CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 1, No. 2, 2007 Chemistry

Zoryan Pikh

OXIDATION OF UNSATURATED ALDEHYDES BY DIFFERENT OXIDANTS

Lviv Polytechnic National University,
12 Bandera Str., Lviv, 79013, Ukraine
pikh@polynet.lviv.ua

Received: May 10, 2007

Abstract. The new data about oxidation of unsaturated aldehydes of a general structure R–CH = C(R)–CHO by molecular oxygen (in liquid and gaseous phase), peracids and hydrogen peroxide were obtained. The composition of reaction products for a series of aldehydes with different structures was determined. The dependencies of the selectivity of reaction from an aldehyde structure and oxidant type have been evaluated. It has been assumed that a stage of aldehyde interaction with peracid determines the formation of reaction products. The common mechanisms of unsaturated aldehydes oxidation by different oxidants have been established on the basis of generalization of obtained results.

Key words: oxidation, unsaturated aldehyds, peracids, hydrogen peroxide, oxygen

1. Introduction

The oxidation of unsaturated aldehydes is an attractive pathway for obtaining unsaturated acids. Aldehydes can be easily oxydized by molecular oxygen, and the oxidation process of acetaldehyde is an important industrial method for production of acetic acid and its anhydride. [1]

Due to the specific chemical structure of unsaturated aldehydes their oxidation leads to the formation of by-products. The presence of two reactive centres in the molecule of unsaturated aldehyde which can undergo oxidation (carbonyl group and C=C double bond) leads to the change of the reaction rate and selectivity as compared to saturated analogues. The above mentioned effects are strongly influenced by the localization of both carbonyl group and C=C double bond in the molecule of aldehyde as well as presence of substitutions. In the case when carbonyl group and double bond are well separated in the aldehyde molecule they behave as independent reactive centres providing formation of carbonyl, carboxyl, epoxy compounds and products of epoxide ring opening. [2,3]

In the case when reactive centres are localized closely they influence each other by varying the oxidation rate and selectivity. Additionally, such aldehydes and corresponding acids undergo polymerization during oxidation. This makes the optimization of the highly selective methods for production of unsaturated acids very difficult. [2]

Two ways for the oxidation of unsaturated aldehydes are frequently reported in the literature: oxidation in the gas phase by using oxide catalyst and oxidation in liquid phase. In both cases complicated mechanisms and formation of the by-products have been reported. The experimental data reported in the literature can be hardly compared due to the specific reaction conditions and different approaches for data analysis.

The detailed studies of the reaction products as well as generalization of the oxidation principles of unsaturated aldehydes with different oxidants allowed us to determine common features and peculiarities of different oxidation methods and to control selectivity of investigated processes.

2. Results and discussion

2.1. Oxidation of unsaturated aldehydes by peracids

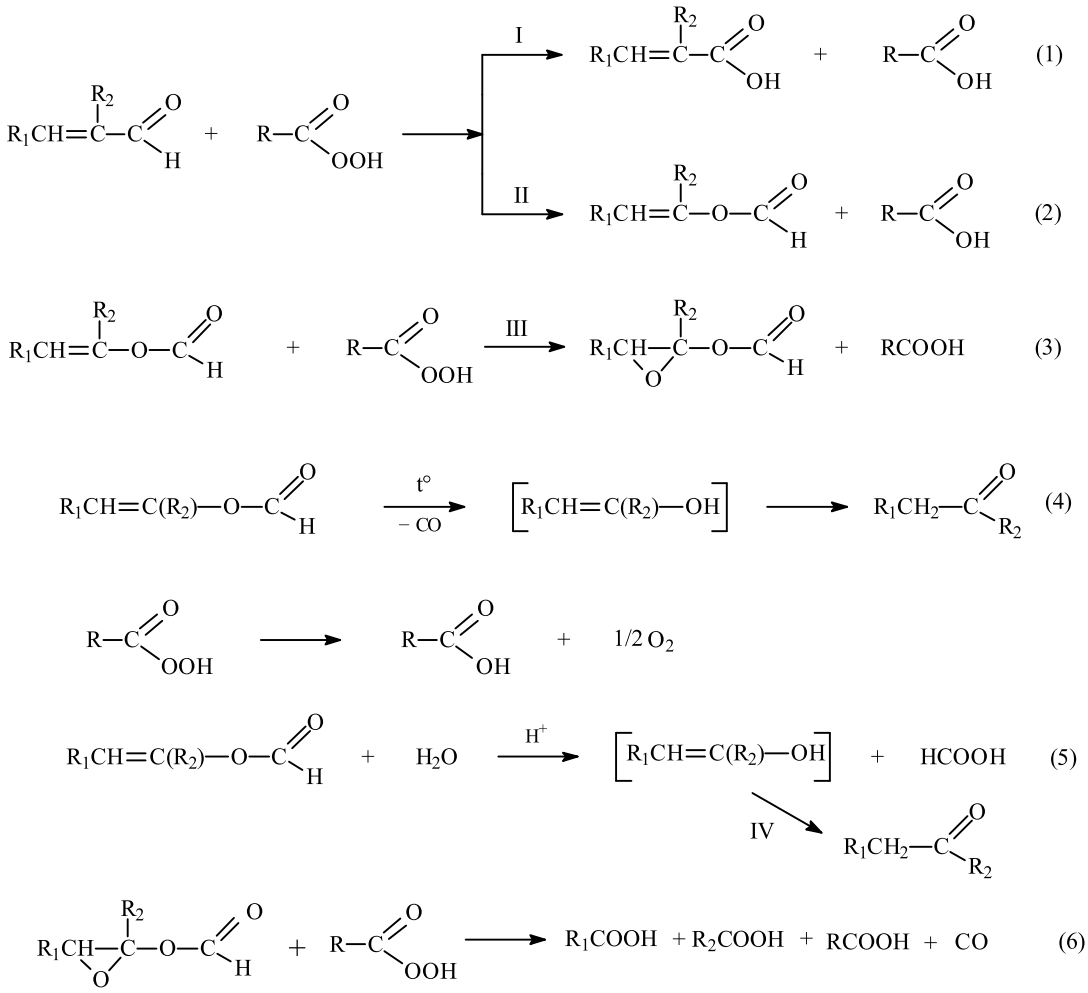
It has been determined experimentally, [4-8] that during oxidation of unsaturated aldehydes (acrylaldehyde, methacrylaldehyde, 2-ethylpropenal, crotonaldehyde, 2-ethyl-2-hexenal) with peracetic acid beside unsaturated acid and acetic acid (originated from peracetic acid) some by-products have been formed such as formates, epoxyformates and products of their further transformations (Table 1).

Table 1

Compounds formed after oxidation of unsaturated aldehydes with peracetic acid

Product name	Chemical formulae
Methacrylaldehyde	
Methacrylic acid	$CH_2=C(CH_3)–COOH$
Isopropenyl formate	$CH_2=C(CH_3)–O–CHO$
1–Methyl–1,2–epoxyethyl formate	$CH_2 – C(CH_3)–O–CHO$ (O)
Acetone	$CH_3–C(O)–CH_3$
Acetic acid	CH_3COOH
Formic acid	HCOOH
2-Ethylpropenal	
2–Ethylpropenoic acid	$CH_2=C(C_2H_5)–COOH$
1–Ethylethenyl formate	$CH_2=C(C_2H_5)–O–CHO$
1–Ethyl–1,2–epoxyethyl formate	$CH_2 – C(C_2H_5)–O–CHO$ (O)
2–Butanone	$CH_3–C(O)–C_2H_5$
Propionic acid	CH_3CH_2COOH
Formic acid	HCOOH
Crotonaldehyde	
Crotonic acid	$CH_3–CH=CH–COOH$
1–Propenyl formate	$CH_3–CH=CH–O–CHO$
1,2–Epoxypropyl formate	$CH_3–CH – CH–O–CHO$ (O)
Propionaldehyde	CH_3CH_2CHO
Propionic acid	CH_3CH_2COOH
Acetic acid	CH_3COOH
Formic acid	HCOOH
2-Ethyl-2-hexenal	
2–Ethyl–2–hexenoic acid	$C_3H_7–CH=C(C_2H_5)–COOH$
1–Ethyl–1–pentenyl formate	$C_3H_7–CH=C(C_2H_5)–O–CHO$
1–Ethyl–1,2–epoxypentenyl formate	$C_3H_7–CH–C(C_2H_5)–O–CHO$ (O)
3–Heptanone	$C_2H_5–C(O)– C_4H_9$
Propionic acid	CH_3CH_2COOH
Butyric acid	$CH_3CH_2CH_2COOH$

Following mechanism of product formation has been proposed based on the structure of the identified compounds in the reaction mixture [6]:



The proposed mechanism indicates that interaction of unsaturated aldehydes with peracetic acid took place by two pathways: oxidation of the carbonyl group leading to formation of unsaturated acid (reaction 1); integration of oxygen between carbon atoms in unsaturated aldehyde leading to formation of formate of unsaturated alcohol (reaction 2). Both pathways are related to the Bayer-Williger mechanism for unsaturated aldehydes. The formate of unsaturated alcohol further decomposes to ketone (reactions 4,5) or is subjected to epoxidation (reaction 3). The formed epoxyformate according to reaction 3 is further oxidized by peracid (reaction 6) leading to unsaturated acids. The selectivity of the unsaturated acid formation is determined by the relation of reaction rates (steps 1 and 2).

Table 2

The selectivity of the unsaturated acid formation during oxidation of unsaturated aldehydes with peracetic acid at the degree of conversion 0.9 (T=303 K)

Aldehyde	Selectivity, %	
	By aldehyde	By peracid
Crotonaldehyde	95	93
2–Ethylpropenal	86	78
Methacryl-aldehyde	49	39
2–Ethyl–2–hexenal	30	26

Figures 1 and 2 represent kinetic curves for reagent consumption and product accumulation during oxidation of 2-ethylpropenal and 2-ethyl-2-hexenal respectively. The experimental data indicate that peracid is consumed faster compared to aldehyde due to the participation of the peracid in reactions (3) and (6). The experimental curves for the reaction products correlate with proposed reaction mechanism.

The experimentally determined selectivity values for unsaturated acid during oxidation of unsaturated aldehydes are presented in Table 2.

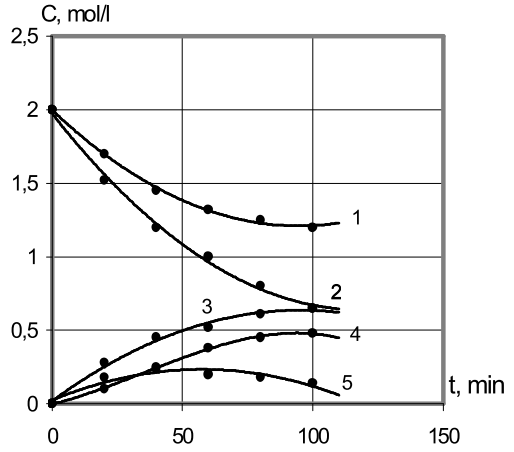


Fig. 1. The kinetic curves for reagent consumption and product accumulation during oxidation of 2-ethylpropenal with peracetic acid in benzene (T=313 K):
1 – 2-ethylpropenal; 2 – peracetic acid;
3 – 2-ethylpropenoic acid; 4 – 1-ethylethenyl-1-formate;
5 – 1-ethyl-1,2-epoxyethylformate

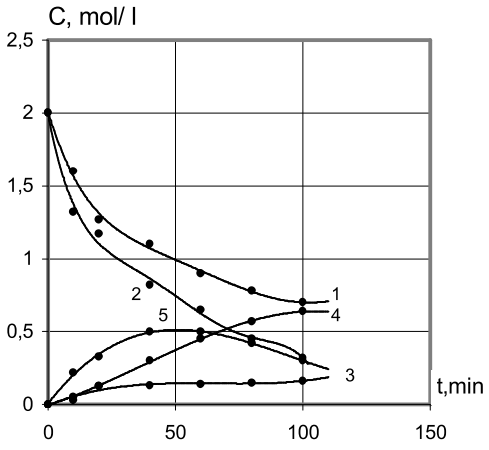


Fig. 2. The kinetic curves for reagent consumption and product accumulation during oxidation of 2-ethyl-2-hexanal with peracetic acid in benzene (T=313 K): 1 – 2-ethyl-2-hexenal; 2 – peracetic acid; 3 – 2-ethyl-2-hexenoic acid; 4 – 1-ethyl-1-pentenylformate; 5 – 1-ethyl-1,2-epoxypentenylformate

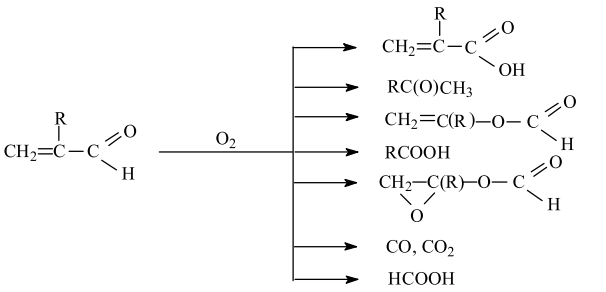
Table 2 indicates that the selectivity of the unsaturated acid formation is lower for the aldehydes with the alkyl substitutents in α-position relatively to carbonyl group or in α,β-positions compared to crotonaldehyde having alkyl substituent in β-position. According to the selectivity of the unsaturated acid formation by oxidation with peracids aldehydes can be positioned in following order: crotonaldehyde (2-butenal) > 2-ethylpropenal > methacrylaldehyde (2-methylpropenal) > 2-ethyl-2-hexanal. Lower selectivity of the unsaturated acid formation by oxidation of methacrylaldehyde compared to 2-ethylpropenal is related to the polymerization ability of methacrylaldehyde and methacrylic acid.

The presented data for the oxidation of unsaturated aldehydes by peracids indicate formation of by-products and the selectivity of the unsaturated acid formation is determined by the aldehyde structure.

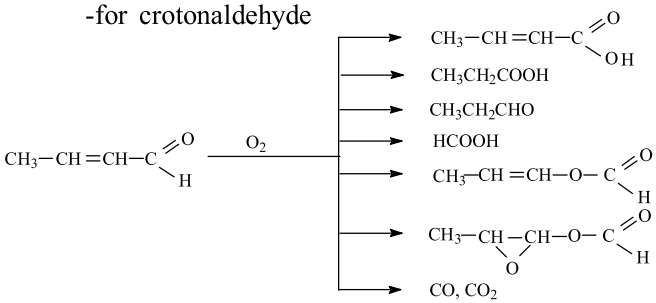
2.2. Liquid-phase oxidation of unsaturated aldehydes by oxygen

The oxidation of unsaturated aldehydes by molecular oxygen in the liquid phase has been studied in the temperature range 293 – 313 K. All experiments have been carried out in thermostated bubble reactor. Following products of the oxidation process have been identified:

-for α-alkyl substituted unsaturated aldehydes

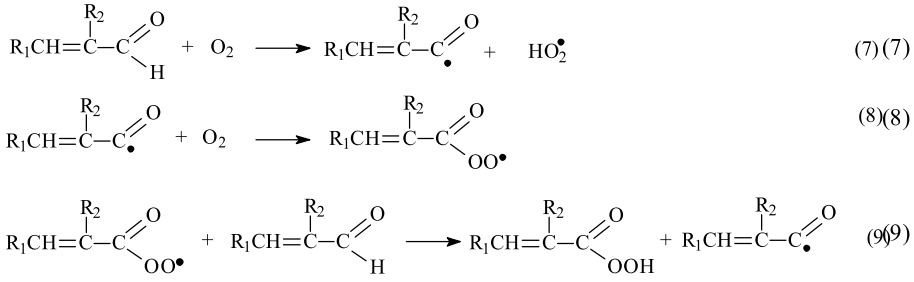


-for crotonaldehyde

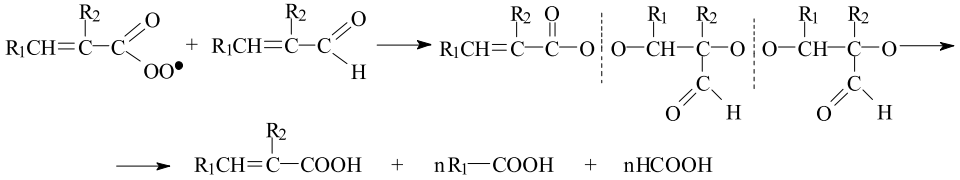


Along with unsaturated acid the unsaturated alcohol and corresponding epoxide, carbonic acids, ketones and carbon oxides are formed during oxidation of the unsaturated aldehyde with oxygen. The main reaction pathway is following radical mechanism determining the formation of the reaction products. However, the primary molecular product of the aldehyde oxidation is peracid which is formed according to reactions 7-9.

The formed peracid reacts with starting aldehyde leading to unsaturated acid and by-products (see part 1). The by-products can be formed additionally during radical transformation stages following another way of the peracyl radical interaction with aldehyde:



The selectivity of the unsaturated acid formation during aldehyde oxidation with molecular oxygen is low due to the formation of the by-products by two different pathways.



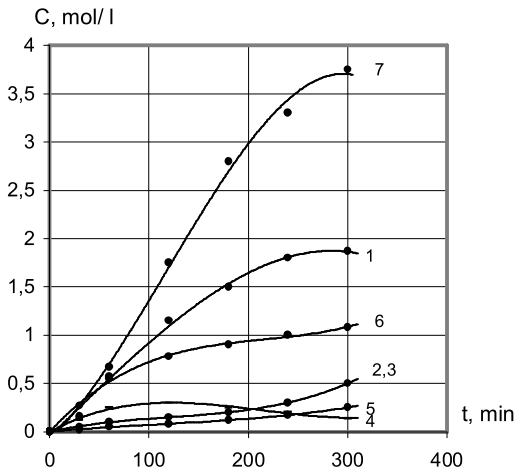


Fig. 3. The kinetic curves of product formation during oxidation of 2-ethylpropenal by molecular oxygen at 303 K: 1 – 2-ethylpropenoic acid; 2 – propionic acid; 3 – formic acid; 4 – 1-ethylethenyl-1-formate; 5 – 1-ethyl-1,2-epoxyethylformate; 6 – peroxides; 7 – total acidity

For example the selectivity of the unsaturated acid formation at 303 K at 50% conversion is 37.7%, 42.5%, 70%, 53% for methacrylaldehyde (2-methylpropenal), 2-ethylpropenal, crotonaldehyde (2-butenal) and 2-ethyl-2-hexenal respectively.

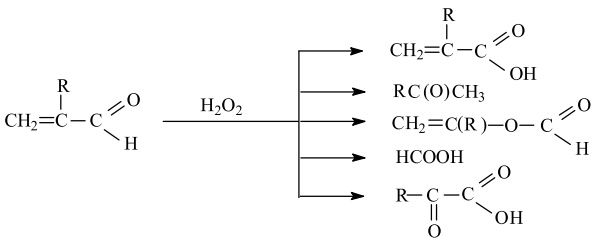
The kinetic curves of the product formation during oxidation of 2-ethylpropenal by molecular oxygen are presented in Figure 3.

2.3. Oxidation of unsaturated aldehydes by hydrogen peroxide

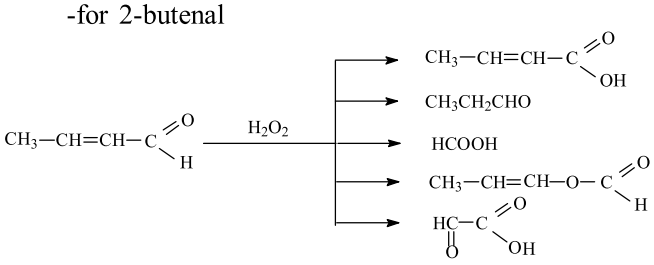
The unsaturated acids can be obtained during oxidation of unsaturated aldehydes by hydrogen peroxide. In the case of unsaturated aldehydes the interaction with hydrogen peroxide takes place in the presence of catalyst (compounds of Se, Te, W, Mo, Ti, Ce, Sb) [11]. As a model system the oxidation of unsaturated aldehydes with hydrogen peroxide in the presence of $H_7[P(Mo_2O_7)_6]\cdot H_2O$ [12] has been used to study the reaction products.

In the presence of this catalyst the reaction is fast, however many by-products are formed:

-for α-alkyl substituted unsaturated aldehydes



-for 2-butenal



The given by-product list indicates that as the consequence of the unsaturated aldehyde oxidation by hydrogen peroxide corresponding unsaturated acid, ketone (or aldehyde), unsaturated formate, acetic acid and keto- (or aldehyde) acids are formed.

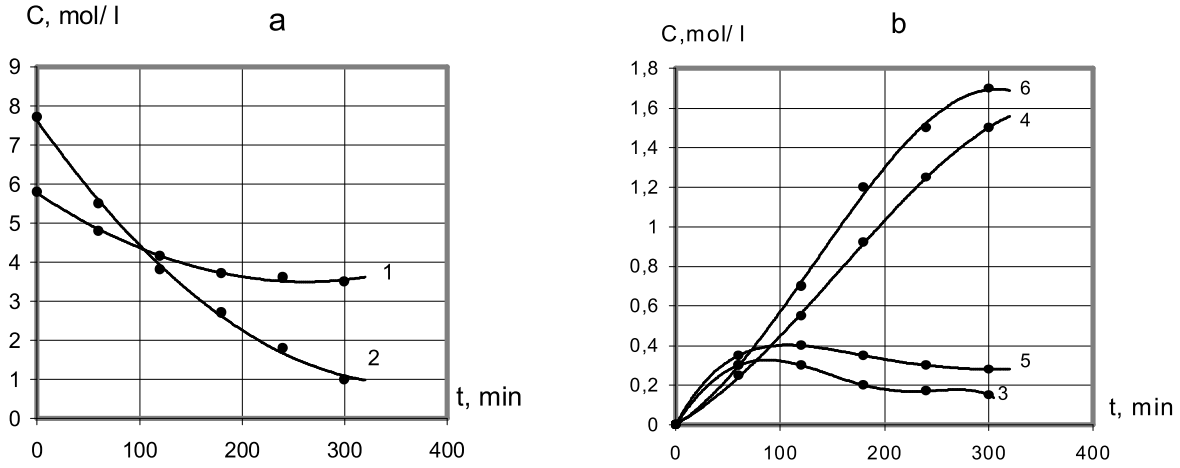
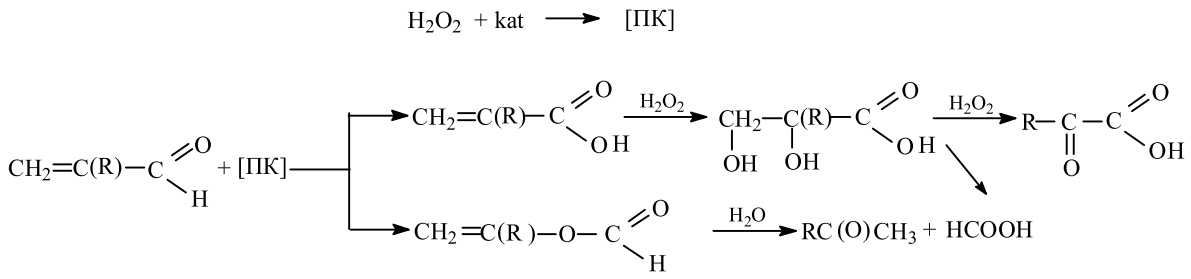


Fig. 4. The kinetic curves for products (**a**) and reactants (**b**) during oxidation of 2-ethylpropenal by hydrogen peroxide in the presence of $H_7[P(Mo_2O_7)_6]\cdot H_2O$:
1 – 2-ethylpropenal; 2 – hydrogen peroxide; 3 – 1-ethylethenylformate;
4 – 2-oxobutanoic acid; 5 – 2-ethylpropenal;
6 – acetic acid (solvent – dioxane; T = 323K)

Fig. 4a indicates that aldehyde and hydrogen peroxide are consumed in non-equivalent amounts. The kinetic curves for reaction products have characteristic shape of continuous reactions. The formation of the reaction products characteristic for the oxidation of unsaturated aldehydes with peracids indicates principal similarity to oxidation mechanisms by hydrogen peroxide. The difference between two oxidants is only presence of the catalyst which is required to transform oxygen from hydrogen peroxide to aldehyde. [12]

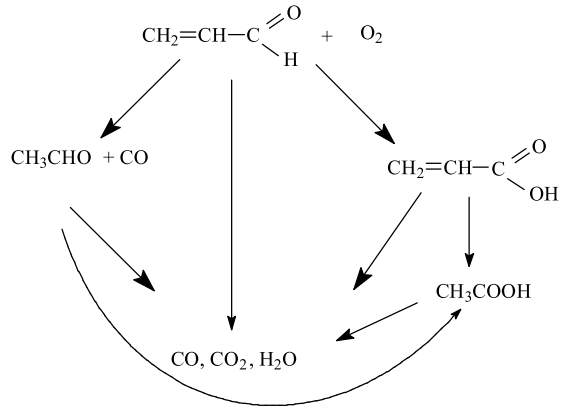
The overall scheme of the catalytic oxidation of unsaturated aldehydes with hydrogen peroxide according to [13, 14] can be presented as follows:

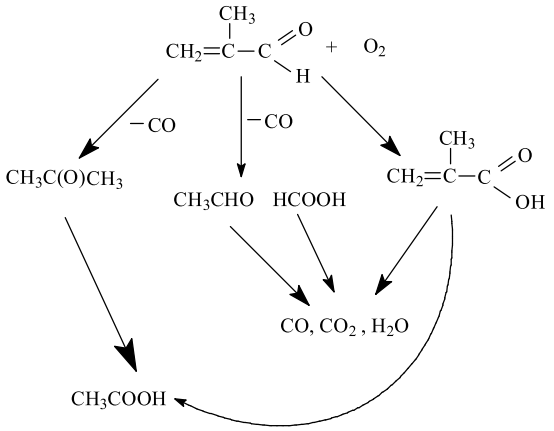


According to this mechanism, hydrogen peroxide interacts with catalyst forming a peroxy-form of a catalyst [PC]. The [PC] further reacts with aldehyde leading to the simultaneous formation of unsaturated acid and unsaturated formate. The formation of the by-products is possible by a) hydroxylation of unsaturated acid with further oxidation of the product to ketoacid and formic acid and b) hydrolysis of the unsaturated formate with formation of ketone and formic acid.

2.4. Vapour-phase oxidation of unsaturated aldehydes by using heterogeneous catalysts

The formation of the reaction products has been studied for the oxidation of unsaturated aldehydes in gas phase with water vapour and $Mo_{12}PCs_2Pb_{0.72}O_x$ as catalyst in the temperature range 583-613 K. Following mechanisms have been established for oxidation of acroleine and methacroleine:





It is known [15] that the oxidation of aldehydes in gas phase follows Red-Ox mechanism and the oxygen integrated into the crystal structure of the catalyst participates actively in this process. At the first stage of the reaction reagents adsorb on the catalyst surface. The adsorbtion of unsaturated aldehydes on the catalyst surface can occur by carbonyl group or C=C double bond. Therefore, the adsorbtion efficiency of above mentioned reactive centres determines the selectivity of the unsaturated acid formation during oxidation of such aldehydes.

It is common that the selectivity of the unsaturated acid formation during oxidation of propenal and 2-methylpropenal is different even at similar reaction conditions. For example the selectivity of the acrylic acid and methacrylic acid formation by using Fe-Te-Mo-O catalyst is 82.8% and 58.8% respectively.[16] Additionally the reaction rate of the methacrylaldehyde oxidation is two times higher compared to acrylaldehyde.

It has been determined [17] that heterogeneous catalysts with the phosphomolibdenic heteropolyacids (PMA) exhibit better selectivity toward formation of unsaturated acid formation during oxidation of methacrylaldehyde. The oxidation efficiency of Mo-ions in PMA increases with increase of the electronegativity for the second cation: P > As > Si.

The reaction rate and selectivity of the aldehyde oxidation process on heterogeneous catalysts depends on the unsaturated aldehyde structure. It has been determined [18] that the reaction rate of the oxidation process for unsaturated aldehydes increases in the line: methacrylaldehyde (2-methylpropenal) > 2-ethylpropenal > 2-propylpropenal > acrylaldehyde (propenal) (catalyst $Mo_{12}PCs_2Pb_{0.72}O_x$; T=580K). The selectivity of the unsaturated acid formation at similar conversion increases in the following way: 2-ethylpropenal > 2-propylpropenal > 2-methylpropenal > propenal. The increase of the selectivity with aldehyde molecular weight can be related to the influence of the substituent on the coupling of double bond and carbonyl group.

The presented above interpretation of the unsaturated aldehyde oxidation processes with heterogeneous catalysts is based on classical theories of heterogeneous catalysis. The important issue is the relation of the mechanisms for the unsaturated aldehyde oxidation in the liquid an gas phases. We made an attempt to correlate the experimental studies of the mechanisms for two processes which have been previously judged from completely different positions. The similarity of the final reaction products is obvious for two oxidation processes; therefore we assume that during the oxidation by using heterogeneous catalyst the composition of the reaction products is determined by peroxy-compounds of catalyst.

Let's consider possible ways for the occurrence of the peroxy-compounds on the surface of solid catalyst. It is known [19] that the interaction of the O^{2-} and O^- ions (formed during adsorbtion of the oxygen on the catalyst' surface) with double bond of the aldehyde can lead to the formation of surface-attached peroxy-complexes. The formation of surface-attached peroxy-compounds is also possible due to the reaction of heteropoly acids of molybdate with oxygen. [11,20] These facts indicate the high probability of the product formation during oxidation of unsaturated aldehydes in the presence of heterogeneous catalysts occurs with participation of peroxides. The best evidence for this is a good correlation of the reaction product composition for the oxidation of unsaturated aldehydes in the presence of heterogeneous catalysts by hydrogen peroxide and peroxy acids. The mechanism of the product formation during the oxidation with

heterogeneous catalysts can be explained considering results of the oxidation of unsaturated aldehydes with hydrogen peroxide in liquid phase in the presence of molybden-containing catalysts. It is clear that more extreme reaction conditions during the oxidation with heterogeneous catalyst and presence of the water vapour eliminate some intermediate products (formates, epoxyformates, peroxides).

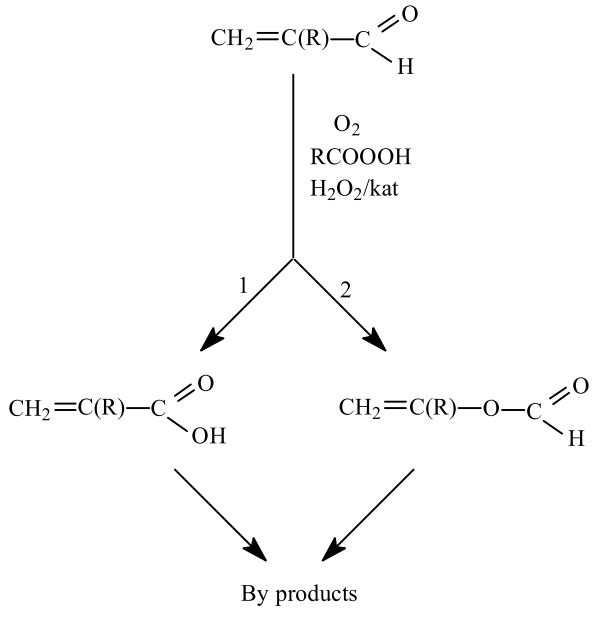
This interpretation of the oxidation processes gives a possibility to formulate a new approach to the selection of the heterogeneous catalyst: the effective catalysts must have components able to create surface-attached peroxy-compounds with certain oxidation ability and stability. The best catalysts in terms of selectivity should be compounds able to create stable enough peroxy-complexes with mild oxidation power.

3. Conclusions

The complex approach for the studies of unsaturated aldehyde oxidation with different oxidants allowed creation of the general mechanism for oxidation processes.

1. The experimental results indicate that the oxidation of unsaturated aldehydes is a complex process where different oxidation mechanisms coexist (radical and molecular processes of the oxidation with oxygen, hydrogen peroxide and peracids).

The general scheme of the unsaturated aldehyde oxidation is presented below:



2. The systematic studies of the oxidation processes for unsaturated aldehydes with different chemical structure led to the important conclusion about principal similarity of the pathways for the product formation in different oxidation methods. The oxidation processes are complicated and often different oxidation processes occur simultaneously.

For example, the oxidation of unsaturated aldehydes with molecular oxygen occurs by radical mechanism under participation of carbonyl group and is accompanied by molecular interactions of unsaturated aldehydes with per acid and hydrogen peroxide. Additionally, polymerization processes take place as well as reactions of radical transformations with participation of C=C double bond.

During interactions of unsaturated aldehydes with peracid beside the oxidation of carbonyl group another process takes place, namely epoxidation of intermediate formates of unsaturated alcohols. During catalytic oxidation of unsaturated aldehydes with hydrogen peroxide the oxidation of carbonyl group is accompanied by hydroxylation of C=C bond leading to the formation of the destructive oxidation products. In all three oxidation methods the key role plays reaction of aldehyde with peracid in terms of the product formation.

3. During oxidation of unsaturated aldehydes with molecular oxygen numerous by-products are formed. This effect has following reasons: a) variability of the reaction between aldehyde and peroxy acid; b) the peracyl radical can participate in the chain extension reaction by elimination of the hydrogen from carbonyl group and addition to C=C bond and formation of less active radical; c) presence of the peroxides with different reactivity in the reaction mixture.

The main problem of the oxidation of unsaturated aldehydes with oxygen in liquid phase is possibility of the addition of peracyl radical to the double bond of aldehyde, what induces polymerization processes. Therefore, the contradiction exists between radical mechanism of the oxidation reaction and selectivity of the unsaturated acid formation.

Another specialty of the oxidation processes with participation of molecular oxygen is formation of the by-products in the reaction mixture with much higher reactivity as compared to the main reagents. For example, the presence of saturated aldehydes in the reaction mixture leads to the fast consumption of saturated aldehyde during oxidation process. The radicals formed by this process are much more active regardless carbonyl group and C=C bond. Therefore such reaction must be considered as simultaneous oxidation of substances with different reactivity. Additionally, one should keep in mind another way of the oxidation process if reaction mixture contains hydrogen peroxide and carboxylic acids. In this case the transfer of the active oxygen from hydrogen peroxide to substrate occurs through the formation of peracid. This is the reason why carboxylic acids are better solvents for the oxidation of aldehydes with oxygen.

4. The oxidation of unsaturated aldehydes with hydrogen peroxide in the presence of catalyst is closely related to the oxidation with peracids since the oxidant for the aldehyde is inorganic peroxy acid formed due to the interaction of catalyst with hydrogen peroxide. Therefore the oxidation scheme is similar to the oxidation with peroxy acids. The peculiarity f this reaction is possible hydroxylation of C=C bond in the presence of different catalysts. This leads to destructive oxidation of aldehyde. A special position among catalysts possesses Se-based compounds [14] which provide high reaction rates and selectivity. The reasons for high selectivity in this case are: a) optimal balance between oxidation strength and stability of Se-peroxide complex and b) formation of the intermediate complex with aldehyde which provides stabilization of carbon backbone of the aldehyde.

References

[1] Maslov S., Blumberg E.: Uspechy Chimij, 1976, **45,** 303.
[2] Haines A.: Method for the oxidation of organic compounds. Academic press, 1986.
[3] Rubailo V.and Maslov S.: Liquid-phase oxidation of unsaturated compounds. Moskwa, Chyimia, 1989.
[4] Pikh Z.: Dopovidi NAN Ukraine, 1996, **3,** 116.
[5] Pikh Z., Kucher R, Iatchishin J.and Gunka M.: Neftechimia, 1983, **23** (3), 368.
[6] Pikh Z., Purig Ia., Iatchishin J. and Horvaty I.: Zhurn. Organ. Chem., 1979, **15** (12), 2459.
[7] Pikh Z. and Samaruk V.: Zhurn. Organ. Chem., 1993, **29** (8), 1553.
[8] Pikh Z., Fedevich M. and Samaruk V.: Dopovidi NAN Ukrainy, 1993, **11**, 144.
[9] Pikh Z., Fedevich M., Iatchishin J. and Tolopko D.: Dopovidi NAN Ukrainy, 1976, **11 (B)**, 1001.
[10] Pikh Z., ,Samaruk V.and Kuptsevich O.: Dopovidi NAN Ukrainy, 1991, **6 (B)**, 121.
[11] Woldman G.: Zhurn. Anorg. Chem., 1977, **22**, 2498.
[12] Pikh Z.,Kosmyna N., Samaruk V. and Sheredko A.: Neftechimia, 1991, **31** (3), 322.
[13] Pikh Z., Denys G. and Iatchishin J.: Zhurn. Organ. Chem., 1979, **XV** (9), 1831.
[14] Pikh Z.,, Samaruk V. and Chajkyvskij T.: Dopovidi NAN Ukrainy, 1991, **7 (B),** 125.
[15] Margolis L.: Oxidation of hydrocarbons on heterogeneous catalysts. Moskwa, Chimia, 1977.
[16] Zhuznevskyj V.,Fedevich E.,,Nykypanchuk M., Golub I., Iakubovska L.and Shupailo V.: Chem. Technol., 1979, **1**, 30.
[17] Chugaev V. and Sagalovich V.: Dopovidi NAN Ukrainy, 1980, **11**, 114.
[18] Zhuznevskyj V., Grumaliuk B. and Agbosu S.: Zhurn. Phys. Chim., 1984, **58** (12), 2968.
[19] Haber J.: Prz. Chem., 1980, **59** (2), 64.
[20] Volnov I.: Peroxocomplex by chrom, wolframum, tungstan. Moskwa, Nauka, 1989.

ОКИСНЕННЯ НЕНАСИЧЕНИХ АЛЬДЕГІДІВ РІЗНИМИ ОКСИДАНТАМИ

Анотація. *Одержано нові дані про окиснення ненасичених альдегідів загальної будови R–CH=C(R)–CHO киснем (у рідкій та газовій фазі) гідропероксикислотами та пероксидом водню. Встановлено склад продуктів окиснення альдегідів різної будови та виявлено залежність селективности реакції від будови альдегіду та оксиданту. Показано, що визначальною у формуванні складу продуктів реакцій окиснення є взаємодія альдегіду з гідропероксикислотою. Узагальнено одержані результати і запропоновано схеми утворення продуктів при окисненні ненасичених альдегідів різними оксидантами.*

Ключові слова: *окиснення, ненасичені альдегіди, надкислоти, пероксид водню, кисень.*