proposed in [4] for the primary decarboxylation is shown below:



## Experimental

The following reagents were used during the research: dihydroxyfumaric acid hydrate 98% purchased from Aldrich, sodium hydroxide, hydrochloric acid, EDTA – titration standards. All solutions were prepared using bidistilled water. Freshly prepared dihydroxyfumaric acid solution was used in each experiment. The investigated solution contained:  $[\text{DFH}_4]_0 = 1 \cdot 10^{-4}$  M,  $[\text{EDTA}] = 5 \cdot 10^{-3}$  M. The anaerobic medium was created by purging argon through the solution. Spectrometric measurements have been made using a Perkin Elmer Lambda 25 Spectrometer at  $\lambda = 290$  nm, the established value of dihydroxyfumaric acid absorption maximum.

## Results

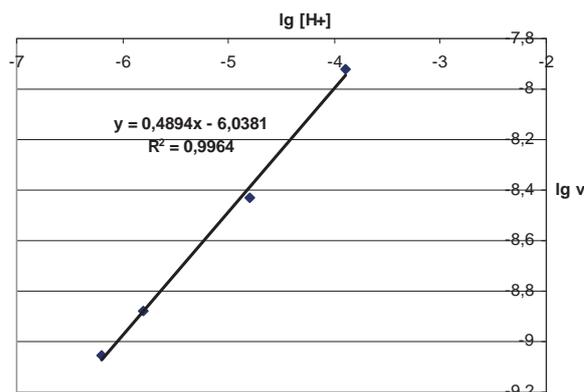


Fig. 1. The decarboxylation velocity of the dihydroxyfumaric acid, as function of the pH value of the solution,  $t = 30^\circ\text{C}$

According to [4], for values of pH > 3, the rate of decrease of the enolic form concentration is equivalent with the velocity of decarboxylation of the dihydroxyfumaric acid, therefore making it possible to investigate the decarboxylation reaction by the decrease in absorbance at 290 nm.

Investigations allowed finding the dependence of the decarboxylation velocity on the pH value of the solution (for  $\text{pH} > 3$ ), the decarboxylation velocity and the rate constant which describe this reaction have been calculated (Table 1 and Figure 1). It was found that the reaction order towards  $[\text{H}^+]$  equals to 0,49.

Table 1

The decarboxylation velocity of the dihydroxyfumaric acid, as function of the pH value of the solution,  $t=30^\circ\text{C}$

pH	$v_p, \text{mol/l}\cdot\text{s}$
3,9	$1,2\cdot 10^{-8}$
4,8	$3,71\cdot 10^{-9}$
5,8	$1,33\cdot 10^{-9}$
6,2	$8,79\cdot 10^{-10}$

During current investigations, the influence of temperature on the rate of the decarboxylation process was established. The decarboxylation rates and the rate constants have been calculated for the temperature range  $20^\circ\text{C} - 60^\circ\text{C}$ . The obtained results are shown in Table 2.

Table 2

The decarboxylation rate of the dihydroxyfumaric acid, as function of the temperature of the solution at pH 4,8

$t, ^\circ\text{C}$	$v_p, \text{mol/l}\cdot\text{s}$	$k_p, \text{s}^{-1}$
20	$5,43\cdot 10^{-10}$	0,0004606
30	$3,71\cdot 10^{-9}$	0,0020727
40	$4,29\cdot 10^{-9}$	0,0027636
50	$1,15\cdot 10^{-8}$	0,0076
60	$1,68\cdot 10^{-8}$	0,011515

Figure 2 illustrates how the rate constant of the decarboxylation reaction depends on the temperature of the investigated solution.

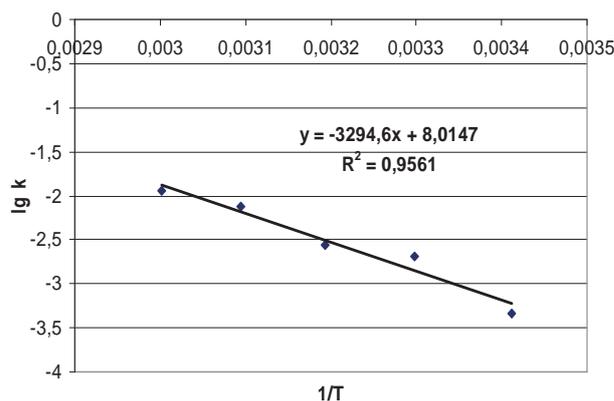


Fig. 2. The rate constant of the decarboxylation, as function of the temperature of the solution at pH 4,8

Using the graphical method, the activation energy and the pre-exponential factor have been determined. There were obtained the following values: for the pre-exponential factor  $-1,034\cdot 10^8$ , for the activation energy calculated by the graphical method  $-63,08 \text{ kJ/mol}$ , and by the analytical method  $-65,3 \text{ kJ/mol}$ .

Therefore, we propose the Arrhenius equation which describes the variation of the rate constant with temperature, of the following form:

$$k = 1.034 \cdot 10^8 \cdot e^{-7.58 \cdot 10^3 / T}$$

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#### References:

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