

Zoryan Pikh¹, Roman Nebesnyi¹, Volodymyr Ivasiv¹, Andriy Pich² and Sofia Vynnytska¹

OXIDATION OF UNSATURATED ALDEHYDES BY PERACETIC ACID

¹ Lviv Polytechnic National University

12 S. Bandery St., 79013 Lviv, Ukraine; pikh@polynet.lviv.ua

² Institute of Technical and Macromolecular Chemistry,

RWTH Aachen University and Leibniz Institute for Interactive Materials, e.V. Aachen, Germany

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Abstract. The paper is dedicated to studies of kinetic regularities of oxidation of unsaturated aldehydes by organic peracids. The routes of products formation were considered, kinetic model of the oxidation reaction was designed and reaction activation parameters were calculated based on experimental data. New data on reactivity of aldehydes with various structures in the reaction with peracids were obtained.

Keywords: oxidation with peracids, unsaturated aldehydes, mechanism of the reaction, kinetic and activation parameters.

1. Introduction

Study of the reaction of unsaturated aldehydes with peracids has practical and theoretical reason. This reaction is among other possible ways of obtaining unsaturated acids, which are valuable products of organic synthesis industry [1-3]. Theoretical value of the study should be considered in a few aspects. Firstly, the interaction of aldehyde with peracid is the key stage responsible for acid formation in the processes of liquid phase aldehydes oxidation by molecular oxygen. Thus, detailed study of the reaction regularities could answer the range of questions about routes of the products formation and role of the peroxide compounds in the processes of liquid phase aldehydes oxidation. Secondly, availability of two functional groups (carbonyl group and >C=C< double bond) capable of interaction with peracids in the molecules of unsaturated aldehydes causes the necessity of considering the mutual influence of these groups and possibility of the reaction by both reaction sites. Because of this circumstance it is necessary to consider the interaction of unsaturated aldehydes with peracids from

the point of view of both the reaction by carbonyl compound and as the reaction by double bond.

2. Experimental

Study of the reaction of unsaturated aldehydes with peracids was carried out in thermostatted 50 ml glass reactor equipped with magnetic stirrer, condenser and thermometer. 0.05 mol of unsaturated aldehyde was fed into the reactor and the solution of peracid in organic solvent was added at constant temperature. Samples of the reaction mixture were periodically taken for the analysis. The peracid content was determined by iodometric method. The unsaturated acid content, as well as content of the formate of unsaturated alcohol and corresponding epoxy formate were determined by chromatography.

The unsaturated aldehyde content in the reaction mixture was determined by photocolometric method through the following methodology [4]: 40 ml of 1 % solution of dimethyl sulfoxide was introduced into a weighted 100 ml flask (dimethyl sulfoxide is used for peroxides decomposition). After that the sample of the reaction mixture was weighted and kept for 30 min. Then the mixture was moved into a volumetric flask and 50 ml of 1 % solution of *p*-phenyldiamine and water were introduced into the flask. Optical density of the resulting solution was determined by photocolometer HOVERLABS PA-35. Molar concentration of the aldehyde (C_A) in the volumetric flask was determined using the calibration graph $C_A(\text{mol/l}) - D$ (optical density). Aldehyde content in the reaction mixture was calculated by the formula:

$$C_A = \frac{M_{mk} V}{V_A} \cdot \frac{(m_3 - m_1)}{(m_2 - m_1)}$$

where C_A – concentration of aldehyde in the reaction mixture, mol/l; M_{mk} – molar concentration of aldehyde in volumetric flask; V – volume of the volumetric flask, ml; V_A – volume of the aliquot moved from the volumetric flask into the cell, ml; m_1 – weight of the flask, g; m_2 – weight of the flask with dimethyl sulfoxide solution, g.

The calibration lines for determination of molar concentration of aldehyde in the reaction mixture are shown in Fig. 1 and the regression equation coefficients for the aldehydes concentration calculation based on optical density values are shown in Table 1.

The structure of the reaction products was determined by IR-spectroscopy using Thermo Nicolet NEXUS-470 and NMR-spectroscopy using Bruker AV600.

3. Results and Discussion

3.1. General Regularities of the Reaction of Unsaturated Aldehydes with Peracids

The regularities of unsaturated aldehydes interaction with peracids and the ratio of the products obtained on both kinds of sites largely depend on aldehyde struc-

ture (relative position of functional groups and availability and properties of substituents). Aldehydes of acrylic range, both functional groups of which are in conjugation, occupy a special place in this sense.

The results of products content determination, the schemes of their formation, and the kinetic of reaction of unsaturated aldehydes of various structures with organic peracids are considered in the article. The objects of investigation includes: acrolein, α -methacrolein, α -ethylacrolein, α -propylacrolein, α -butylacrolein, α -amylacrolein, 2-ethyl-2-hexenal, 2-isopropyl-5-methyl-2-hexenal, crotonaldehyde and benzaldehyde. Peracetic acid was used as oxidant.

Based on the kinetic curves of peracid consumption and unsaturated acid formation during oxidation of the range of unsaturated aldehydes with peracetic acid in dichloroethane at 313 K (Fig. 2) it is obvious that:

- i) aldehyde and the peracid are consumed in nonequivalent amounts (higher consumption of the peracid than that of aldehyde are observed in all cases);
- ii) the amount of obtained unsaturated acid does not match the amount of reacted aldehyde and peracid.

Table 1

Factors of regression equation $M_{mk} = k \cdot D$ for photocolorimetric analysis of aldehydes

Aldehyde	Thickness of the cell, mm		
	50	30	20
Methacrolein	$(9.5 \pm 0.2) \cdot 10^{-4}$	$(16.8 \pm 0.5) \cdot 10^{-4}$	$(20.8 \pm 0.5) \cdot 10^{-4}$
α -Ethylacrolein	$(8.3 \pm 0.3) \cdot 10^{-4}$	$(15.9 \pm 0.6) \cdot 10^{-4}$	$(20.1 \pm 0.3) \cdot 10^{-4}$
2-Ethyl-2-hexenal	$(8.6 \pm 0.4) \cdot 10^{-4}$	$(16.1 \pm 0.6) \cdot 10^{-4}$	$(20.0 \pm 0.5) \cdot 10^{-4}$
Crotonaldehyde	$(9.2 \pm 0.2) \cdot 10^{-4}$	$(16.3 \pm 0.3) \cdot 10^{-4}$	$(20.5 \pm 0.4) \cdot 10^{-4}$

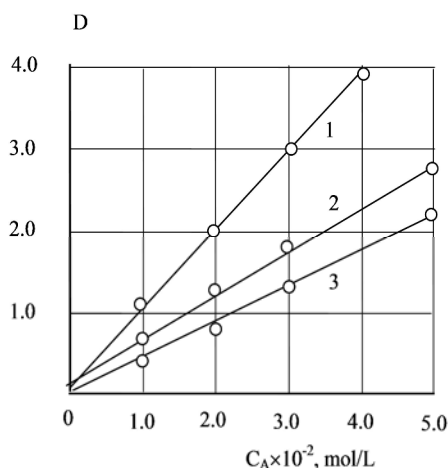


Fig. 1. Gauge curves for photocolorimetric analysis of ethylacrolein by *p*-phenylenediamine. The thickness of the cell (mm): 50 (1); 30 (2) and 20 (3)

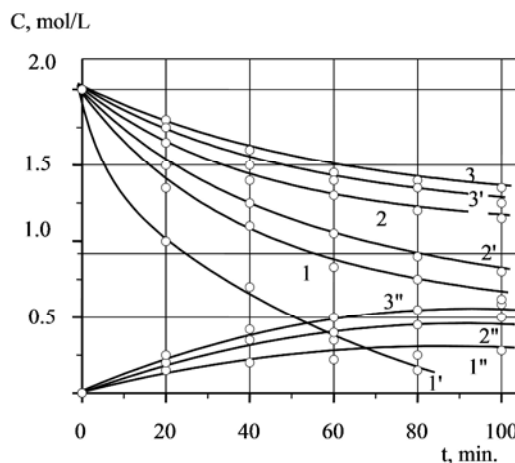


Fig. 2. Kinetic curves of peracetic acid (') and aldehyde consumption, and unsaturated acid (") accumulation in dichloroethane: 2-ethyl-2-hexenal (1); α -ethylacrolein (2) and crotonaldehyde (3). $T = 313$ K

These data indicate complicated nature of the reaction of unsaturated aldehydes with peracids: low unsaturated acid yield indicates by-products formation, and nonequivalent consumption of aldehyde and peracid indicates consumption of peracid in consecutive reactions.

It was determined [5] that the following products form during oxidation of unsaturated aldehydes with peracids: corresponding unsaturated acid, formate of unsaturated alcohol and corresponding epoxide, carbonyl compounds (saturated aldehyde or ketone depending on aldehyde structure), and carboxylic acids with lower carbon atoms number than that of oxidized aldehyde. Small amount of gaseous products (less than 3–5 % of reacted acid) is formed during the interaction between unsaturated aldehydes and peracids. Among gaseous products CO (70 %), CO₂ (12 %), O₂ (18 %) have been identified. Complete list of products of unsaturated aldehydes oxidation by peracids is given in [6].

Kinetic curves of reagents consumption and products accumulation during interaction of α -ethylpropenal with peracetic acid are shown in Fig. 3.

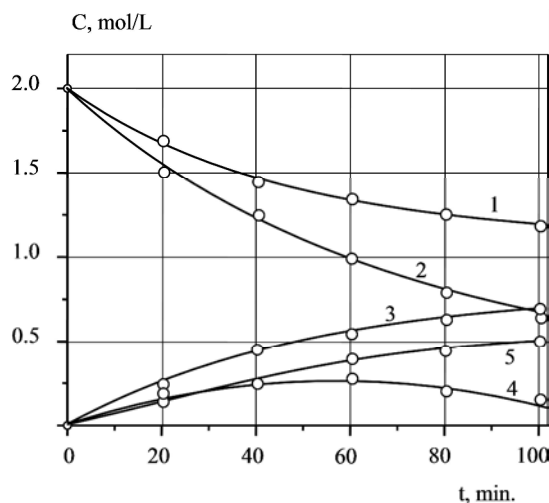
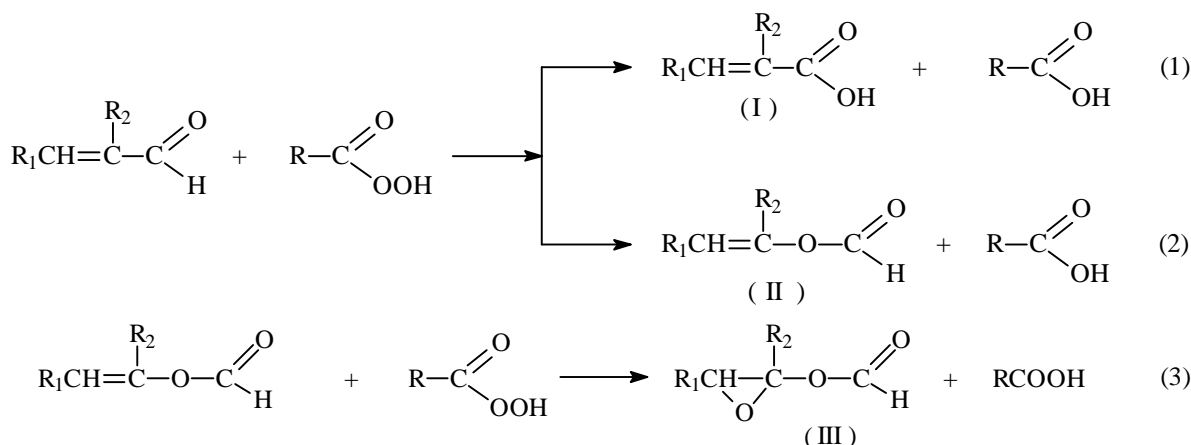
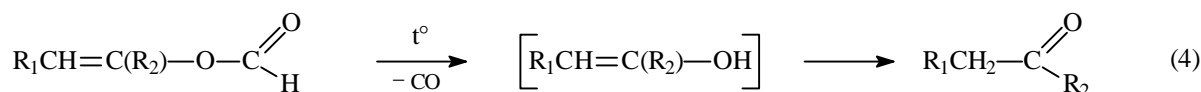


Fig. 3. Kinetic curves of the reagent consumption and products accumulation during ethylacrolein oxidation with peracetic acid in benzene: ethylacrolein (1); peracetic acid (2); ethylacrylic acid (3); 1-ethenylformiate (4) and 1-ethyl-1,2-epoxyenylformiate (5). $T = 313 \text{ K}$

Products composition and character of the kinetic curves of reactants and ratio of aldehyde and peracid consumption allows to suggest the following scheme of converting:



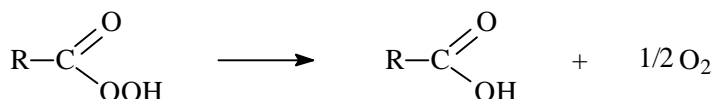
Formates of unsaturated alcohols (compound II) can decompose during the reaction and products separation:



where $\text{R}_1 = \text{CH}_3, \text{C}_3\text{H}_7$; $\text{R}_2 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$.

The evidence of this reaction is carbonyl compounds (ketones and aldehydes, depending on the initial aldehyde structure) and carbon oxide formation.

Presence of carbon dioxide and oxygen among gaseous products could be explained by partial decomposition of peracid by reaction:



Suggested reaction scheme conforms to kinetics of reagents consumption and products accumulation. It explains extreme character of accumulation curve of unsaturated alcohol formate (II) and S-like character of accumulation curve of epoxy formate (product III). The scheme also explains non-equivalence of aldehyde and peracid consumption (the peracid takes part in consecutive reactions).

When carrying out the reaction in the presence of water, the decrease of amount of unsaturated alcohol formate (product II) and its epoxide (product III) and simultaneous increase of product IV amount in the oxidate were observed. Besides, appearance of new reaction products such as formic acid and keto-alcohol (product V) was observed, which forms as a result of hydrolysis of products II and III by reactions [7]:

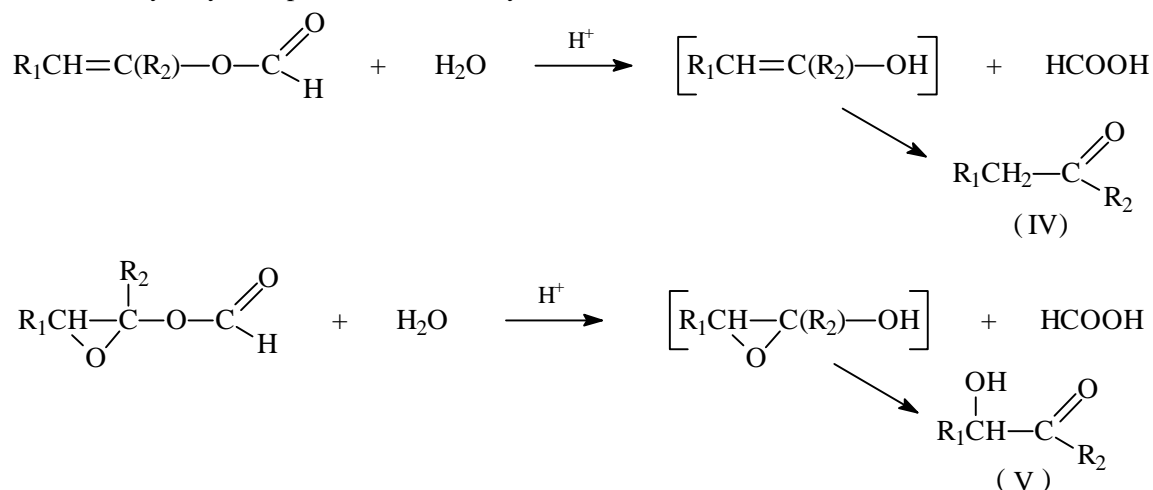


Table 2

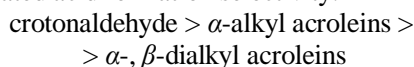
Selectivity of unsaturated acid formation (%) in reaction of aldehydes with peracetic acid at different temperatures (conversion of aldehydes is 50 %)

Solvent	313 K		323 K		333 K	
	$\Delta C_{MA}/\Delta C_A$	$\Delta C_{MA}/C_{PA}$	$\Delta C_{MA}/\Delta C_A$	$\Delta C_{MA}/C_{PA}$	$\Delta C_{MA}/\Delta C_A$	$\Delta C_{MA}/C_{PA}$
<i>α</i>-Methacrolein						
Acetic acid	35	30	39	32	34	29
Dioxane	79	72	82	74	77	69
Tetrahydrofurane	85	78	91	80	89	77
Benzene	34	24	37	28	35	22
<i>α</i>-Ethylacrolein						
Acetic acid	80	74	85	78	80	70
Dioxane	79	72	84	76	78	70
Tetrahydrofurane	92	85	95	88	89	81
Benzene	37	31	39	32	31	30
Crotonaldehyde						
Acetic acid	89	74	89	78	86	71
Dioxane	94	85	95	88	91	82
Tetrahydrofurane	96	85	97	89	93	82
Benzene	88	79	92	81	89	77
2-Ethyl-2-hexenal						
Acetic acid	17	14	22	15	19	13
Dioxane	24	18	28	22	25	20
Tetrahydrofurane	27	20	33	25	29	21
Benzene	16	11	21	17	18	12

3.2. Unsaturated Acids Formation Selectivity during Interaction of Unsaturated Aldehydes with Peracids

Selectivity of unsaturated acids formation during oxidation of corresponding aldehydes with peracids strongly depends on the reaction conditions (solvent, temperature, reagents concentration, conversion of reagents, and aldehyde structure). Table 2 shows the dependence of unsaturated acids selectivity on solvent used as reaction medium, and on temperature. This table shows that the highest selectivity is observed in case of croton aldehyde oxidation (yield is higher than 89%). Yield of unsaturated acid in case of α -alkyl acroleins oxidation is 25–92%, depending on reaction conditions.

The lowest yield of unsaturated acid (less than 21%) is observed in case of α -, β -dialkylacroleins oxidation. Unsaturated aldehydes form a series by change of unsaturated acid formation selectivity:



The highest acid formation selectivity is achieved when carrying out the reaction in dioxane and tetrahydrofurane.

3.3. Kinetic Regularities of Unsaturated Aldehydes Reaction with Peracids

To determine the reaction orders with respect to reagents (peracid and aldehyde) a series of experiments were carried out with different concentrations of reagent, for which reaction order is determined, and at constant concentration of another reagent. The method of excess was used [8], *i.e.* the concentration of reactant for which reaction order is being determined was 4–5 times lower

than the concentration of another reactant. Thus, while determining reaction order with respect to peracid, a series of experiments was carried out with different initial concentrations of peracid and with constant excessive concentration of the aldehyde (Fig. 4). Initial concentration of acid was kept constant in this series of experiments in order to avoid the influence of acid.

To determine the reaction order with respect to peracid the curves of this series of experiments were differentiated and dependence of reaction rate on peracid concentration was analyzed. Fig. 5 shows data concerning dependence of peracid consumption rate on peracid concentration for oxidation of 2-ethyl-2-hexenal with peracetic acid.

Dependence of reaction rate on the peracid concentration is non-linear (Fig. 5), indicating the reaction order with respect to peracid is not equal to 1. Correlation coefficients were calculated to quantify the deviation of the curves of peracid consumption rate dependence on peracid concentration from straight lines. Correlation coefficients for 2-ethyl-2-hexenal, α -ethylacrolein and crotonaldehyde are 0.6–0.7, 0.85–0.9 and 0.95, respectively. High correlation coefficient for crotonaldehyde indicates linear dependence of peracid consumption rate on peracid concentration for this aldehyde, therefore oxidation of crotonaldehyde is the first-order reaction with respect to peracid. It is noteworthy that the order of increasing of correlation coefficients matches the order of increasing of reaction selectivity with respect to unsaturated acid. Therefore, there is a correlation between reaction kinetics and the ratio of different reaction scheme stages: the more unsaturated aldehyde is capable of formates forming while interacting with peracid, the less is unsaturated acid selectivity and the bigger is deviation of curves of reaction rate dependence on peracid concentration from straight line.

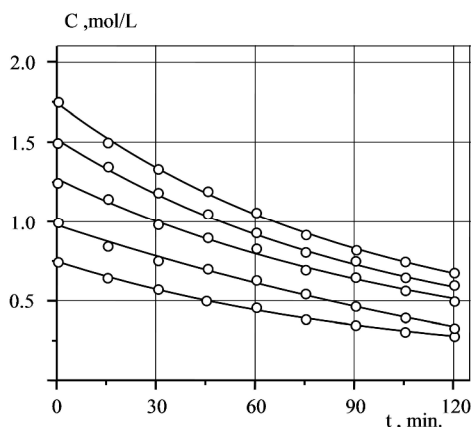


Fig. 4. Kinetic curves of peracetic acid consumption at its different initial concentrations (oxidation of α -ethylacrolein in dichlorethane). Initial concentration of aldehyde is 6.5 mol/l

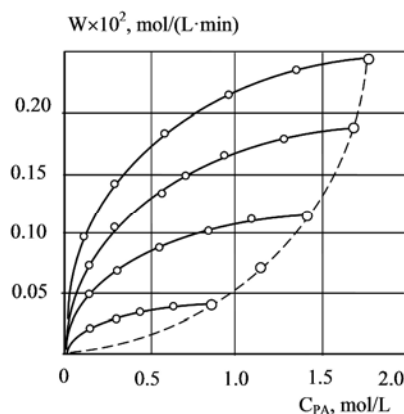


Fig. 5. Dependence of reaction rate on concentration of peracetic acid (oxidation of 2-ethyl-2-hexenal in dichlorethane). Initial concentration of aldehyde is 5 mol/l. $T = 313$ K

Fig. 5 also shows that dependence of initial reaction rate on initial peracid concentration is non-linear (dashed line in Fig. 5). For determining functional dependence of peracid consumption rate on its concentration a number of experiments were done with the same initial aldehyde concentration and different molar ratios aldehyde : peracid (1:0.4; 1:0.6; 1:0.8; 1:1).

Fig. 6 shows the dependence of initial reaction rate on peracid concentration during oxidation of α -ethylacrolein in benzene at 303 K. The dependence of initial reaction rate on initial peracid concentration has the form of parabola (curve 1), which turns linear with 0.998 correlation coefficient in coordinates $W_0/[PA]_0 - [PA]_0$ (line 3). Linearization of curve 1 in this coordinates indicates quadratic dependence of initial reaction rate on peracid concentration. Such dependence of peracid consumption rate on its initial concentration is observed only in oxygen-free solvents. Thus, the dependence of initial peracid consumption on its initial concentration is linear (line 2) with 0.997 correlation coefficient while carrying out the reaction in acetic acid. This indicates strictly first-order reaction with respect to peracid while carrying out reaction of unsaturated aldehydes with peracids in organic solvents.

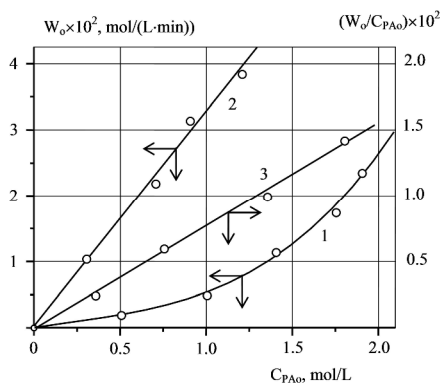
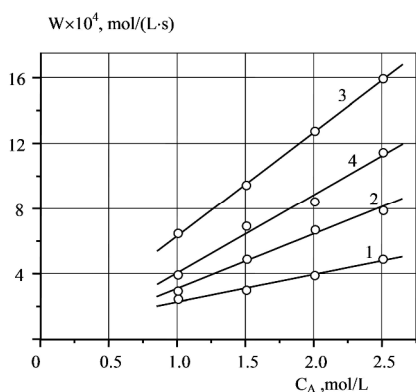


Fig. 6. Dependence of initial rate of peracetic acid consumption on initial concentration of peracid: in benzene (1); in acetic acid (2); curve 1 in coordinates $W_0/C_{PA0} - C_{PA0}$. (3)



Considering specific reaction nature in organic solvents, a number of experiments were done in order to study the dependence of initial reaction rate on initial organic acid concentration. The results of experiments which were done at peracid concentration of 0.1 mol/l are shown at Fig. 7. It is clear that at acetic acid concentration in the mixture up to 2.5 mol/l the initial reaction rate is directly proportional to acetic acid concentration. When acetic acid concentration is 2.5–4.4 mol/l it has almost no effect on the reaction rate and with further increasing of acetic acid concentration reaction rate decreases. Therefore, the effect of acid formed from peracid during reaction and participation of acid in reaction mechanism should be considered for kinetic studies.

To determine the reaction order with respect to aldehyde a series of experiments were done with constant initial peracid concentration and various initial concentrations of unsaturated aldehyde. Dependences of reaction rate on aldehyde concentration were obtained by differentiation of obtained curves. Strictly linear dependence of reaction rate on aldehyde concentration at various temperatures (Fig. 8) indicates first-order reaction with respect to aldehyde.

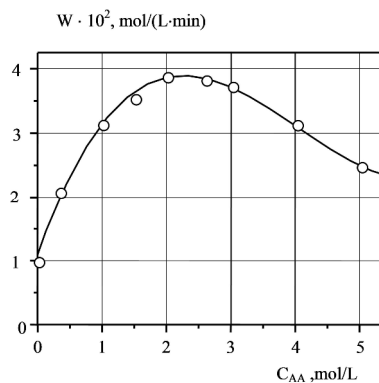
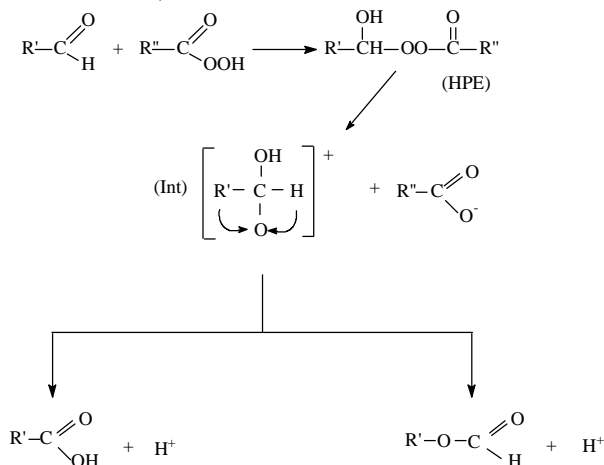


Fig. 7. Dependence of initial reaction rate on the initial concentration of acetic acid in case of α -ethylacrolein oxidation with peracetic acid in dichloroethane. Concentration of reagent is 1 mol/l; $T = 313$ K

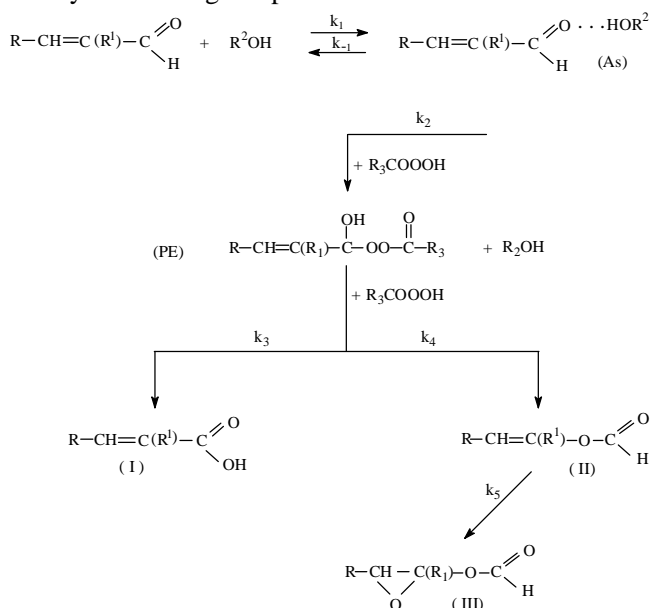
Fig. 8. Dependence of initial reaction rate on aldehyde concentration (oxidation of α -ethylacrolein in benzene) at 303 K (1); 313 K (2); 323 K (3) and oxidation of 2-ethyl-2-hexenal in tetrahydrofuran at 313 K (4). he oxidant is 2 mol/l peracetic acid solution

Simultaneous formation of primary stable products by reaction of unsaturated aldehyde with peracid (or unsaturated acid with formate of unsaturated alcohol) indicates that they are formed from one intermediate compound and can be explained in terms of Baeyer-Villiger mechanism (interaction of carbonyl compounds with peracids). According to this mechanism [9], during interaction between carbonyl compound and peracid α -hydroxyperester (HPE) forms at the first stage and decomposes by $-OO-$ bond, forming the cation (Int), which undergoes rearrangement with proton transfer (unsaturated acid forms) or with alkyl transfer (thus isomer of unsaturated acid – formate of unsaturated alcohol – forms):



Forming of α -oxyperacetate is certainly proven for oxidation of saturated aldehydes by peracids [10].

Considering the transformation scheme and specific effect of acid on reaction kinetics, the following mechanism could be suggested for reaction of unsaturated aldehydes with organic peracids:



The first stage of suggested mechanism is activation of aldehyde by forming of associate (As) of aldehyde and molecule of acid or peracid. Then the activated aldehyde molecule interacts with peracid forming intermediate – hydroxyperester (HPE), which decomposes by above-mentioned scheme forming unsaturated acid (I) or formate of unsaturated alcohol (II), which in turns is epoxidized to corresponding epoxide (III). The kinetic model of the reaction was constructed using this reaction scheme. Abbreviations for concentrations of compounds and intermediates used for kinetic equations are listed below:

aldehyde	[A]
peracid	[PA]
acid (formed from peracid)	[AA]
α -hydroxyperester	[PE]
solvated aldehyde	[AS]
unsaturated acid (target product)	[MA]
formate of unsaturated alcohol	[F]
epoxyformate	[E]
the sum of peracid and acid	[K] = [PA] + [AP]

In terms of stationarity for solvated aldehyde and α -oxyperester concentrations of associated aldehyde and α -oxyperester are:

$$[AS] = \frac{k_1 [PA][K]}{k_{-1} + k_2 [PA]} \quad (1)$$

$$[PE] = \frac{k_1 k_2 [K][PA][A]}{(k_3 + k_4)(k_{-1} + k_2 [PA])} \quad (2)$$

The system of differential equations of reagents consumption and products accumulation rate considering (1) and (2) is:

$$\frac{d[A]}{dt} = -\frac{k_1 k_2 [A][K][PA]}{k_{-1} + k_2 [PA]} \quad (3)$$

$$\frac{d[PA]}{dt} = -\frac{k_1 k_2 [A][K][PA]}{k_{-1} + k_2 [PA]} - k_5 [F][PA] \quad (4)$$

$$\frac{d[MA]}{dt} = -\frac{k_1 k_2 k_3 [K][PA][A]}{(k_3 + k_4)(k_{-1} + k_2 [PA])} \quad (5)$$

$$\frac{d[F]}{dt} = -\frac{k_1 k_2 k_4 [K][PA][A]}{(k_3 + k_4)(k_{-1} + k_2 [PA])} \quad (6)$$

$$\frac{d[E]}{dt} = k_5 [\Phi][PA] \quad (7)$$

As the limiting stage of Baeyer-Villiger reaction is α -oxyperester formation it can be taken that $k_{-1} \gg k_2$ and $(k_{-1} + k_2 [PA]) \approx k_{-1}$. Considering this for initial conditions ($[K] = [PA]_0$ and $[F]_0 = 0$), Eq. (4) for initial peracid consumption rate is:

$$W_0 = k_1 k_2 (k_{-1})^{-1} [A]_0 [PA]_0^2$$

This equation shows that quadratic dependence of initial reaction rate on peracid concentration should be observed during experiment. This equation is correct for cases when reaction is carried out in oxygen-free solvents. When carrying out the reaction in acetic acid, [K] is constant, therefore equation for the initial rate is:

$$W_o = k^* [A]_o [PA]_o$$

where: $k^* = \frac{k_1 k_2}{k_{-1}}$

We can see that equations for initial rates for both cases conform to the data in Fig. 5.

3.4. Calculation of Kinetic Model Parameters for Reaction of Unsaturated Aldehydes with Peracids

The derived kinetic model was the basis for calculation of kinetic parameters of the reaction. Complexity of the model does not allow calculating constants for each stage separately, but only complexes of the constants. The methodology of constants calculating is described in [5]. Let's denote them as follows:

$$k_p = Kk_2 \quad k_{MA} = Kk_2k_3(k_3 + k_4)^{-1}$$

$$k_F = Kk_2k_4(k_3 + k_4)^{-1} \quad k_E = k_5$$

Constant k_p characterizes reactivity of aldehyde during its interaction with peracid. Constants k_{MA} and k_F only differ in that k_{MA} contains rate constant of intermediate α -oxyperester decomposition to unsaturated acid (k_3) and k_F contains rate constant of intermediate product decomposition to formate of unsaturated alcohol (k_4). Therefore ratio of k_3 and k_4 constants indicates ratio of two main directions of reaction (formation of unsaturated acid and formate of unsaturated alcohol). Constant k_{MA} is a characteristic of reaction of unsaturated acid formation and constant k_F is a characteristic of reaction of formate formation. Comparing Eqs. (5) and (3) we can see that complex of constants $k_3/(k_3 + k_4)$ characterizes differential selectivity of unsaturated acid formation with respect to reacted aldehyde.

Constants k_p and k_{MA} at various temperatures are presented in Table 3.

Whereas $k_p = K \cdot k_2$ and $k_{MA} = K \cdot k_2(k_3/(k_3 + k_4))$, using constants k_{MA} and k_p in Table 3 we can calculate complex of constants $k_3/(k_3 + k_4)$. Therefore if suggested kinetic model of reaction and calculation methodology of kinetic parameters of reaction are correct then values of $k_3/(k_3 + k_4)$ calculated using data from Table 3 should correlate with selectivity determined experimentally.

Table 4 contains values of $k_3/(k_3 + k_4)$ complex of constants. Satisfactory conformity of Table 3 and Table 1 data indicates good conformity of reaction products composition data and kinetic studies data.

Table 3

Values of constant k_p and k_{MA} for reaction of unsaturated aldehydes with peracetic acid

Solvent	$k_p \cdot 10^3, l^2/(mol^2 \cdot s)$				$k_{MA} \cdot 10^3, l^2/(mol^2 \cdot s)$			
	293 K	303 K	313 K	323 K	293 K	303 K	313 K	323 K
α-Methacrolein								
Dioxane	0.47±0.06	1.09±0.07	2.51±0.1	5.49±0.11	0.35±0.04	0.92±0.04	2.38±0.05	5.27±0.08
Tetrahydrofurane	0.78±0.05	1.82±0.08	4.23±0.09	9.43±0.08	0.67±0.03	1.65±0.08	4.06±0.06	9.34±0.08
Acetic acid*	3.4±0.04	9.10±0.07	22.11±0.08	47.15±0.09	2.54±0.04	1.65±0.08	4.06±0.04	9.34±0.08
Benzene	0.92±0.06	2.18±0.09	5.42±0.07	11.63±0.05	0.77±0.04	1.58±0.06	3.84±0.08	8.34±0.07
α-Ethylacrolein								
Dichlorethane	0.79±0.04	1.31±0.05	3.28±0.08	7.71±0.06	0.38±0.03	0.73±0.05	0.850.04	1.62±0.04
Benzene	1.51±0.04	3.38±0.08	7.22±0.03	14.71±0.07	1.17±0.06	2.10±0.06	3.750.08	7.35±0.08
Dioxane	0.78±0.05	1.86±0.03	4.20±0.05	9.08±0.08	0.63±0.07	1.490.04	3.530.07	8.63±0.1
Ethylacetate	0.42±0.04	1.13±0.08	2.20±0.04	4.19±0.03	0.29±0.03	0.590.03	1.20±0.09	2.54±0.07
Tetrahydrofurane	1.15±0.05	2.64±0.09	5.85±0.05	1.91±0.08	1.13±0.06	2.510.05	5.55±0.09	12.63±0.12
Acetic acid*	1.81±0.06	5.44±0.05	10.31±0.09	18.92±0.09	1.06±0.05	1.950.04	3.43±0.08	6.24±0.09
2-Ethyl-2-hexenal								
Dichlorethane	1.11±0.04	3.14±0.05	8.87±0.07	22.61±0.3	0.19±0.1	0.45±0.05	0.78±0.02	1.81±0.07
Benzen	4.12±0.04	8.59±0.07	18.00±0.09	39.52±0.3	0.44±0.02	0.94±0.05	1.98±0.05	4.35±0.06
Dioxane	1.32±0.05	3.10±0.03	7.28±0.04	16.22±0.09	0.21±0.02	0.52±0.03	1.73±0.06	4.54±0.06
Ethylacetate	1.15±0.03	2.30±0.06	4.53±0.08	8.73±0.09	0.23±0.03	0.49±0.05	1.09±0.07	2.09±0.09
Tetrahydrofurane	1.92±0.08	4.51±0.06	10.72±0.11	24.00±0.2	0.370.04	1.03±0.05	2.89±0.07	6.86±0.09
Acetic acid*	13.35±0.08	25.42±0.09	48.33±0.3	82.2±0.7	2.93±0.07	3.86±0.06	4.35±0.09	8.45±0.09
Crotonaldehyde								
Dioxane	0.34±0.04	0.83±0.04	2.03±0.08	4.20±0.09	0.29±0.02	0.75±0.03	1.92±0.04	4.03±0.04
Tetrahydrofurane	0.84±0.05	1.91±0.07	4.33±0.1	9.76±0.12	0.72±0.04	1.75±0.08	4.24±0.05	9.55±0.09

Note: *value of constant in acetic acid l/(mol·s)

Table 4

Values $k_3/(k_3+k_4)$ for reaction of unsaturated aldehydes oxidation with peracetic acid

Solvent	Temperature, K		
	303 K	313 K	323 K
α -Methacrolein			
Dioxane	0.85	0.95	0.96
Tetrahydrofurane	0.80	0.96	0.97
α -Ethylacrolein			
Dichlorethane	0.56	0.31	0.21
Benzene	0.62	0.52	0.50
Dioxane	0.80	0.84	0.94
Tetrahydrofurane	0.90	0.95	0.98
Acetic acid*	0.35	0.33	0.33
2-Ethyl-2-hexenal			
Dichlorethane	0.14	0.09	0.08
Benzene	0.11	0.11	0.11
Dioxane	0.18	0.24	0.28
Ethylacetate	0.21	0.23	0.24
Tetrahydrofurane	0.23	0.27	0.29
Acetic acid*	0.15	0.09	0.09
Crotonaldehyde			
Dioxane	0.91	0.94	0.96
Tetrahydrofurane	0.92	0.98	0.98

Note: *value of constant in acetic acid l/(mol·s)

Table 5

Activation parameters of reaction of unsaturated aldehydes oxidation with peracetic acid

Solvent	k_0	E_a , kJ/mol	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , J/(mol·K)
α -Methacrolein				
Dioxane	$(2.4 \pm 0.2) \cdot 10^6$	65.8 ± 0.5	63.2	-152.4
Tetrahydrofurane	$(6.4 \pm 0.4) \cdot 10^6$	67.0 ± 0.4	64.4	-144.3
Acetic acid*	$(3.4 \pm 0.3) \cdot 10^4$	50.7 ± 0.4	48.1	-189.4
Benzene	$(7.54 \pm 0.4) \cdot 10^5$	63.4 ± 0.5	60.9	-165.2
α -Ethylacrolein				
Dichloroethane	$(3.6 \pm 0.1) \cdot 10^7$	72.2 ± 0.4	69.6	-129.9
Benzene	$(7.02 \pm 0.04) \cdot 10^5$	60.3 ± 0.5	57.3	-162.7
Dioxane	$(2.49 \pm 0.05) \cdot 10^6$	64.5 ± 0.4	61.9	-152.2
Tetrahydrofurane	$(3.51 \pm 0.06) \cdot 10^6$	64.6 ± 0.6	62.0	-149.2
Ethylacetate	$(1.76 \pm 0.04) \cdot 10^4$	53.3 ± 0.3	50.7	-193.3
Acetic acid*	$(2.98 \pm 0.05) \cdot 10^4$	52.5 ± 0.6	50.1	-177.4
2-Ethyl-2-hexenal				
Dichloroethane	$(2.28 \pm 0.5) \cdot 10^9$	80.4 ± 0.5	77.8	-95.5
Benzene	$(4.26 \pm 0.04) \cdot 10^6$	62.1 ± 0.4	59.5	-147.7
Dioxane	$(1.27 \pm 0.06) \cdot 10^7$	67.3 ± 0.6	67.7	-138.7
Tetrahydrofurane	$(2.50 \pm 0.07) \cdot 10^7$	68.1 ± 0.4	65.5	-133.2
Ethylacetate	$(5.22 \pm 0.05) \cdot 10^4$	54.3 ± 0.5	51.7	-184.3
Acetic acid*	$(3.93 \pm 0.06) \cdot 10^5$	53.3 ± 0.4	50.7	-167.5
Crotonaldehyde				
Dioxane	$(2.03 \pm 0.07) \cdot 10^6$	66.0 ± 0.5	63.5	-153.7
Tetrahydrofurane	$(5.29 \pm 0.05) \cdot 10^6$	66.3 ± 0.6	63.8	-145.9

Note: *value of constant in acetic acid l/(mol·s)

**Value of constant k_p for oxidation of aldehydes
with different structure by peracetic acid at 293 K**

Aldehyde	$k_p \cdot 10^5, \text{l}/(\text{mol} \cdot \text{s})$
Acetaldehyde	19.24
Propionaldehyde	13.55
Butanal	13.11
2-Ethyl-2-hexenal	13.37
2-Isopropyl-5-methyl-2-hexenal	7.52
Benzaldehyde	5.26
Acrolein	2.96
α -Methacrolein	1.63
α -Ethylacrolein	1.51
α -Propylacrolein	1.52
α -Butylacrolein	1.50
α -Amylacrolein	1.49
Crotonaldehyde	1.88

As we failed to determine constants k_3 and k_4 separately, we did not get specific activation energies for these reactions. But increase of $k_3/(k_3 + k_4)$ constants complex with temperature increasing (Table 4) is possible only when k_3 is more dependent on temperature than k_4 . Therefore unsaturated acid formation selectivity with respect to reacted aldehyde increases with temperature increasing.

Data on dependence of activation parameters on peracid structure are shown in Table 5. We see that rate constants and activation energies weakly depend on peracid structure.

Value of k_p , which characterizes the rate of limiting reaction stage, should be taken as a characteristic of aldehyde reactivity. Aldehydes form a series by reactivity with respect to peracids (using data from Table 6): saturated aldehydes > α -, β -dialkyl acroleins > benzaldehyde > crotonaldehyde >> α -alkyl acroleins.

This Table shows that the rate of saturated aldehydes interaction with peracids is greater than that of unsaturated aldehydes.

Noteworthy, the fundamental difference between oxidation of saturated aldehydes, benzaldehyde and unsaturated aldehydes is that there are no consecutive reactions of peracid consumption for saturated aldehydes, as formates formed at first stages do not further react with peracid due to the specifics of their structure.

4. Conclusions

It was determined that in the reaction of unsaturated aldehydes of various structure with peracids C_2 – C_4 apart from the main product (unsaturated acid) products of oxygen introduction into carbon chain of the aldehyde and products of their further transformations are also formed.

Kinetic regularities of unsaturated aldehydes reaction with peracids were studied and kinetic model for this reaction was constructed. It was found that it is first-order reaction with respect to unsaturated aldehyde. Kinetic model parameters (constants complexes (k_p , k_{MA} , k_E)) characterizing the main stages of the reaction and confidence intervals for these parameters were calculated. Adequacy of the model was determined. Specifics of mathematical description while carrying out reaction in carboxylic acids were explained.

New data on reactivity of aldehydes with various structures in the reaction with peracids were obtained. By reaction rate with peracids aldehydes form the following series: saturated aldehydes > α -, β -dialkyl acroleins > benzaldehyde > crotonaldehyde > α -alkyl acroleins.

The dependence of unsaturated acid formation selectivity on reaction conditions was determined. Aldehydes structure, properties of solvent and initial concentration of the reagents have the main effect on the reaction selectivity. Aldehydes form a series by unsaturated acid formation selectivity: β -alkyl acroleins > α -alkyl acroleins > α -, β -dialkyl acroleins

The highest selectivity is in base solvents. The optimal temperature is 313–323 K and reagents concentration 2.5–3 mol/l. Under these conditions unsaturated acid selectivity is 80–92 %.

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ОКИСНЕННЯ НЕНАСИЧЕНИХ АЛЬДЕГІДІВ ОРГАНІЧНИМИ ПЕРКИСЛОТАМИ

Анотація. Стаття присвячена дослідженню кінетичних закономірностей реакції окиснення ненасичених альдегідів органічними перкислотами. На основі експериментальних даних запропоновано шляхи утворення продуктів, розроблено кінетичну модель реакції окиснення та розраховано активаційні параметри реакції. Наведено нові дані про реакційну здатність альдегідів різної будови в реакції з перкислотами.

Ключові слова: окиснення перкислотами, ненасичені альдегіди, механізм реакції, кінетичні та активаційні параметри реакції.