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KINETICS OF LEVULINIC ACID FORMATION FROM CARBOHYDRATES AT MODERATE TEMPERATURES

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Abstract

The kinetic curves of levulinic acid accumulation in the process of saccharide dehydration at 80-98°C are compared. The structural features of the substrates and 5-hydroxymethylfurfural, which is the intermediate of the process, explain the observed difference in the rates of fructose and glucose conversion. Sulfuric acid can be effectively used under moderate conditions to synthesize levulinic acid with yields exceeding 35 mol % for glucose and 50% for sucrose at 98°C.

Keywords: Carbohydrates, levulinic acid, acid-catalyzed degradation, Hammett acidity function

INTRODUCTION

Levulinic acid (LA) is an important product of processing the hexose sugars, including cellulose. Its synthesis from petroleum type raw materials origin is known to be more complicated [1, 2]. Cellulose and sucrose are renewable raw materials of relatively low price [2]. LA production from carbohydrates has been intensively studied [1-10].

The acid-catalyzed conversion of carbohydrates into levulinic acid, as well as cellulose into glucose, can be carried out in concentrated solutions of acids at moderate temperature ($\approx$100°C) or in their dilute solutions at elevated temperature (>160°C) [6, 7, 9-12]. Both approaches have advantages and disadvantages. Hydrolysis by dilute acids is used in industry and does not require high consumption of the acid. This high-temperature

hydrolysis of polysaccharides, however, does not allow attaining high yields of monocarbohydrates and LA (20-40 wt. %) [4, 9, 10, 12]. An increase in the yields can be attained at low temperatures.

Most papers devoted to the kinetics and mechanism of LA formation [1, 5-7] consider fructose hydrolysis by hydrochloric acid, which is also the most popular catalyst for the low-temperature synthesis of LA [1, 5-7, 11]. The influence of the carbohydrate and of the acid catalyst on the formation of LA has not been sufficiently studied. The most widespread hypothesis on the hydrolysis of hexoses into 5-hydroxymethylfurfural (HMF), which is a precursor of LA, through enediols [1, 13, 14] was not comprehensively proved [15].

The goal of the present work is to study and compare the kinetics of levulinic acid formation from different substrates (wood, cellulose, fructose, glucose and sucrose) in the presence of mineral acids (hydrochloric, sulfuric and phosphoric) at moderate temperatures.

EXPERIMENTAL

The catalytic experiments were carried out in a 250 mL thermostated magnetically stirred glass flask. The temperature of $98^{\circ}C$, 3-7 M acid and 0.33 M of sugar were used in the main experiments. The proper amount of the catalyst was heated to the required temperature and then added to an aqueous solution or suspension of the carbohydrate. In order to obtain the kinetic curves, the reaction mixture was sampled periodically, quickly cooled and analyzed. The humic substances were filtered and dried to a constant weight. Then the humic substances and the reaction mixture were extracted with ethyl acetate and the extract was analyzed by GLC. The byproducts and intermediates were analyzed by GC-MS with a Hewlett-Packard GCD Plus spectrometer. HMF, α- and β-angelicalactones were detected among the intermediates of the fructose hydrolysis.

The Hammett acidity function H^0 was calculated according to the data of [16] neglecting an influence of carbohydrates and the other components of the reaction mixture on the acidity.

RESULTS AND DISCUSSION

Figure 1 demonstrates the kinetic curves of LA accumulation in the hydrolysis of various carbohydrates, as well as aspen (*Populus tremuloides M.*) and fir (*Abies Alba*) wood. The initial reaction rates are given in Table 1. The maximum rates of LA formation were observed for the fructose and sucrose

hydrolysis, while the rate of glucose conversion was about 30 times lower. Cellulose and wood were three orders of magnitude less reactive than fructose. The low activity of polymeric substrates is obviously caused by the slow hydrolysis of the polysaccharides [3, 12].
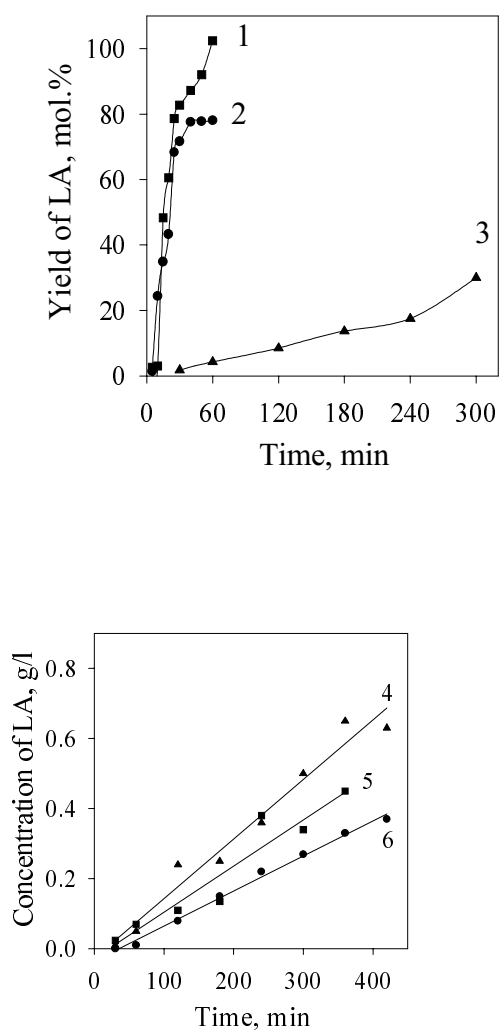

Fig. 1. Kinetic curves of levulinic acid formation from sucrose (1), fructose (2), glucose (3), fir wood (4), aspen wood (5) and cellulose (6). The reaction conditions are in Table 1

Table 1

Initial rates W of the levulinic acid accumulation during hexose and wood dehydration (98°C, 3.84 M hydrochloric acid)

	Fructose	Sucrose	Glucose	Cellulose	Aspen wood	Fir wood
Substrate concentration (M)	0.33	0.33	0.33	–	–	–
Substrate loading (g/L)	60	114	60	27	54	54
W (M/min)	9.1×10^{-3}	9.5×10^{-3}	2.6×10^{-4}	8.5×10^{-6}	1.1×10^{-5}	1.8×10^{-5}
Yield of LA (mol %)	75 ± 5	105 ± 5	27 ± 3	–	–	–

The structural features of the substrates and HMF, which is an intermediate of the process [1, 2, 4, 13, 14], can cause the distinctions in the rates of the transformation of fructose and glucose. An equilibrium solution of fructose contains more than 50% of fructofuranose (I) at 100°C [2]. The fructofuranose (I) and HMF (II) molecules have identical carbon skeletons, and the rates of the fructose transformation can be governed only by the dehydration reactions, which proceed fast in acidic medium:


$$+ \ 3 \, H_2O \qquad (1)$$
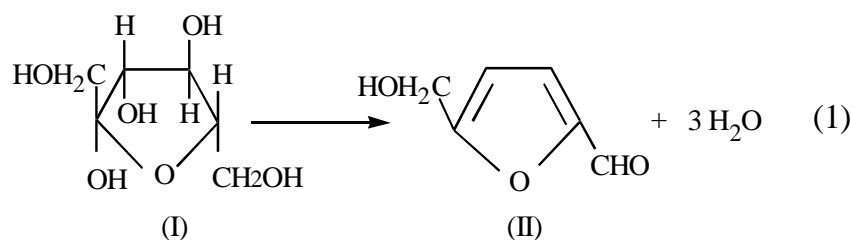
Glucose (III) conversion into HMF (II) can proceed through the rearrangement of aldose into ketose, and this step is rather slow in acidic medium: glucose transforms into fructose in a 1 M solution of sulfuric acid at 110-120°C in 10 h [17]. The rates of conversion of glucose (III) into LA have the close values (Figs 1, 4). So, glucose transformation into fructose can limit HMF and LA formation from (III):

$$(2)$$
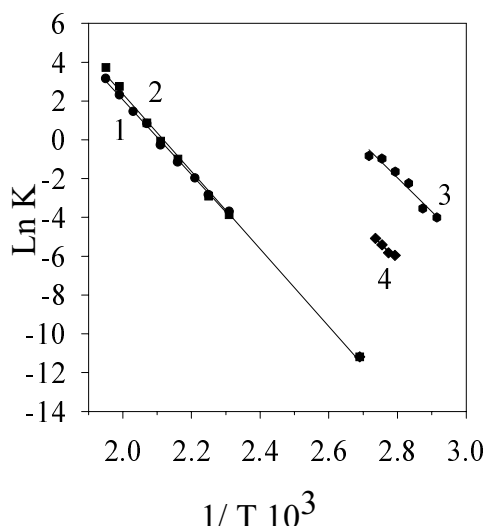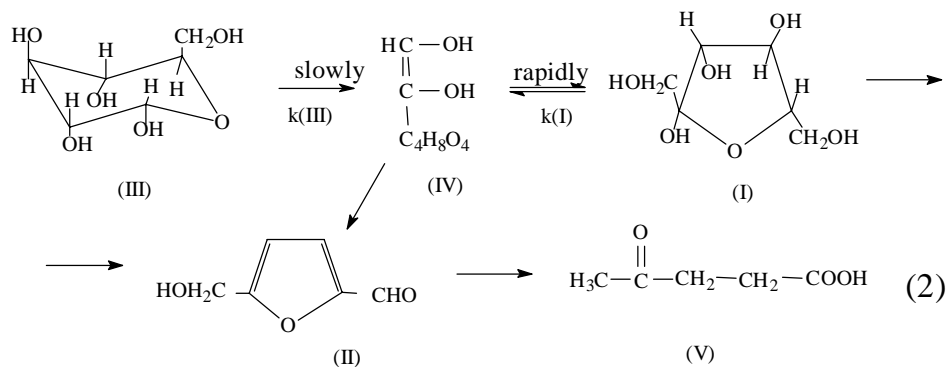
Fig. 2. Arrhenius plots for the effective rate constant k of the conversion of glucose (1 [3]), cellulose (2 [3]) fructose (3), and glucose (4)

The possibility of LA and HMF formation through the frequently cited pathway (I) → (IV) → (II) [1, 13, 14] seems to be implausible also from the viewpoint of known data on thermodynamics of fructose and glucose interconversion. The ratio of the equilibrium concentrations of glucose and fructose in a water solution is 63 : 31 [18], *i.e.*, the equilibrium constant of the

reaction (III) ⇆ (I) is about 0.5. This value is equal to the ratio k_{III}/k_I of the corresponding rate constants of the slow steps of carbohydrate enolization into enediol (IV). In the framework of the pathways (I) → (IV) →(II) and (III) → (IV) → (II), this corresponds to the ratio of the rates of the levulinic acid formation from glucose and fructose. According to the experimental results (Table 1) and the data in [6], this ratio is much smaller: $k_{III}/k_I = 0.03–0.02$.
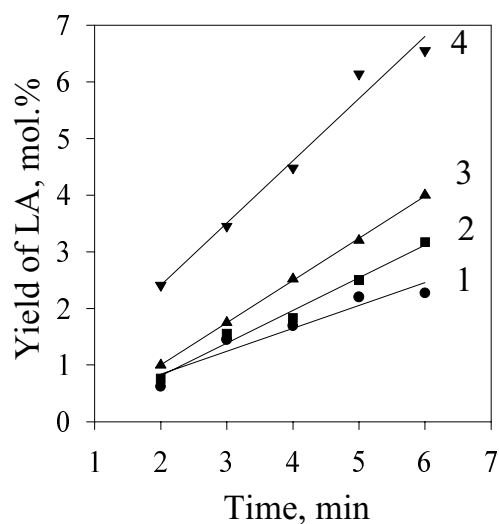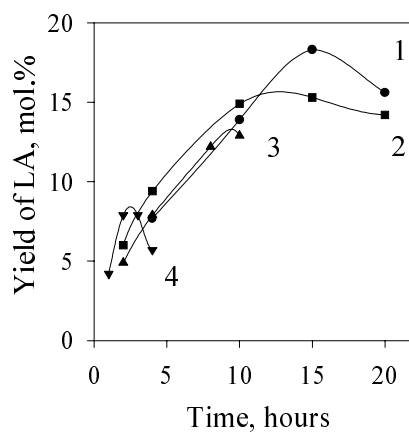

Fig. 3. Kinetic curves of levulinic acid formation from 0.25 M glucose. The reaction conditions: 4.125 M HCl, 85.0°C (1), 87.2°C (2), 90.0°C (3) and 92.5°C (4)

Raising the temperature of glucose hydrolysis by 5–10°C increases the rate and selectivity of the process by a factor of two–three (Figs 2, 3, Table 2). The activation energies estimated from the data of Fig. 3 are 130±6 kJ/mol for glucose and 140±5 kJ/mol for fructose. The literature data [3] permit an estimation of activation energy of hydrolysis of glucose (160±2 kJ/mol) and cellulose (176±3 kJ/mol) by dilute sulfuric acid in the range of temperatures 160-240°C (Fig. 3). It should be noted that the estimated rate of cellulose hydrolysis at 98°C (Fig. 3) corresponds to the data of [3] after recalculating the sulfuric acid concentration.

Table 2

Influence of temperature and nature of acid on the kinetics of LA formation during the glucose hydrolysis (0.35 M)

Temper-ature	Acid and its concentration	Acidity function	Initial rate of LA	Parameters of appearance of maximum concentration of LA		
(^{o}C)	(M)	(H^0)	accumulation (M/min x 10^4)	Concentration of LA (g/l)	Yield (mol %)	Time (min)
80	HCl, 7.5 M	-2.8	14 ± 0.08	6.86	12	360
90	HCl, 7.5 M	-2.8	27 ± 0.1	12.90	23	240
98	HCl, 7.5 M	-2.8	64 ± 0.18	19.00	34	180
98	HCl, 7.2 M	-2.6	21 ± 0.9	19.80	35	180
98	H_2SO_4, 5.8 M	-2.6	1.8 ± 0.07	21.50	38	720
98	H_3PO_4, 10 M	-2.6	0.52 ± 0.012	2.80	5	360

Fig. 4. Kinetic curves of levulinic acid formation from 0.55 M glucose at different HCl concentrations at 95°C. 5.0 M (1), 5.8 M (2), 6.6 M (3), 7.9 M (4)
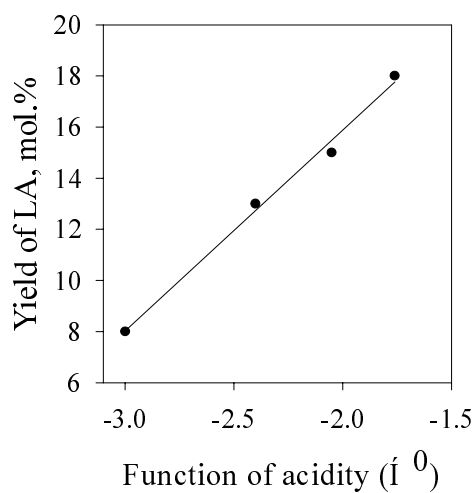
Fig. 5. Influence of Hammett acidity function H^0 on the yield of LA (conditions are the same as in Fig. 4)
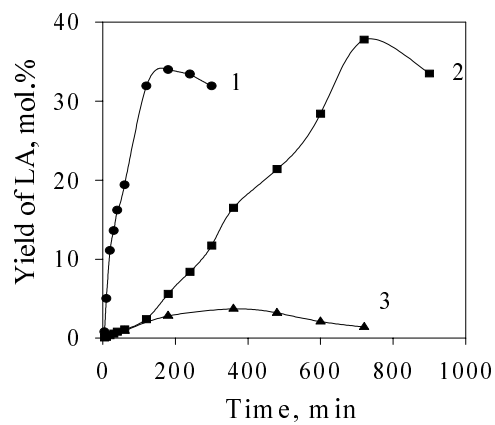
Fig. 6. Influence of the acid on the kinetics of levulinic acid formation from 0.35 M glucose at 98°C and H^o = -2.6: 1 – 7.2 M HCl, 2 – 5.8 M H_2SO_4, 3 – 10 M H_3PO_4

The rate of LA formation from glucose depends slightly on the HCl concentration (Fig. 4), but the selectivity of the process strongly increases with raising H^0 (Fig. 5). Such a selectivity gain can be explained by a rise of the water activity and hence by a decrease in the contribution of the pathways related to the reactant and intermediate condensation into humic substances.

Figure 6 shows the influence of the acid on the kinetics of glucose conversion at constant H^0. The hydrochloric acid is twelve times more active than sulfuric acid, but the selectivities of LA formation are practically the same in both cases. Such difference in the rates is caused, probably, by the greater activity of protons in the former case. Phosphoric acid is too weak for its application as a catalyst of the process: the maximum yield of levulinic acid does not exceed 5 mol %, and the rate of process is small (Fig. 6, Table 2).

Thus, despite the relatively high oxidative potential and the low acidity, sulfuric acid can be effectively applied to synthesize levulinic acid. A comparison of the kinetic results with the known data on the thermodynamics of glucose and fructose interconversion shows that the formation of LA from glucose can proceed through fructofuranose as intermediate.

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