

## LIQUID PHASE NON-CATALYTIC AND CATALYTIC OXIDATION PROCESSES OF HALOGEN-VINYLIC COMPOUNDS VIA MOLECULAR OXYGEN

**Allen S. Baghdasaryan**

National Polytechnic University of Armenia  
105 Teryan St., Yerevan 0009, RA  
[allenbagdasaryan@gmail.com](mailto:allenbagdasaryan@gmail.com)  
ORCID iD: 0000-0002-4111-8596  
Republic of Armenia

**Mher Peltekian**

National Polytechnic University of Armenia  
105 Teryan St., Yerevan 0009, RA  
[mherpeltekian@gmail.com](mailto:mherpeltekian@gmail.com)  
ORCID iD: 0000-0002-7598-5030  
Republic of Armenia

**Nona L. Asatryan**

National Polytechnic University of Armenia  
105 Teryan St., Yerevan 0009, RA  
[asatryannona@gmail.com](mailto:asatryannona@gmail.com)  
ORCID iD: 0000-0001-8827-349X  
Republic of Armenia

**Aram R. Mikaelyan**

National Polytechnic University of Armenia  
105 Teryan St., Yerevan 0009, RA  
[aramrm@suea.am](mailto:aramrm@suea.am)  
ORCID iD: 0000-0002-4668-3498  
Republic of Armenia

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### Abstract

Oxidation reactions continue to play an important role in organic chemistry, and the increasing demand for selective oxidation methods in modern organic synthesis had led to rich development in the field during recent decades. Oxidation of organic compounds has been widely used in laboratory and industrial applications for creating various fine organic compounds, and also from the rise of ecological issues, it has found more importance for utilization of environmental pollutants. Liquid phase oxidation (LPO) with molecular oxygen is one of the prominent methods in this sphere that allows us the use of affordable and effective technology, also it opens a great prospect for future development. In this paper the comparative research results of non-catalytic and catalytic LPO of some *gem*-dichlorovinyl substrates [1,1,5-trichloropent-1-ene (Ia), 1,1-dichloro-5-brompent-1-ene (Ib)] have been presented. For catalytic processes significant advancements such as greater yield, low duration and selective formations of targeted compounds ( $\alpha$ -chloro carboxylic acid chlorides) has been recorded. As

catalyst transitional metals and their oxides (e.g., TiO<sub>2</sub>, Ag/SiO<sub>2</sub>) has been investigated. For more active Ag/SiO<sub>2</sub> catalytic system's the process is characterized by a pronounced induction period of 1.5-2 h. At the same time, after 2-2.5 h of interaction, there is complete homogenization of the metallic silver into the organic phase was observed.

**Key words:** aerobic oxidation, liquid phase oxidation, bubble reactor, transition metal catalysis, halogen vinylic compounds,  $\alpha$ -halogen carboxylic acids.

### Introduction

Application of selective oxidation of alkenes by molecular oxygen is one of the current challenges in the manufacture of organic building blocks and industrial intermediates [1, 2]. Liquid phase oxidation (LPO) of vinyl halides with molecular oxygen is a simple and affordable method for the synthesis of functionally substituted  $\alpha$ -halogen carboxylic acid chlorides [3, 4, 5]. The latter have found wide application for the production of various medicine, plant protection chemicals and other valuable products [6, 7]. In this sense this reaction has become subject in many studies and in recent times because of the rise of ecological issues, it has started to gain attention for further development as a green chemistry perspective tool [8].

Based on LPO of hydrocarbons with air or oxygen industrial processes gained importance [9], due the following factors:

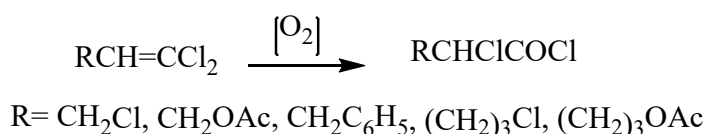
1. The significance of resulting products (alcohols, aldehydes, carbonic acids and their acid chlorides, oxides of olefines etc.), which are starting products for creating valuable compounds.
2. Many varieties of oxidation reactions, which are applicable for hydrocarbons of all classes of organic substances.
3. The low cost and availability of applied oxidizer. In this case the atmospheric oxygen has a special role.

The technological issues from the reaction compounds further separation and recycling of the catalyst are still the main disadvantages that this method has. The kinetic aspects and regulation of processes by liquid phase auto-oxidation of hydrocarbons have been presented in several monographs and review articles [10].

One of the first LPO processes of *gem*-dichlovinyl compounds experiments have been done by academician A.N. Nesmeyanov and coworkers. The oxidation has been implemented in high temperature and pressure (till 20 atm.) conditions, in this case the yeilds of targeted  $\alpha$ -chloro acids chlorides did not exceed 50% [11].

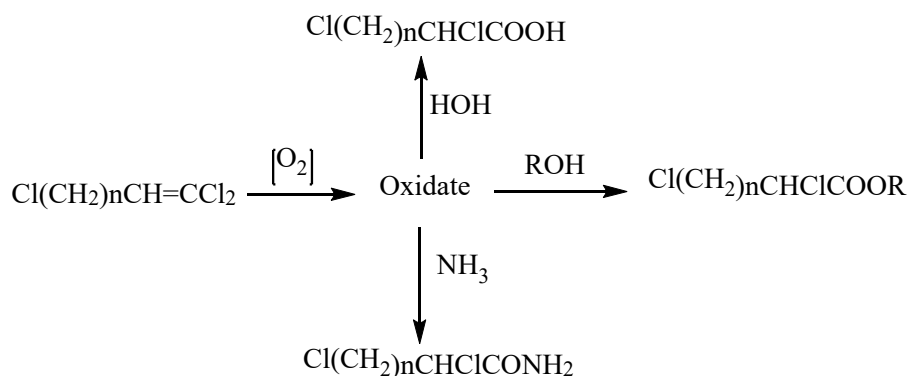
### Conflict setting

The authors Shakhnazaryan G.M., Bayatyan B.E. showed that for a number of *gem*-halogen vinylic compounds by non-catalytic LPO processes with molecular oxygen as the main reaction product forms  $\alpha$ -halogen carboxylic acid chloride (yield 70 ÷ 90%), for principal scheme see Fig. 1 [12, 13].



**Fig. 1 General oxidation conversion of *gem*-halogen vinylic compounds by molecular oxygen**

Although it must be noted, that in majority of cases by active oxidation temperature range (90-130 °C) the duration of the process lasted 30 hours, for some substrates even reached 60 hours. Hydrolysis, alcoholysis and aminolysis of the oxidate has been conducted to form acids, esters and amides of  $\alpha$ -chlorocarboxylic acids (Fig. 2).

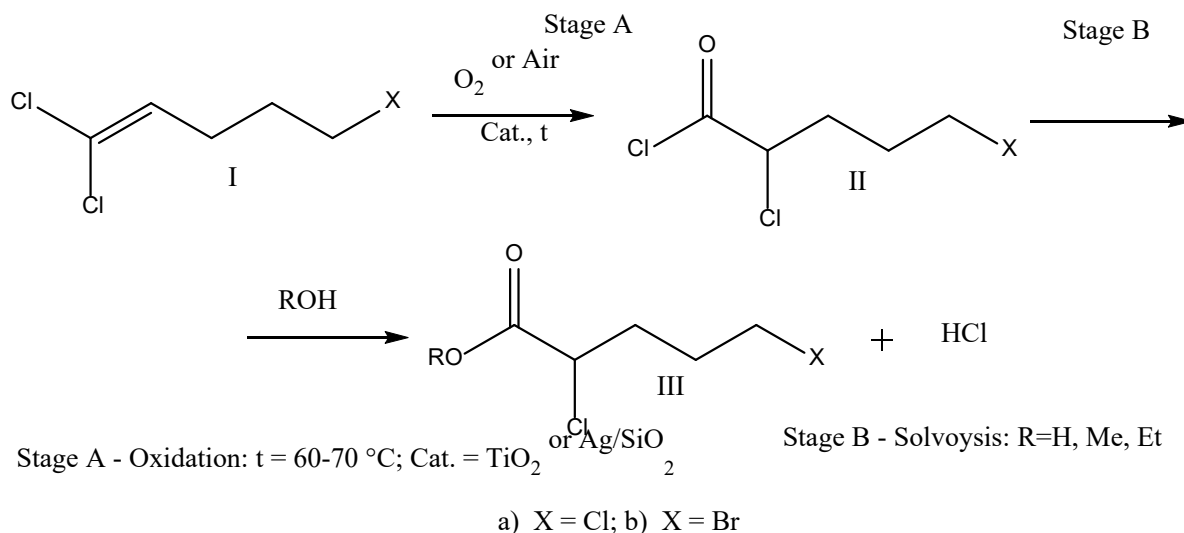


**Fig. 2 Derivatization of the oxidate**

It should be mentioned that further increases of temperature, even though insignificantly decreases oxidation duration, but it results in increase of side products yield and vaporizing of substrate with significant losses. It is obvious, that the any increase in heterogeneous reaction's speed will lead to shortening of long term thermic effect on the reaction product, which in its turn will raise the yield and selectivity of the formation of targeted acid chlorides. To maximize the contact surface of the gas-phase (oxygen, air) and liquid substrate we have used packed-bubbling reactor with glass ring (3x3x1 mm) packings. Such construction of reaction unit with application of different types of packs and/or solid catalyst in bubble reactor, can make this reaction into safe neutralization and utilization methods for halogen vinyl waste (such as,  $\alpha$ -chloroprene, 1,3-dichlorobut-2-ene, trichlorobutenes etc.) which are emerged from wholesale production of halogen organic compound: mainly chloroprene rubber [14]. The results of auto-oxidation in packed-bubble reactors with oxygen or air both non-catalytic [15] and catalytic ( $\text{TiO}_2$ ) [14, 16] of several functionalized halogen vinyl compounds (1,1,5-trichloropent-1-ene (Ia), 1,1-dichloro-5-acetoxypent-1-ene (Ib), 1,3-dichlorobut-2-ene) have been presented. The kinetics studies of catalytic ( $\text{TiO}_2$ ) oxidation of 1,1,5-trichloropent-1-ene (Ia) and 1,1-dichloro-5-acetoxypent-1-ene by oxygen has been studied. The data results compared to the previously mentioned studies had significant progress, however, sufficient improvements from further development of  $\text{TiO}_2$  catalyst from technological standpoint was not recorded. By these reactions as end product similarly was observed formation of appropriate carboxylic acid chloride, that was isolated from reaction mixture in forms of corresponding esters by means of alcoholysis (MeOH or EtOH).

It is well known one of widely used catalytic system for industrial and laboratory scale app by heterogeneous catalysis for aerobic oxidation of broad spectrum of hydrocarbons are Ag-based catalysts on different supports [17]. As a promising catalyst, we have investigated Ag/ $\text{SiO}_2$  system and perform their application in packed column bubbling reactor [18].

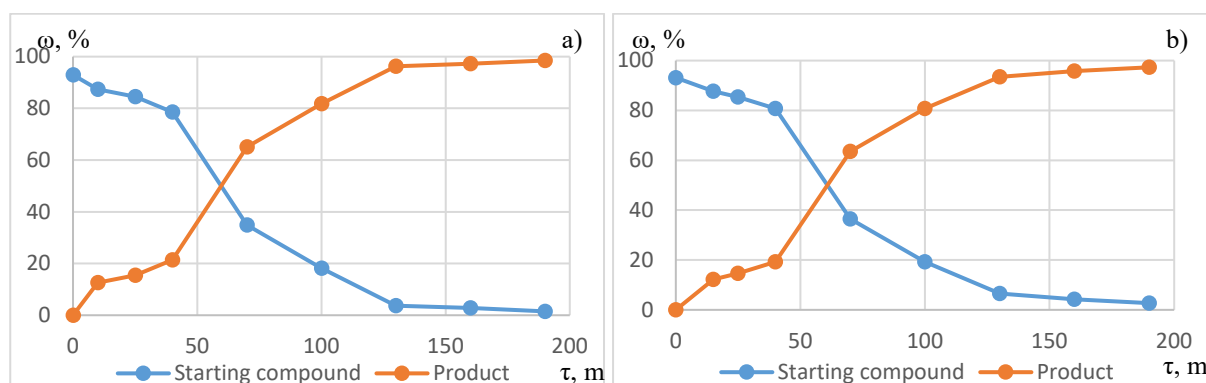
For general catalytic transformation strategy we propose one pot to stage procedure: oxidation and subsequent solvolysis of the formed acids chloride II into the corresponding acid or esters III. The interaction can be presented by the following scheme (Fig. 3).



**Fig. 3 One pot to stage procedure: oxidation and subsequent solvolysis of the formed acids chloride**

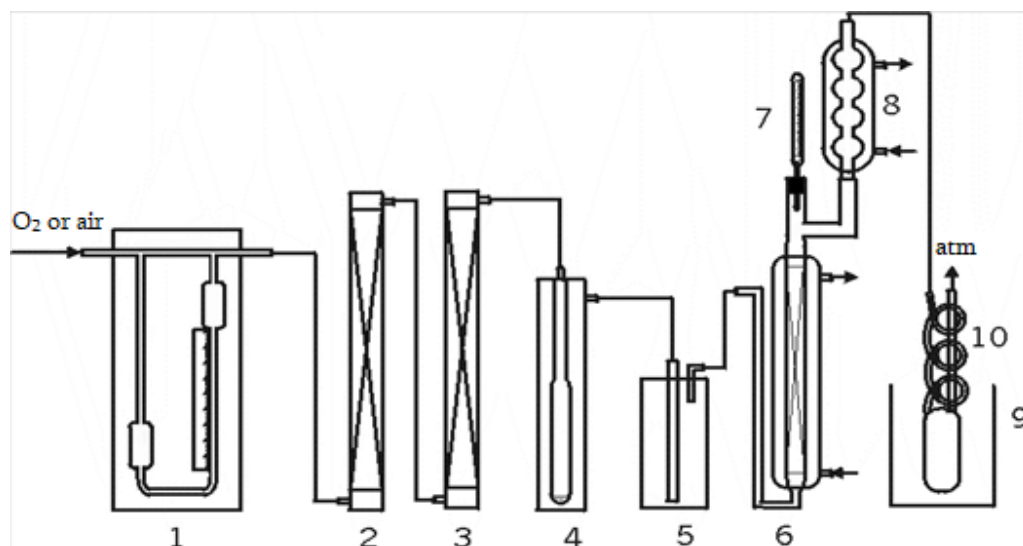
### Material and method

*Gem*-dihalogen vinylic compounds (Ia and Ib) have been obtained from corresponding 1,1,1-trichloropentane via dehydrochlorination in a presents of Lewis acid (anhydrous  $\text{FeCl}_3$ ) catalytic amount in non-solvent media. The kinetic curves of formation of Ia and Ib are presented in Fig. 4.



**Fig. 4 Synthesis of 1,1,5-trichloropent-1-ene (Ia) and 1,1-dichloro-5-bromopent-1-ene (Ib)**

Oxidation has been realised in reaction unit with the following installation (Fig. 5). Substrate (*gem*-dihalogen vinylic model compounds: Ia and Ib) was situated in the packet reactor (filled with glass ring packings:  $3 \times 3 \times 1$  mm) in the presence of 10mg catalyst to 1mmol substrate:  $\text{TiO}_2$  (alpha lead dioxide form) or  $\text{Ag/SiO}_2$  ( $100-200\text{ }\mu\text{m}$ , 5% w/w Ag). The oxygen/or air flow was dried beforehand, is provided to the reactor with 4-6 l/h expenditure. The reactor heating jacket has a supplied by temperature-controlled heat carrier (water-ethylene glycol mixture) at different temperatures so that the reaction mixture temperature won't exceed range of  $60-70\text{ }^{\circ}\text{C}$ .



**Fig. 5 Oxidation laboratory installation with glass ring packed-bed-bubble reactor unit.**

1. Rheometer, 2. Basic dryer (KOH), 3. Calcium chloride dryer, 4. Acidic dryer (sulfuric acid),
5. Trap for acid drops, 6. Packet-bed-bubble reactor, 7. Thermometer, 8. Reflux condenser,
- 9/10. Cold trap on liquid nitrogen or dry ice/acetone mixture.

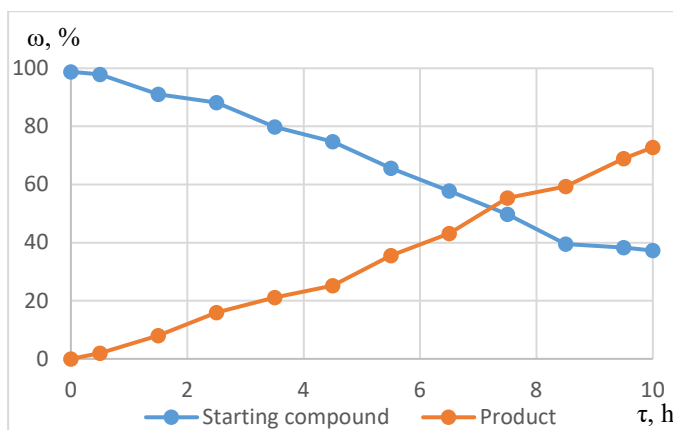
### Research results

The main focus of this paper is improving the LPO by catalytic process. So, the liquid phase oxidations of 1,1,5-trichloropent-1-ene (Ia - as a model compound) over a  $\text{TiO}_2$  catalyst by molecular oxygen in glass-ring packed reactor with oxygen-spray have been investigated. It has been shown, that titanium dioxide (10 mg  $\text{TiO}_2$  to 1 mmol substrate) has catalytic activity in this oxidation reactions, so by 70 °C after 6.0 hour the yield of acid chloride arrived at 41% (by non-catalytic oxidation in glass-ring packed reactor this rate has been attained more than 9 hours reaction time).

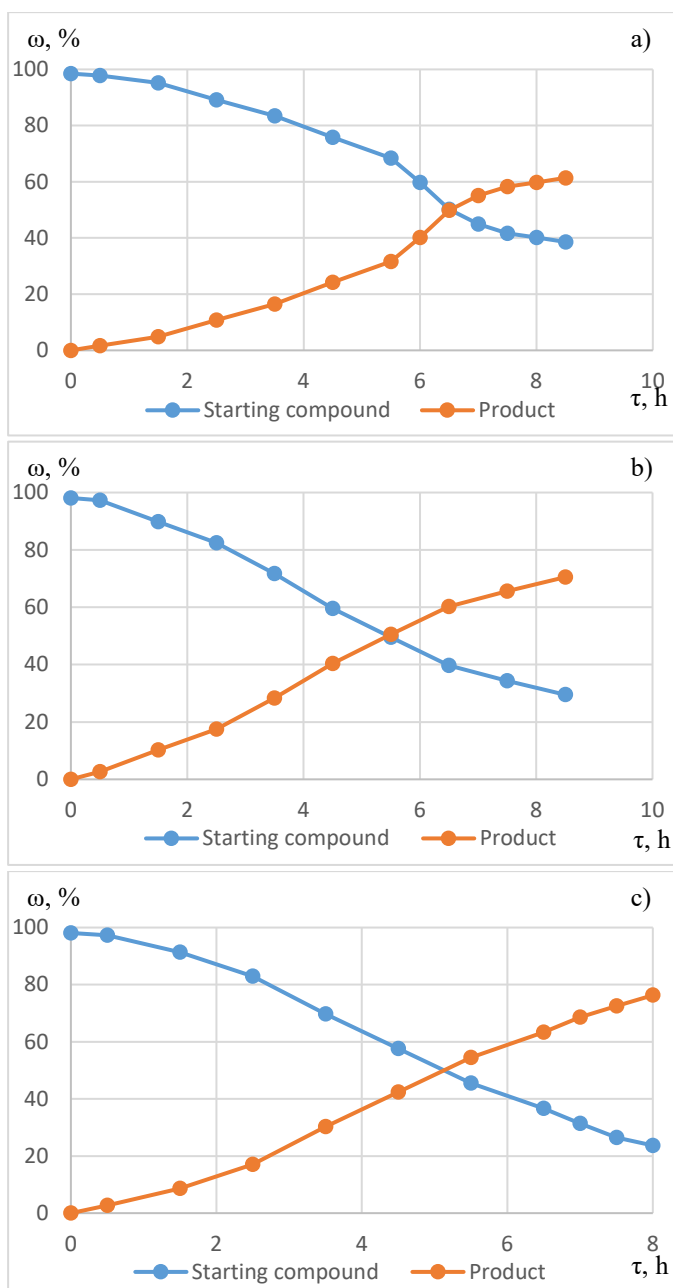
We have noticed that the  $\text{Ag}/\text{SiO}_2$  catalytic LPO had larger potential for future development. For same model compound Ia, by analogs conditions (70 °C, 6.0 hour) the yield of corresponding acid chloride already reaching over 55%. It must be mentioned, that after oxidative transformation, subsequent alcoholysis and removal of rest of methanol/ethanol, the formation of crystals was observed.

This compound is high photo-stable, solution in ethanol-water is stable in strong acidic media (up to  $\text{pH}=1$ ). By melting, heating higher 200 °C temperatures, decomposes to  $\text{AgCl}$  with gas release (preliminary  $\text{Cl}_2$ ).

Kinetic studies of liquid-phase oxidation reaction of *gem*-dihalogen olefines are based on the determination of speeds of consumption of halogen-vinyl compounds and the formation of the products. The correlation of products, dynamics of their formation and changes in quantities of stable intermediary products are determined by the following methods: the starting *gem*-dihalogen vinyl compounds, 2,5-dichlorovaleric and 2-chloro-5-bromovaleric acid chlorides (after alcoholysis) - by GC method in isothermal and programming regimes (Fig.6 and Fig.7). The obtained experimental data shows that the increase in oxygen flow speed more than 4-4.5 l/h does not affect the process itself.



**Fig. 6** LPO of 1,1,5-trichloropent-1-ene in 70 °C temperature over catalyst TiO<sub>2</sub> by oxygen in the packed bubbling reactor



**Fig. 7** LPO over catalyst Ag/SiO<sub>2</sub> by oxygen in the packed bubbling reactor:  
 a); b) 1,1,5-trichloropent-1-ene in 60 °C and 70 °C  
 c) 1,1-dichloro-5-bromopent-1-ene in 70 °C

### Experimental procedures

Reaction monitoring via chromatographic analysis were carried out on a gas chromatograph - Agilent Technologies GC-7809B, capillary column - DB-WAX-30m x 320 $\mu$ m x 0.25 $\mu$ m, FID detector, detector temperature 300 $^{\circ}$ C, injector temperature 250  $^{\circ}$ C, flow rate gas (N<sub>2</sub>) 6 ml/min, column temperature 40  $^{\circ}$ C hold for 2 min, 7  $^{\circ}$ C/min 235  $^{\circ}$ C hold for 5 min.

The NMR spectra (<sup>1</sup>H and <sup>13</sup>C NMR) were registered on a spectrometer Varian Mercury-300 at operating frequencies 300.077 MHz (<sup>1</sup>H), 75.46 MHz (<sup>13</sup>C), Chemical shifts are given in ppm ( $\delta$ ) and were referenced to TMS used as an internal standard. The signal assignment in the <sup>1</sup>H and <sup>13</sup>C NMR spectra was performed with the use of methods Noedif, HMQC, and also registering <sup>13</sup>C NMR spectra without decoupling from protons.

Synthesis of starting gem-dihalogen vinylic compounds:

#### 1,1,5-trichloropent-1-ene (Ia)

1,1,1,5-tetrachloropentane (106g, 0.5mol) and anhydrous ferric chloride (FeCl<sub>3</sub>, 2g) have been heated at 45-55 $^{\circ}$ C for 3 hours and in final 1 hour at 60  $^{\circ}$ C, by intensive stirring. During the process violent discharge of hydrogen chloride (HCl) has been observed. The reaction mixture was cooled to room temperature, 50 ml chloroform was added and washed with Na<sub>2</sub>CO<sub>3</sub> solution (5%) until neutral reaction. Water layer was extracted with chloroform (2x20ml). Combined organic extracts was dried over CaCl<sub>2</sub>. The solvents were removed and residue was distilled under vacuum. Yield 75.7g (86%) of 1,1,5-trichloropent-1-ene (Ia), purity 96,5% (GC),  $t_{b.p.}$  = 100-105  $^{\circ}$ C/85-90 mmHg,  $d_{20}^4$  = 1.272,  $n_D^{20}$  = 1.4892.

#### 1,1-dichloro-5-bromopent-1-ene (Ib)

Analogue to previous procedure from 1,1,1-trichloro-5-bromopentane (128.25g, 0.5mol) and anhydrous ferric chloride (FeCl<sub>3</sub>, 2g) 97.5g (yield: 88%) of 1,1-dichloro-5-bromopent-1-ene (Ib) has been isolated. Purity 94,5% (GC),  $t_{b.p.}$  = 68-69  $^{\circ}$ C/7 mmHg,  $d_{20}^4$  = 1.544,  $n_D^{20}$  = 1.4892.

General methodology for catalytic LPO of model compounds:

The experimental set-up used for catalytic oxidation is presented in Fig 6. beforehand dried oxygen (from gas cylinder) with an expenditure of 4-6 l/h has introduced in the reactor filled with pre-weighed model compounds Ia or Ib and catalyst (10 mg catalyst to 1mmol substrate). The temperature was regulated via reactors heating jacket supplied temperature-controlled heat carrier (50% aqueous solution of ethylene glycol). The mixture was bubbled by oxygen for 8-10 h at 60  $^{\circ}$ C (or 70  $^{\circ}$ C), reaction monitoring via GC and TLC. On cooling to room temperature, the mixture was diluted with alcohol (methanol or ethanol) in 5-fold excess of the theoretically required amount, the organic suspension was filtered through a paper filter, reactor and glass rings were washed with diethyl ether (2 x 20 ml) and the ether solution was also filtered. The summarized organic solutions were dried over MgSO<sub>4</sub>. The solvents were removed off, the residue was distilled in a vacuum.

#### a) LPO of 1,1,5-trichloropent-1-ene (Ia) over TiO<sub>2</sub>:

The reaction temperature was controlled at 70 $^{\circ}$ C. After 10 hours of interaction formation of 2,5-dichlorovaleric acid chloride (IIa) by 72.8% yield was observed.

#### b) LPO of 1,1,5-trichloropent-1-ene (Ia) over Ag/SiO<sub>2</sub>:

In experiments the reaction temperature was controlled at 60  $^{\circ}$ C (or 70  $^{\circ}$ C). After 8.5 hours of interaction formation of 2,5-dichlorovaleric acid chloride (IIa) by 61.4% (or 70.5% corresponding to 70  $^{\circ}$ C) yields was observed.

#### c) LPO of 1,1-dichloro-5-bromopent-1-ene (Ib) over Ag/SiO<sub>2</sub>:

The reaction temperature was controlled at 70°C. After 8 hours of interaction formation of 2-chloro-5-bromovaleric acid chloride (IIb) by 76.3% yield was observed.

NMR spectral characteristics of some end-products:

2,5-dichlorovaleric acid (IIIa, R=H)

<sup>1</sup>H NMR spectrum 1.88÷2.32 m(4H, -CH<sub>2</sub>-CH<sub>2</sub>-), 3.58 t(2H, CH<sub>2</sub>Cl, J=6.2.), 4.35 dd(1H, CHCl, J<sub>1</sub>=8.1, J<sub>2</sub>=5.3), 11.67 bs(1H, COOH),

<sup>13</sup>C NMR spectrum 28.94(CH<sub>2</sub>), 32.13(CH<sub>2</sub>), 43.69(CH<sub>2</sub>Cl), 56.30(CHCl), 175.55 (C=O).

2,5-dichlorovaleric acid methyl ester (IIIa, R=Me)

<sup>1</sup>H NMR spectrum: 1.84÷2.29 m(4H, -CH<sub>2</sub>-CH<sub>2</sub>-), 3.57 t(2H, CH<sub>2</sub>Cl, J=6.3), 3.81 s(3H, OCH<sub>3</sub>), 4.30 dd (1H, CHCl, J<sub>1</sub>=8.0, J<sub>2</sub>=5.5,)

<sup>13</sup>C spectrum: 29.11(CH<sub>2</sub>), 32.37(CH<sub>2</sub>), 43.79(CH<sub>2</sub>Cl), 53.07(OCH<sub>3</sub>), 56.39(CHCl), 169.66(C=O).

2,5-dichlorovaleric acid methyl ester (IIIa, R=Et)

<sup>1</sup>H NMR spectrum: 1.34 t (3H, CH<sub>3</sub>, J=7.1), 1.85÷2.28 m(4H, -CH<sub>2</sub>-CH<sub>2</sub>-), 3.58 t(2H, CH<sub>2</sub>Cl, J=6.3), 4.26 q(2H, OCH<sub>2</sub>, J=7.1), 4.27 dd(1H, CHCl, J<sub>1</sub>=7.7, J<sub>2</sub>=6.8),

<sup>13</sup>C NMR spectrum: 14.44(CH<sub>3</sub>), 29.24(CH<sub>2</sub>), 32.37(CH<sub>2</sub>), 43.87(CH<sub>2</sub>Cl), 56.66(OCH<sub>2</sub>), 62.23(CHCl), 169.17(C=O).

### Conclusion

It has been shown, that performance of variable valence metals and inorganic carriers based heterogeneous catalysts in LPO process will offer synthetic utility since reaction proceeds readily, does not require any solvent (which would usually introduce problems for purifying of products) and provide selective formation of valuable products: α-halogen acid chlorides. On the basis of the obtained results on direct liquid phase oxidation of halogenolefines by oxygen or air, it is supposed to find the opportunities for application of these reactions for solution of environmental problems related particularly to the problems of utilization, mineralization and metabolism in the biosphere of halogenorganic compounds and industrial wastes.

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ՄՈԼԵԿՈՒԼԱՅԻՆ ԹԹՎԱԾՆՈՎ ՀԱԼՈԳԵՆ-ՎԻՆԻԼԱՅԻՆ  
ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ ՈՉ ԿԱՏԱԼԻՏԻԿ ԵՎ ԿԱՏԱԼԻՏԻԿ  
ՀԵՂՈԼԿԱՖԱԶ ՕՔՍԻԴԱՑՄԱՆ ԳՈՐԾԸՆԹԱՅՆԵՐ

Բաղդասարյան Ա.Ս., Փելթիկյան Մ., Ասատրյան Ն.Լ., Միքաելյան Ա.Ռ.

*Հայաստանի ազգային պոլիտեխնիկական համալսարան*

Օքսիդացման ռեակցիաները շարունակում են կարևոր դեր խաղալ օրգանական քիմիայում, և ժամանակակից օրգանական սինթեզներում ընտրողական օքսիդացման մեթոդների նկատմամբ աճող պահանջարկը հանգեցրել է այս ուղղության արագ զարգացմանը վերջին տասնամյակներում: Օրգանական միացությունների օքսիդացումը լայնորեն օգտագործվում է լաբորատոր սինթեզներում և ունի արդյունաբերական կիրառություններ՝ զանազան նուրբ օրգանական միացություններ ստանալու համար, իսկ բնապահպանական խնդիրների նկատմամբ աճող ուշադրությունը այն ավելի կարևոր է դարձրել շրջակա միջավայրի աղտոտիչների վնասասագերծման համար: Հեղուկաֆազ օքսիդացումը (<math>C\_3O</math>) մոլեկուլային թթվածնով այս ոլորտում խոստումնալից մեթոդներից մեկն է, որը թույլ է տալիս օգտագործել մատչելի և արդյունավետ տեխնոլոգիա, ինչպես նաև մեծ հեռանկարներ է բացում հետագա զարգացման համար: Աշխատանքում ներկայացված են որոշ *գեմ-դիքլորովինիլային* սուբստրատների [1,1,5-տրիքլորպենտ-1-են (Ia), 1,1-դիքլոր-5-բրոմպենտ-1-են (Ib)] ոչ կատալիտիկ և կատալիտիկ <math>C\_3O</math> համեմատական ուսումնասիրությունների արդյունքները: Զգալի բարելավումներ են արձանագրվել կատալիտիկ գործընթացների համար, ինչպիսիք են բարձր ելքերը, ավելի կարճ տևողությունը և թիրախային միացությունների ընտրողական գոյացումը ( $\alpha$ -քլորկարբոնաթթուների քլորանհիդրիդներ): Որպես կատալիզատորներ ուսումնասիրվել են անցումային մետաղները և դրանց օքսիդները (օրինակ՝  $TiO_2$ ,  $Ag/SiO_2$ ): Ավելի ակտիվ  $Ag/SiO_2$  կատալիտիկ համակարգի համար գործընթացը բնութագրվում է 1,5-2 ժամ ընդգծված ինդուկցիոն շրջանով: Այս դեպքում 2-2,5 ժամ փոխազդեցությունից հետո տեղի է ունենում մետաղական արծաթի ամբողջական համասեռացում դեպի օրգանական ֆազ:

**Բանալի բաներ.** աերոբային օքսիդացում, հեղուկաֆազ օքսիդացում, բարբոտաժային ռեակտոր, անցումային մետաղներով կատալիզ, հալոգենվինիլային միացություններ,  $\alpha$ -հալոգեն կարբոնաթթուներ:

НЕКАТАЛИТИЧЕСКИЕ И КАТАЛИТИЧЕСКИЕ ПРОЦЕССЫ  
ЖИДКОФАЗНОГО ОКИСЛЕНИЯ ГАЛОГЕН-ВИНИЛОВЫХ  
СОЕДИНЕНИЙ МОЛЕКУЛЯРНЫМ КИСЛОРОДОМ

Багдасарян А.С., Пелтикян М., Асатрян Н.Л., Микаелян А.Р.

*Национальный политехнический университет Армении*

Реакция окисления продолжает играть важную роль в органической химии, а растущий спрос на методы селективного окисления в современном органическом синтезе в последние десятилетия привел к бурному развитию в этой области. Окисление

органических соединений широко используется в лабораторных и промышленных целях для создания различных тонких органических соединений, а также в связи с возникновением экологических проблем оно приобрело большее значение для утилизации загрязнителей окружающей среды. Жидкофазное окисление (ЖФО) молекулярным кислородом является одним из перспективных методов в этой области, что позволяет использовать доступную и эффективную технологию, а также открывает большие перспективы для дальнейшего развития. В работе представлены результаты сравнительных исследований некаталитического и каталитического ЖФО некоторых *гем*-дихлорвиниловых субстратов [1,1,5-трихлорпент-1-ен (Ia), 1,1-дихлор-5-бромпент-1-ен ( Ib)]. Для каталитических процессов были зарегистрированы значительные улучшения, такие как более высокий выход, низкая продолжительность и селективное образование целевых соединений (хлориды  $\alpha$ -хлоркарбоновых кислот). В качестве катализаторов исследованы переходные металлы и их оксиды (например,  $\text{TiO}_2$ ,  $\text{Ag/SiO}_2$ ). Для более активных каталитических систем  $\text{Ag/SiO}_2$  процесс характеризуется выраженным индукционным периодом 1,5-2 часа. При этом через 2-2,5 ч взаимодействия происходит полная гомогенизация металлического серебра в органическую фазу.

**Ключевые слова:** аэробное окисление, жидкофазное окисление, барботажный реактор, катализ переходными металлами, галогенвиниловые соединения,  $\alpha$ -галогенкарбоновые кислоты.

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