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OXIDATION OF UNSATURATED ALDEHYDES BY HYDROGEN PEROXIDE IN ALCOHOLS MEDIUM

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Abstract. Kinetic regularities of *α*-ethylacrolein and crotonic aldehyde oxidation in methanol, allyl alcohol and glycidol were studied. Rate constants of hydrogen peroxide consumption and rate constants of unsaturated acid and its ester accumulation for both aldehydes in different alcohols at various catalyst concentrations and temperatures were calculated. The reaction activation parameters were also calculated. Dependences of ester/acid ratio on the reaction conditions were ascertained. Dependence of the reaction rate and the reaction products composition on aldehyde and alcohol structures was shown. Data of the reaction products composition dependence on the reaction conditions conform to the reaction kinetic parameters.

Keywords: *α*-ethylacrolein, crotonic aldehyde, oxidation with hydrogen peroxide, oxidative alkoxylation, H_2SeO_3 catalyst, ester/acid ratio, kinetic and activation parameters of reaction.

1. Introduction

The interaction of unsaturated aldehydes with hydrogen peroxide in a liquid phase of organic solvent, which is necessary for reaction mixture homogenization, may proceed only in the presence of a catalyst. It was determined that Selene compounds having oxidation level +4 (H_2SeO_3, SeO_2) are the best catalysts of this reaction. The reaction proceeds with a high selectivity for unsaturated acid (92 %) [1-3].

If the catalytic reaction of unsaturated aldehydes with hydrogen peroxide is carried out in alcohol mediums, the unsaturated acid and its ester are produced simultaneously (both oxidation and oxidative alkoxylation of unsaturated aldehydes proceed simultaneously). This is very important from the point of view of practice since this reaction is a method of one-stage simultaneous production of unsaturated acid and its ester [4-6].

The aim of the work was study of kinetic regularities of the reaction of unsaturated aldehydes oxidation with hydrogen peroxide in alcohol medium, as well as determination of the reaction products ratio (ester/acid) dependence on the reaction conditions. For ascertainment of the reaction regularities dependence on aldehyde and alcohol structure the oxidation of two unsaturated aldehydes: *α*-ethylacrolein (EA) and crotonic aldehyde (CA) in methanol (ME), allyl alcohol (AA) and glycidol (GL) at various temperatures and reagents ratios (aldehyde/alcohol) was studied.

2. Experimental

The reaction was carried out in the liquid phase. The aldehyde, hydrogen peroxide and the catalyst solution in alcohol were mixed in a batch temperature-stabilized reactor. Change in amount of hydrogen peroxide was monitored by the iodometric method. The amounts of unsaturated acid and its ester were determined by chromatography. The H_2SeO_3 was used as a catalyst.

Experiments were carried out in a temperature-stabilized glass three-necked reactor with the volume of 100 sm^3. Calculated amount of alcohol, 0.05 mol of aldehyde, 90 % aqueous solution of H_2O_2 and the catalyst were charged into the reactor. Moment of the catalyst addition was considered to be the reaction starting point. The reaction mixture was sampled from the reactor for analytical control of the reaction proceeding.

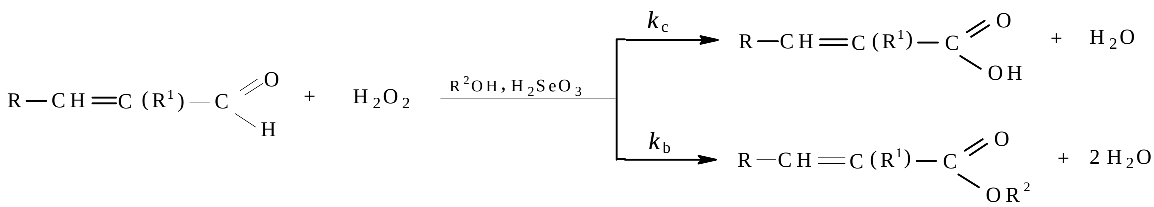
Chromatographic analysis was carried out by the internal standard method in a gas-liquid chromatograph with a thermal conductivity based detector. Helium was used as a carrier gas. Volumetric rate of the carrier gas in the chromatographic column was 1.45 l/h. We used 1.5 meters long chromatographic column filled with

Chromaton NAW and 15 % of PEGA. Signal processing was conducted through a differentiating amplifier.

For the reaction kinetic regularities ascertainment sets of experiments were carried out. Kinetic curves of the hydrogen peroxide consumption and kinetic curves of the unsaturated acid and its ester accumulation were obtained.

3. Results and Discussion

When aldehyde interacts with hydrogen peroxide in alcohol mediums the parallel formation of both unsaturated acid and its ester occurs. And the reaction proceeding may be represented by the following scheme:



R — H, CH_3; R^1 — H, C_2H_5; R^2 — CH_3, $-CH_2-CH{=}CH_2$, $-CH_2-CH-CH_2$ (epoxide, –O–) .

In case of unsaturated aldehyde oxidation with hydrogen peroxide in alcohol medium in the presence of a catalyst the reagents are consumed in two ways: the reaction of unsaturated acid formation with a rate constant k_c and the reaction of ester formation with the rate constant k_b proceeds simultaneously.

It was determined that the curve of hydrogen peroxide consumption and the curve of the reaction products accumulation are characterized by kinetic equations for a second order reaction. And using the integral method the equations describing hydrogen peroxide consumption were obtained:

$$\left(\frac{1}{[P]}\right)-\left(\frac{1}{[P_0]}\right)=k_p\cdot t \quad \text{or} \quad \frac{1}{[P]}=\frac{1}{[P_0]}+k_p\cdot t\,, \qquad (1)$$

ester accumulation:

$$\frac{[P_0]\cdot k_b}{[B]\cdot k_p}=1+\frac{1}{k_p\cdot t\cdot[P_0]} \quad \text{or} \quad \frac{1}{[B]}=\frac{k_p}{k_b\cdot[P_0]}+\frac{1}{k_b\cdot[P_0]^2}\cdot\frac{1}{t} \qquad (2)$$

and unsaturated acid accumulation:

$$\frac{[P_0]\cdot k_c}{[C]\cdot k_p}=1+\frac{1}{k_p\cdot t\cdot[P_0]} \quad \text{or} \quad \frac{1}{[C]}=\frac{k_p}{k_c\cdot[P_0]}+\frac{1}{k_c\cdot[P_0]^2}\cdot\frac{1}{t}\,, \qquad (3)$$

where: $[P_o]$, $[P]$ – initial and current concentration of hydrogen peroxide, respectively, mol/l; $[B]$ – ester concentration, mol/l; $[C]$ – acid concentration, mol/l; k_p – rate constant of hydrogen peroxide consumption, l/(mol·s); k_b – rate constant of ester accumulation, l/(mol·s); k_c – rate constant of acid accumulation, l/(mol·s); t – time.

It is evident from the Eqs. (1), (2) and (3) that the kinetic curve of hydrogen peroxide consumption should have the appearance of a straight line in the $1/[P] = f(t)$ coordinates, the curve of the ester accumulation should have the appearance of the straight line in the $1/[B] = f(1/t)$ coordinates, and the curve of the acid accumulation should have the appearance of the straight line in the $1/[C] = f(1/t)$ coordinates.

Respective charts are given in Fig. 1.

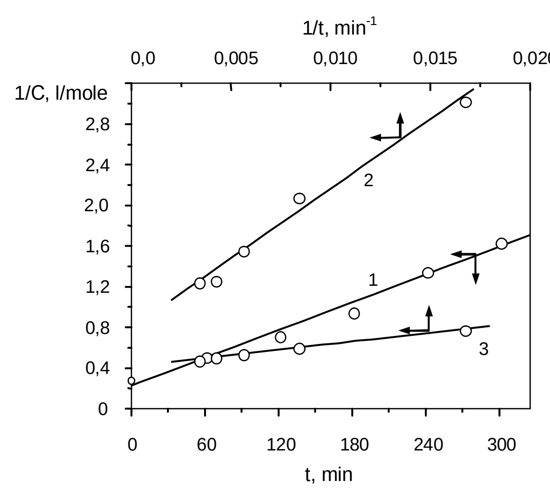


Fig. 1. Rectification of the kinetic curves of the hydrogen peroxide consumption (1), α-ethacrylic acid (2) and allylacrylate accumulation (3) in case of α-ethylacrolein interaction with the hydrogen peroxide in the presence of H_2SeO_3 in the allyl alcohol medium. T = 313K; $C_{cat.}$ = 0.1 mol/l; the alcohol:aldehyde molar ratio is 2:1

Rectification of the kinetic curves for hydrogen peroxide, ester and acid in mentioned coordinates confirms the proceeding of the investigated reaction according to the laws of the parallel second order reaction. That is why for calculation of the rate constants of hydrogen peroxide consumption (k_p), the ester accumulation (k_b) and the unsaturated acid accumulation (k_c) the following expressions obtained from the Eqs. (1)-(3), relatively, were used:

$$k_p = \frac{\left(\frac{1}{[P]} - \frac{1}{[P_0]}\right)}{t} \quad (4)$$

$$k_b = \frac{[B] \cdot \left(k_p [P_0] \cdot t + 1\right)}{[P_0]^2 \cdot t} \quad (5)$$

$$k_c = \frac{[C] \cdot \left(k_p [P_0] \cdot t + 1\right)}{[P_0]^2 \cdot t}. \quad (6)$$

Table 1

Model parameters of the oxidation reaction of a-ethylacrolein and crotonic aldehyde in methanol

T, K	C_{cat}, mol/l	$k_P \cdot 10^5$, l/(mol·s)	$k_c \cdot 10^5$, l/(mol·s)	$k_b \cdot 10^5$, l/(mol·s)	k_b / k_c
		a-Ethylacrolein			
293	0.1	1.65	0.49	1.04	2.12
303	0.1	4.41	1.73	2.52	1.457
313	0.1	8.70	5.20	3.35	0.644
323	0.1	24.1	17.4	4.40	0.253
303	0.05	2.65	1.48	1.05	0.709
303	0.1	4.42	1.72	2.51	1.459
303	0.15	6.01	3.41	2.25	0.660
		Crotonic aldehyde			
293	0.05	2.30	0.89	1.40	1.573
303	0.05	6.36	3.10	2.93	0.945
313	0.05	17.5	10.8	6.00	0.556
303	0.025	3.33	1.70	1.52	0.894
303	0.05	6.36	3.10	2.93	0.945
303	0.1	11.0	7.51	3.35	0.446

The rate constants of hydrogen peroxide consumption, ester and unsaturated acid accumulation, calculated by the Eqs. (4)-(6) for a-ethylacrolein and crotonic aldehyde oxidation in methanol, allyl alcohol and glycidol, are given in Tables 1, 2 and 3.

It is evident from the tables, that the rates of hydrogen peroxide consumption, ester and unsaturated acid accumulation depend on temperature and alcohol/ aldehyde ratio, and they are proportional to the catalyst concentration.

The values of the rate constants ratio k_b / k_c , given in Tables 1, 2 and 3 are an important characteristic of the parallel reaction. This ratio numerically corresponds to the ratio of parallel reactions rates of products accumulation. And because of the fact that the parallel reactions have the same order, it indicates the ratio of the products molar amounts.

It is very important to analyze the dependence of products ratios (ester/acid) on the reaction conditions (temperature, the catalyst concentration, the reagents ratio and its conversion degree) when choosing optimal conditions of the reaction realization, since the ester is a more valuable product of the reaction.

The constancy of the ester/unsaturated acid ratio in time is common for both aldehydes oxidation in various alcohols. This is confirmed by data of Fig. 1, corresponding to the model of the parallel reaction of the same order. And it can be stated that the reaction products amounts ratio doesn't depend on the reagents conversion degree.

Dependences of the reaction products ratio on the catalyst concentration, temperature and the alcohol/ aldehyde ratio are given in Figs. 2, 3 and 4, respectively. These data show that when the catalyst concentration increases (Fig. 2) the ester/acid ratio decreases. So, the increase in the catalyst concentration affects the increase in rate of unsaturated acid formation to a larger extent than it affects the increase in its ester formation rate. Comparison of the products ratios for alcohols of different structure indicates that this ratio is larger for allyl alcohol (curves 1 and 2 in Fig. 2) then for glycidol (curves 3 and 4 in Fig. 2).

Table 2

Model parameters of the oxidation reaction of a-ethylacrolein and crotonic aldehyde in allyl alcohol

T, K	Alcohol/ aldhyde	$C_{cat.}$, mol/l	$k_P \cdot 10^5$, l/(mol·s)	$k_c \cdot 10^5$, l/(mol·s)	$k_b \cdot 10^5$, l/(mol·s)	k_b / k_c
			a-Ethylacrolein			
293	2/1	0.1	2.51	1.51	0.69	0.445
303	2/1	0.1	7.84	4.99	2.03	0.407
313	2/1	0.1	13.58	8.81	3.38	0.384
323	2/1	0.1	42.52	27.92	10.29	0.369
313	2/1	0.05	4.79	2.99	1.28	0.428
313	2/1	0.1	7.84	4.99	2.03	0.407
313	2/1	0.15	11.11	7.03	2.78	0.395
313	1/1	0.1	5.99	3.39	2.60	0.45
313	2/1	0.1	7.84	4.99	2.03	0.407
313	3/1	0.1	8.51	5.72	1.83	0.321
313	5/1	0.1	17.15	12.51	2.61	0.209
313	10/1	0.1	24.14	17.8	3.51	0.197
			Crotonic aldehyde			
293	2/1	0.1	2.29	1.22	0.85	0.697
303	2/1	0.1	4.38	2.29	1.60	0.669
313	2/1	0.1	8.26	4.60	2.91	0.633
323	2/1	0.1	22.65	12.94	7.44	0.575
313	2/1	0.05	2.26	1.20	0.83	0.692
313	2/1	0.1	4.38	2.39	1.6	0.669
313	2/1	0.15	12.89	7.26	4.22	0.581
313	1/1	0.1	4.15	2.38	1.73	0.73
313	2/1	0.1	4.38	2.39	1.60	0.669
313	3/1	0.1	6.81	3.87	2.25	0.581
313	5/1	0.1	9.40	5.96	2.47	0.414
313	10/1	0.1	14.52	9.55	3.53	0.370

Table 3

Model parameters of the oxidation reaction of *α*-ethylacrolein and crotonic aldehyde in glycidol

T, K	Alcohol/ aldhyde	$C_{cat.}$, mol/l	$k_P \cdot 10^5$, l/(mol·s)	$k_c \cdot 10^5$, l/(mol·s)	$k_b \cdot 10^5$, l/(mol·s)	k_b / k_c
α-Ethylacrolein						
293	1/1	0.1	1.10	0.78	0.21	0.269
303	1/1	0.1	2.74	2.07	0.39	0.188
313	1/1	0.1	4.75	3.64	0.63	0.173
323	1/1	0.1	21.91	17.10	2.57	0.150
313	1/1	0.05	0.92	0.67	0.16	0.239
313	1/1	0.1	2.74	2.07	0.39	0.188
313	1/1	0.15	3.63	2.73	0.51	0.186
313	0.35/1	0.1	1.44	0.97	0.32	0.330
313	1/1	0.1	2.74	2.07	0.39	0.188
313	1.25/1	0.1	2.61	2.02	0.33	0.163
313	1.5/1	0.1	3.52	2.76	0.41	0.145
313	2/1	0.1	4.81	3.81	0.51	0.134
Crotonic aldehyde						
293	1/1	0.1	1.33	0.87	0.33	0.379
303	1/1	0.1	3.11	2.17	0.62	0.286
313	1/1	0.1	4.48	3.19	0.84	0.263
323	1/1	0.1	7.50	5.38	1.37	0.255
313	1/1	0.05	1.09	0.72	0.26	0.361
313	1/1	0.1	3.11	2.17	0.62	0.286
313	1/1	0.15	4.99	3.54	0.95	0.268
313	0.35/1	0.1	2.19	1.38	0.58	0.420
313	1/1	0.1	3.11	2.17	0.62	0.286
313	1.25/1	0.1	3.62	2.58	0.67	0.260
313	1.5/1	0.1	5.10	3.68	0.91	0.247
313	2/1	0.1	7.98	5.85	1.33	0.227

Data of the ester/acid ratio dependence on temperature conform to data of activation parameters for the rate constants, given in Table 4.

It is evident from Table 4 that the activation energy of the acid formation reaction (E_A^C) is larger than the activation energy of the ester formation reaction (E_A^B) for the oxidation of both aldehydes in all studied alcohols. This fact conforms to the obtained data of the reaction products ratio (ester/acid) dependence on the reaction temperature, since the temperature increase affects the unsaturated acid formation rate to a larger extent than it affects the ester formation rate.

When the alcohol/aldehyde ratio increases the ester/acid ratio decreases (Fig. 4). So, excess of the alcohol related to the aldehyde promotes the reaction of the unsaturated acid formation. This fact confirms that the reaction proceeds according to the parallel products formation scheme given above, and denies the possibility of direct esterification of formed unsaturated acid under conditions, on which the reaction was investigated.

The ester/acid ratio decreases when the reaction temperature increases (Fig. 3). This decrease is especially essential when the reaction is carried out in the methanol medium (curves 1 and 2 in Fig. 3). Besides, it is clear from Fig. 3 that the ester formation prevails when the reaction is carried out at low temperatures in methanol. When the reaction is carried out in allyl alcohol or glycidol the unsaturated acid is mainly formed.

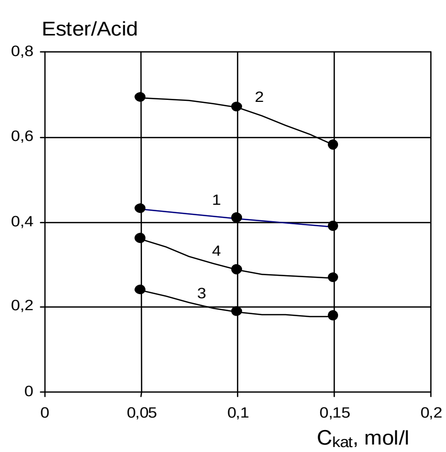


Fig. 2. Dependence of ester/acid ratio on the catalyst concentration at *T* = 313 K: EA in AA (1); CA in AA (2); EA in GL (3) and CA in GL (4)

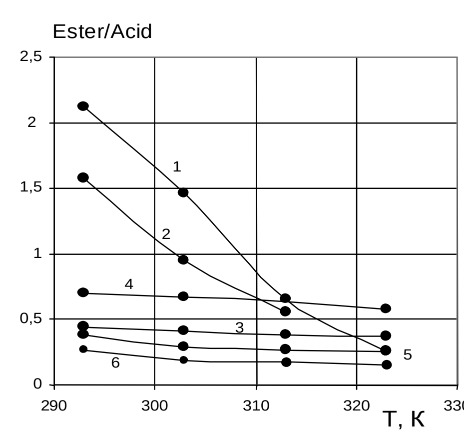


Fig. 3. Dependence of the products ratio on temperature at $C_{cat.}$ = 0.1 mol/l: EA in ME (1); CA in ME (2); EA in AA (3); CA in AA (4); EA in GL (5) and CA in GL (6)

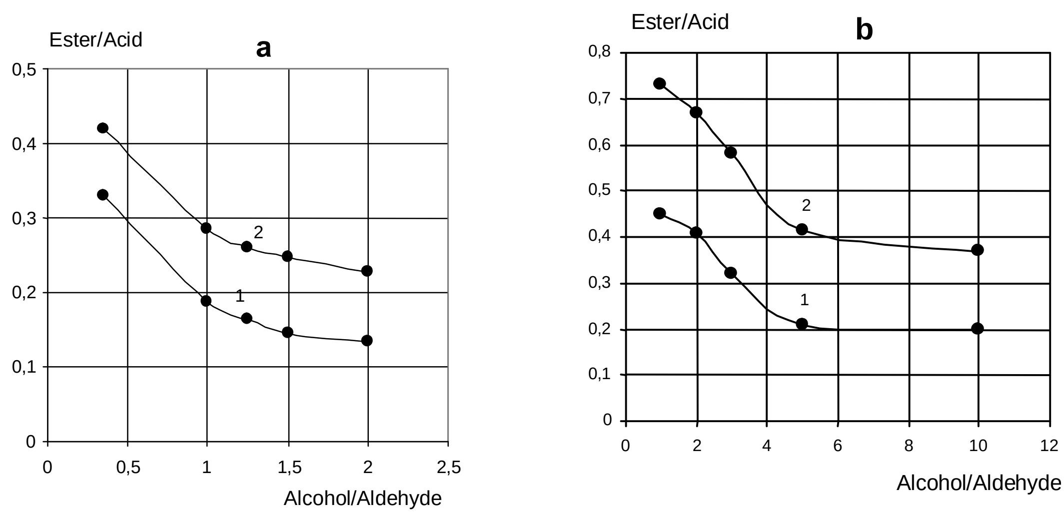


Fig. 4. Dependence of the reaction products ratio on the alcohol/aldehyde ratio in glycidol (a) and in allyl alcohol (b): EA (1) and CA (2). T = 313 K, $C_{cat.}$ = 0.1 mol/l

Table 4

Activation parameters of the reaction of ethylacrolein (EA) and crotonic aldehyde (CA) oxidation in alcohols

Aldehyde	E_A^P, kJ/mol	E_A^C, kJ/mol	E_A^B, kJ/mol	k_0^P, l/(mol·s)	k_0^C, l/(mol·s)	k_0^B, l/(mol·s)
Methanol						
EA	68.6	93.6	50.0	$2.78 \cdot 10^7$	$2.4 \cdot 10^{11}$	$9.3 \cdot 10^3$
CA	77.3	93.7	55.5	$1.4 \cdot 10^9$	$4.5 \cdot 10^{11}$	$1.08 \cdot 10^5$
Allyl alcohol						
EA	72.1	71.8	66.8	$1.65 \cdot 10^8$	$9.6 \cdot 10^7$	$5.5 \cdot 10^6$
CA	57.1	59.8	54.9	$4.1 \cdot 10^5$	$5.9 \cdot 10^5$	$5.6 \cdot 10^5$
Glycidol						
EA	78.6	81.0	66.1	$1.10 \cdot 10^9$	$2.1 \cdot 10^9$	$1.3 \cdot 10^6$
CA	45.4	47.9	37.3	$1.6 \cdot 10^3$	$2.9 \cdot 10^3$	$1.5 \cdot 10^3$

4. Conclusions

The kinetic regularities of a-ethylacrolein and crotonic aldehyde oxidation reaction in methanol, allyl alcohol and glycidol were studied. It was shown that this reaction is characterized by kinetic laws for second order parallel reactions. Rate constants of hydrogen peroxide consumption and the unsaturated acid and its ester accumulation, as well as activation parameters of these reactions, for both aldehydes in various alcohols at various temperatures and concentrations of the catalyst were calculated. Dependences of the ester/acid ratio on temperature, the catalyst concentration and the alcohol/aldehyde ratio were ascertained. Dependences of the reaction kinetic parameters and the products composition on the aldehyde and the alcohol structure were ascertained. It was shown that data of the dependence of the reaction products composition on the reaction conditions conforms to the reaction kinetic parameters.

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ОКИСНЕННЯ НЕНАСИЧЕНИХ АЛЬДЕГІДІВ ПЕРОКСИДОМ ВОДНЮ В СПИРТАХ

Анотація. *Вивчено кінетичні закономірності реакції окиснення α-етилакролеїну та кротонового альдегіду в метанолі, аліловому спирті та гліцидолі. Обчислені константи швидкостей витрати пероксиду водню і нагромадження ненасиченої кислоти і її естеру для обох альдегідів в різних спиртах при різних концентраціях каталізатора і температурах та обчислені активаційні параметри реакції. Встановлено залежності відношення естер : кислота від умов проведення реакції. Показана залежність швидкості та складу продуктів реакції від будови альдегіду і спирту. Дані про залежність складу продуктів реакції від умов її проведення узгоджується з кінетичними параметрами реакції.*

Ключові слова: *α-етилакролеїн, кротоновий альдегід, окиснення пероксидом водню, окиснювальне алкоксилювання, каталізатор H_2SeO_3, співвідношення естер/кислота, кінетичні та активаційні параметри реакції.*