

## Article

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Irada G. Melikova<sup>1\*</sup>, Arif J. Efendi<sup>1</sup>, Manaf R. Manafov<sup>1</sup>, Natavan F. Aykan<sup>1</sup>,  
Guseyn M. Faradjev<sup>1</sup>, Ceyran T. Rustamova<sup>1</sup>, Nizami I. Shikhaliyev<sup>2</sup>

<sup>1</sup>*Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev,*

*Ministry of Science and Education of Republic of Azerbaijan, Baku, Azerbaijan;*

<sup>2</sup>*Azerbaijan Technical University, Ministry of Education of the Republic of Azerbaijan, Baku, Azerbaijan*

(\*Corresponding author's e-mail: [iradam@rambler.ru](mailto:iradam@rambler.ru))

## Kinetics and Mechanism of the Oxidation Reaction of Chlorine-Containing Hydrocarbons on a Vanadium Phosphorus Catalyst

The kinetic regularities of oxidation reactions of 1,2,4-trichlorobutene-2, 2,3,3-trichlorobutene-1, 1,2,3-trichlorobutene-2 and pentachlorobutene-1 on vanadium phosphorus catalyst exhibiting high activity and selectivity were studied. The presence of parallel-sequential pathways of XY oxidation with the formation of the main organochlorine compounds and deep oxidation products was established. It was shown that presence and location of the double bond and the number of chlorine atoms affected the direction of the oxidation reaction. The rate of XY consumption in a fixed catalyst bed exceeds that in a fluidized bed, although the rate of formation of the target product is higher in a fluidized bed. Hypotheses reflecting the possibility of a staged reaction mechanism taking into account the modification of the surface of the vanadium-phosphorus oxide system by the main and by-products of the oxidation reactions of chlorobutenes, as well as the competition of substances for active centers were investigated. Discrimination of these hypotheses was carried out on the basis of the Bartlett's criterion and Powell's method, and the mechanism that most fully explains the experimental results was selected. The calculated hardness values were obtained according to the proposed kinetic model by the Kutta-Meyerson and Runge-Kutta methods. A more detailed study of the mechanism of the oxidation reaction of chlorinated hydrocarbons will allow for effective control of its course and the achievement of selective oxidation of chlorinated hydrocarbons.

**Keywords:** kinetic regularities, mechanism, vanadium-phosphorus catalyst, oxidation reactions, chlorinated hydrocarbons, product formation rate, fluidized bed, fixed catalyst bed, Bartlett's criterion.

### Abbreviations

chlorohydrocarbons	—	CH
1,1,3-dichlorobutene-2	—	1,3-DCB-2
1,2,4-trichlorobutene-2	—	1,2,4-TCB-2
1,2,3,4-pentachlorobutene-1	—	PCB-1
chloropropanoic acid	—	CPA
chloroacetic acid	—	CAA
chloroacrylic acid	—	CA
monochloromaleic anhydride	—	m-ChMA
dichloromaleic anhydride	—	d-ChMA
acetic acid	—	AA
fixed bed	—	F
fluidized bed	—	Fl

### Introduction

The study of the kinetics and mechanism of the oxidation reaction of chlorinated hydrocarbons on a vanadium phosphorus catalyst is important both for understanding the mechanism of interactions and for developing more efficient processes in the chemical industry, such as obtaining valuable products from hydrocarbons.

Numerous scientific papers are devoted to the oxidation of hydrocarbons on various catalysts and identifying their mechanism [1–6]. However, there are few works devoted to the oxidation of their chlorinated derivatives. In this regard, the study of the kinetic patterns of oxidation reactions of chlorinated hydrocarbons (CH) is important for establishing the directions and mechanism of their oxidation, as well as for constructing kinetic models.

It is known that for process calculations it is necessary to determine the yields of products, reaction rates, the amount and composition of material flows, raw material consumption, heat, etc. A special place in this is occupied by the analysis of the kinetics of a chemical reaction on a selected catalytic system to identify the kinetic equation of the reaction rate and construct a mathematical model of the process [7–8]. In the presented work, when studying the heterogeneous catalytic oxidation of chlorohydrocarbons (CH), it was noted that it is expedient to study the kinetic patterns of the oxidation reaction using the example of various chlorine-containing hydrocarbons  $C_4$  as the most pronounced representatives of CH on V–P–O/SiO<sub>2</sub>, V–P–O/SiO<sub>2</sub>+MoO<sub>3</sub>, V–Mo–O/Al<sub>2</sub>O<sub>3</sub>+P<sub>2</sub>O<sub>5</sub> catalysts, exhibiting high activity and selectivity [9–11].

Another factor influencing the oxidation process is the concentration of O<sub>2</sub>. The results obtained showed that high oxygen concentrations provide high selectivity.

The results of the oxidation process in a stationary and fluidized bed catalyst are, of course, not the same. This is of great importance in the oxidation of CH, especially in the case of the need to utilize them [12]. The description of the rates of heterogeneous catalytic processes occurring in flow systems in a fluidized bed of catalyst has some difficulties associated with their hydrodynamics. These problems are reflected in the works [13], where an analysis of the kinetic description of heterogeneous catalytic reactions occurring in a fluidized bed of catalyst is carried out, and various models of their implementation are proposed [14–16].

The purpose of the conducted studies is to establish the kinetic patterns of the oxidation process of various chlorohydrocarbons in a stationary and fluidized bed of catalyst, as well as to propose a relatively simplified mechanism that includes the key stages of chlorohydrocarbon oxidation.

### Experimental

Carrying out heterogeneous catalytic oxidation of HC in a fluidized bed of V–P–O/SiO<sub>2</sub>, V–P–O/SiO<sub>2</sub>+MoO<sub>3</sub>, V–Mo–O/Al<sub>2</sub>O<sub>3</sub>+P<sub>2</sub>O<sub>5</sub> catalysts is characterized by a number of advantages: high heat transfer, low intra-diffusion resistance due to the use of small grains (0.4–0.8 mm) of the catalyst, simple reactor design, ease of input and output of particles and products, ease of regeneration, etc. A series of special experiments established the necessary fluidization rates, selected catalyst granules of certain sizes and linear velocity of the gas flow. Another series of experiments showed the oxidation reaction in the kinetic region [17–20].

It should be noted that chlorohydrocarbons without catalysts are not subject to selective oxidation, and at very high temperatures of 600–700 °C they decompose or are completely oxidized to CO<sub>2</sub>. The used V–P–O/SiO<sub>2</sub>, V–P–O/SiO<sub>2</sub>+MoO<sub>3</sub>, V–Mo–O/Al<sub>2</sub>O<sub>3</sub>+P<sub>2</sub>O<sub>5</sub> catalysts were synthesized by the known method of co-precipitation from the corresponding nitrate salts and supported on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [6]. Only in the presence of these catalysts at relatively low temperatures of 673–793 K (400–500 °C) chlorohydrocarbons are selectively oxidized to valuable petrochemical products such as monochloromaleic and dichloromaleic anhydrides. The effect of the catalyst granule size on the degree of HC conversion at temperatures of 673–773 K was studied by varying the catalyst particle size from 0.25÷0.5 to 0.6÷0.8 mm. The degree of HC conversion, as well as the selectivity of the process at the same temperature, remain virtually unchanged, indicating the absence of diffusion complications. Changing the feed rate of the initial gas flow also does not affect the process parameters, which indicates the absence of external diffusion inhibition, i.e. the oxidation reaction occurs in the kinetic region. The data obtained during the study in the gradient-free flow-circulation and flow-through installations are consistent with each other and with the results of [4, 5, 21–24].

In order to identify the kinetic patterns of oxidation reactions of chlorine-containing hydrocarbons  $C_4$  and to construct kinetic models that make it possible to control the oxidation process, the effect of various parameters on its course was studied in a wide range of their change:  $T = 673–793$  K,  $C_{O_2} = 1 \cdot 10^{-4}–20 \cdot 10^{-5}$ ,

$C_{XY} = 1 \cdot 10^{-4} - 20 \cdot 10^{-3}$  mol/l,  $\tau = 0.1 - 1.0$  s using examples of oxidation reactions of 12-DCButene, 1,3-dichlorobutene-2 (1,3-DCB-2), 1,2,4-trichlorobutene-2 (1,2,4-TCB-2), 2,3,3-trichlorobutene-1 (2,3,3-TCB-1), 1,2,3-trichlorobutene-2 (1,2,3-TCB-2), 1,2,3,4-pentachlorobutene-1 (PCB-1). The oxidation products of Ch-Butenes are chloropropanoic acid (CPA), chloroacetic acid (CAC), HCl, CO<sub>2</sub>, CO, H<sub>2</sub>O; 1,2-DCB-2 — chloroacrylic acid (CA), monochloromaleic anhydride (m-ChMA), dichloromaleic anhydride (d-ChMA), acetic acid (AA), CO, CO<sub>2</sub>, HCl, H<sub>2</sub>O, Cl<sub>2</sub>.

The statistical manipulation of the experimental results was ultimately aimed at determining the confidence interval boundary:

$$\left[ M - t_{n,p} \frac{S}{\sqrt{n}}; M + t_{n,p} \frac{S}{\sqrt{n}} \right],$$

where  $M$  — is the average value of the data extraction;  $S$  — is the standard deviation;  $t_{n,p}$  — is a table value of Student's distribution with a number of degrees of freedom ( $n$ ) and confidence factor ( $P$ );  $n$  — is a number of elements in taken extraction of corresponding experiments.

The calculation was carried out using the Excel software package with a confidence probability of  $P = 95\%$  and a preliminary calculation of the standard deviation ( $S$ ), with a sample size of  $n = 4 - 12$ . To find the confidence interval of all curves on graphs 1–4, given in the work, we use the “descriptive statistics” of the Excel program.

### Results and Discussion

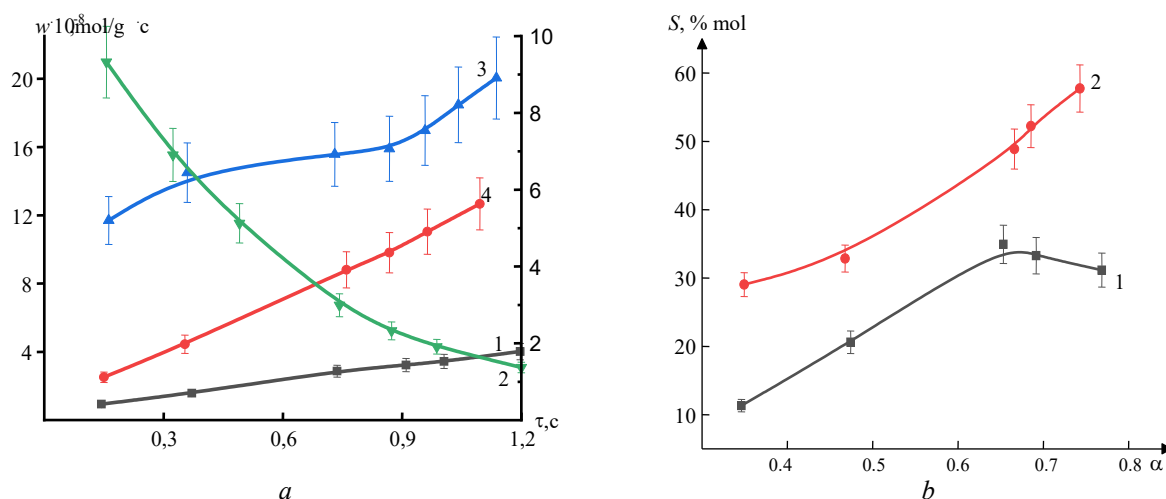
Catalysts containing vanadium and phosphorus oxides were previously used in the oxidation of four-carbon chlorohydrocarbons, such as *n*-butane, *n*-butene, 1,3-butadiene chlorides, or their mixtures with molecular oxygen or oxygen-containing gas to produce chloromaleic anhydrides. Conventional methods for preparing such catalysts involve reducing a pentavalent vanadium compound and combining it with a phosphorus compound and, optionally, promoter compounds under conditions where the valence of vanadium is below +5 to form catalyst precursors capable of being converted to vanadium phosphorus oxide. The oxide catalyst precursor is then isolated and converted to the active catalyst before or after forming suitable catalyst particles for either a fixed bed or a fluidized bed.

In the experimental work, catalytic systems were synthesized from water-soluble salts of vanadium and phosphorus (also molybdenum as a promoter) by impregnation on a carrier (SiO<sub>2</sub>) and subsequent annealing at various temperatures, and were studied in both fluidized and fixed-bed oxidation processes in an open-flow reactor. From the study of the nature of active centers on the surface of synthesized V–P–O/SiO<sub>2</sub>, V–P–O/SiO<sub>2</sub>+MoO<sub>3</sub>, V–Mo–O/Al<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub>, etc. catalysts by derivatographic method with acetone, phenol, butylamine, CO<sub>2</sub> and in pure form, it was found that there are a number of weak, medium, strong, very strong electron-acceptor, oxidizing and acid-base centers on the surface of the catalysts, which differ in energy and concentration. It has been proven by the X-ray phase method that during the activation of catalytic systems in air, O<sub>2</sub>, and chlorohydrocarbons, the phase formation processes continue and the phases that provide activity and selectivity are V<sub>2</sub>MoO<sub>8</sub> and V<sub>9</sub>Mo<sub>6</sub>O<sub>40</sub>. Here, the main oxidizing components are considered to be V and Mo. According to our previous studies (EPR), the catalyst is more active in the oxidation states of V<sup>+4</sup> and V<sup>+5</sup>, Mo<sup>+6</sup> and Mo<sup>+5</sup>. The ratio of V<sup>+4</sup>/V<sup>+5</sup>, Mo<sup>+6</sup>/Mo<sup>+5</sup> plays a decisive role. At the same time, the role of phosphorus is to regulate the ratios of V<sup>+4</sup>/V<sup>+5</sup>, Mo<sup>+6</sup>/Mo<sup>+5</sup> and the amount of weakly adsorbed oxygen, which causes deep oxidation. The fact that the amount of oxygen required for the oxidation reaction of chlorohydrocarbons exceeds stoichiometry is due to the consumption of oxygen in several directions: the creation of catalyst-environment equilibrium, prevention of the transition of reduced active components to a lower oxidation state (V<sup>+5</sup>→V<sup>+4</sup>→V<sup>+3</sup>), oxidation of active centers. At the beginning of the oxidation process, oxidation occurs due to oxygen escaping from the crystal lattice of the catalyst to the surface. Exposure of the surface of the catalysts to the oxidation-reduction process affects the nature of the active centers on the surface and directs the process in a selective direction.

The objects of the study were 1,2,4-trichlorobutene-2 (1,2,4-TCB-2), 1,2,3-trichlorobutene-1 (1,2,3-TCB-1), 2,3,3-trichlorobutene-1 (2,3,3-TCB-1), 1,1,2,3,4-pentachlorobutene-1 (PCB-1). It was of interest to study the kinetic patterns of tri- and pentachlorobutenes from the point of view of clarifying the role of the double bond and chlorine atoms in the formation of monochloromaleic (*m*-ChMA) and dichloromaleic (*d*-ChMA) anhydride. It was also important to clarify the conditions for the deep oxidation reaction and compare its rate with the rate of the reaction of formation of the target product. The kinetic curves of the oxidation reaction of 1,2,4-TCB-2 are shown in Fig. 1. As can be seen from Fig. 1, the rate of consumption of

the initial 1,2,4-TCB-2 gradually increases, while the rates of formation of *m*-ChMA, CO<sub>2</sub> and freely splitting chlorine increase simultaneously. The rate of the deep oxidation reaction exceeds the rate of the main reaction of *m*-ChMA formation by more than an order of magnitude, however, some parallelism of the graphs of these rates is observed up to  $\tau = 0.6$  s, after which  $w_{\text{CO}_2}$  increases sharply. Description of the results in  $w_i - C_i$  coordinates for the corresponding substances shows that they comply with a linear dependence (Fig. 1, *a*, *b*).

Comparison of the rates of the main reaction of *m*-ChMA formation and the deep oxidation reaction shows that CO<sub>2</sub> is formed in a parallel-sequential scheme both from the initial raw material and from the target product under certain conditions, which follows from the analysis of the curve of the selectivity dependence on the degree of conversion (Fig. 1 *b*).



*a* — Kinetic curves of the dependences of the oxidation reaction rate of 1,2,4-TCB-2 on the contact time.  
 1 — the rate of consumption of TCButene,  $w_{1,2,4\text{-TCB-2}}$ ; 2 — the rate of formation of *m*-ChMA— $w_{m\text{-ChMA}}$ ,  
 3 —  $w_{\text{CO}_2}$ ; 4 —  $w_{\text{Cl}_2}$ ; *b* — The dependence of selectivity on the degree of conversion of 1,2,4-TCB-2:  
 1 — *m*-ChMA; 2 — CO<sub>2</sub>. Confidence level  $P = 95\%$

Figure 1

The results of statistical processing of the experimental data in Figures 1–4 and the confidence intervals of the curves are shown in Table 1.

Table 1

Statistical analysis of experimental data and confidence intervals for the kinetic and selectivity curves presented in Figures 1–4 (confidence level  $P = 95\%$ )

Figure	Curve No.	$\bar{y} \pm \Delta$ ( $P = 0.95$ )	Range	Sample size, $n$
Figure 1a	1	$10.3 \pm 4.4$	(5.9; 14.7)	8
	2	$16.9 \pm 1.6$	(15.3; 18.5)	6
	3	$8.2 \pm 3.2$	(5.0; 11.4)	6
	4	$2.55 \pm 0.95$	(1.6; 3.5)	6
Figure 1b	1	$44 \pm 11$	(33; 55)	5
	2	$26.1 \pm 8.8$	(17.3; 34.9)	5
Figure 2	1	$14.8 \pm 7.0$	(7.8; 21.8)	7
	2	$5.7 \pm 3.1$	(2.6; 8.8)	5
	3	$12.9 \pm 6.6$	(6.3; 19.5)	7
	4	$5.7 \pm 3.8$	(1.9; 9.5)	6
Figure 3	1	$3.35 \pm 0.64$	(2.71; 3.99)	8
	1'	$2.91 \pm 0.88$	(2.03; 3.79)	8
	2	$0.59 \pm 0.20$	(0.39; 0.79)	12
	2'	$0.46 \pm 0.27$	(0.19; 0.73)	8
	3	$8.13 \pm 0.45$	(7.68; 8.58)	4

Continuation of Table 1

Figure	Curve No.	$\bar{y} \pm \Delta$ ( $P = 0.95$ )	Range	Sample size, $n$
Figure 3	3'	$7.84 \pm 0.64$	(7.20; 8.48)	4
	4	$5.88 \pm 0.17$	(5.71; 6.05)	6
	4'	$5.76 \pm 0.23$	(5.53; 5.99)	4
Figure 4	1	$3.5 \pm 2.1$	(2.4; 5.6)	4
	2	$5.29 \pm 0.87$	(4.42; 6.16)	4
	3	$8.0 \pm 2.6$	(5.4; 10.6)	4

The results of the study of the kinetic patterns of the oxidation reaction of 2,3,3-TCB-1 are shown in Fig. 2.

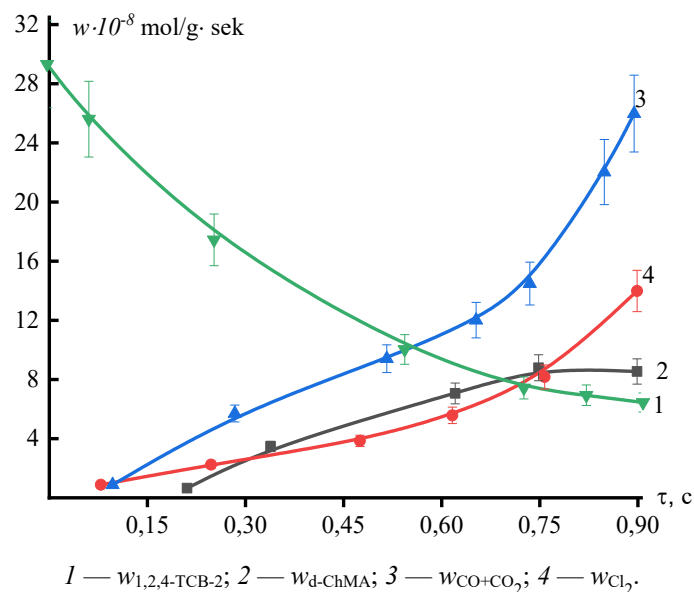


Figure 2. Results of kinetic studies of the oxidation reaction of 2,3,3-TCB-1, dependence of the accumulation rate on the contact time. Confidence level  $P = 95\%$

As can be seen from the presented dependencies (Fig. 2), the oxidation rate of the original 2,3,3-TCB-1 exceeds the rate of formation of d-ChMA and is comparable with the rate of formation of  $\text{CO}_2$ . Carbon dioxide is formed from the beginning of the reaction and then at small  $\tau$  as well, but after the value  $\tau = 0.7$  s, a sharp jump in the rate of formation of  $\text{CO}_2$  is observed. The curve of the rate of formation of chlorine (4) behaves similarly to the curve of the rate of formation of  $\text{CO}_2$  (3), which confirms the idea of the presence of an additional path of formation of  $\text{CO}_2$  (3) and a chlorine-containing compound. This is also evident from Fig. 2, where the dependences of the rates of formation of  $\text{CO}_2$  and  $\text{Cl}_2$  on their concentrations grow in parallel at close values.

The study of the kinetics of 1,2,3-TCB-2, the results of which are presented in Fig. 3, also confirmed the stated assumption about the formation of  $\text{CO}_2$ . The patterns revealed for 1,2,4-TCB-2 and 2,3,3-TCB-1 are also preserved in this case. Comparison of the rates of the main reaction and the deep oxidation reaction here more expressively indicates the presence of a parallel-sequential path of  $\text{CO}_2$  formation.

To clarify the role of the location of chlorine atoms in pentachlor-containing hydrocarbons, a detailed study of the kinetic regularities was carried out using 1,1,2,3,4-PCB-1 as an example.

The results of the influence of various parameters on the rates of the PCB-1 oxidation reaction in both fixed and fluidized beds of V-P-O/ $\text{SiO}_2$  catalyst at different ratios of 1,1,2,3,4-PCB-1: $\text{O}_2$  (1:6 and 1:35) are shown in Figs. 3 and 4. Comparison of the rate of total PCB-1 consumption in a fixed bed (Fig. 3) with the rate in a fluidized bed (Fig. 4) showed that  $w_{\text{PCB}}^F = 7.4 \cdot 10^{-8}$  mol/g is almost 2.0 times higher than  $w_{\text{PCB}}^{FI} = 3.58 \cdot 10^{-8}$  mol/g under the same reaction conditions ( $\tau = 0.6$  s). In this case, the rates of formation  $w_{\text{DCMA}}^{FFI}$  are higher, and the rate of deep oxidation reaction decreases almost 2.0 times.

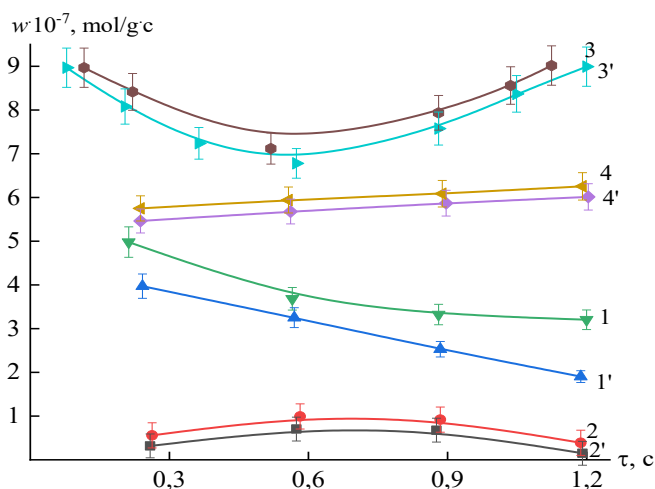


Figure 3. Results of the study of kinetic regularities of the oxidation reaction of 1,1,2,3,4-PCB-1, dependence of the reaction rate on the contact time in a fixed catalyst bed with PCB:O<sub>2</sub>. Confidence level  $P = 95\%$

And if the latter in the case of a fixed bed passes through a minimum, then in the case of a fluidized bed it is almost constant (at  $\tau = 0.15$  s,  $w_{\text{CO}_2} = 4.04 \cdot 10^{-7}$  mol/g s,  $\tau = 0.7$  s,  $w_{\text{CO}_2} = 4.33 \cdot 10^{-7}$  mol/g s — the increase is insignificant). When analyzing the obtained results, attention is drawn to the fact that in a fixed bed at a molar ratio of PCB:O<sub>2</sub> = 1:6 and  $\tau = 0.6$  s, the PCB consumption rate  $w_{\text{PCB}} = 3.85 \cdot 10^{-8}$  mol/g s, and at a ratio of PCB:O<sub>2</sub> = 1:35  $w_{\text{PCB}} = 3.52 \cdot 10^{-8}$  mol/g s. In the fluidized bed, the  $w_{\text{PCB}}$  values are  $7.68 \cdot 10^{-8}$  and  $7.44 \cdot 10^{-8}$  mol/g, respectively. The rates of d-ChMA formation are also higher, which confirms the correctness of the transition to studying reactions in the fluidized bed. The study of the effect of oxygen concentration at different temperatures on the oxidation rate of PCB and the rates of formation of reaction products in the fluidized bed is shown in Fig. 4.

Here, a somewhat strange behavior of the dependence of  $w_{\text{PCB}}$  on CO<sub>2</sub> is also observed (Fig. 4), namely, at very low concentrations of O<sub>2</sub> — in the range from  $0.08 \cdot 10^{-3}$  mol/l to  $0.8 \cdot 10^{-3}$  mol/l, a decrease in the rate of PCB consumption is observed.

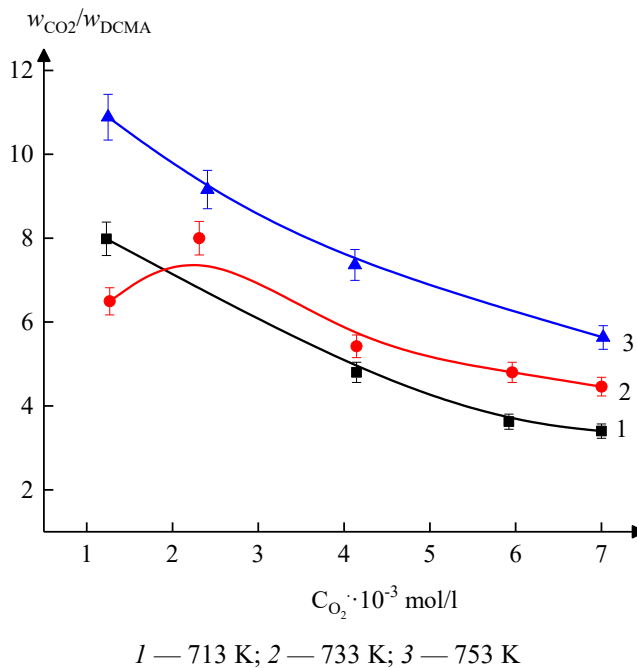
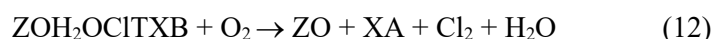
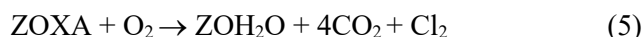
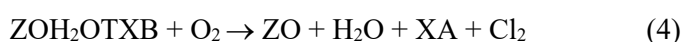
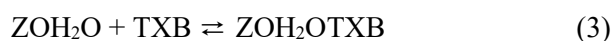


Figure 4. Results of the study of the kinetics of PCB-1 oxidation in a fluidized bed of catalyst at different temperatures. Confidence level  $P = 95\%$

A further increase in  $\text{CO}_2$  to  $7.15 \cdot 10^{-3}$  has almost no effect on the PCB oxidation rate. Only with an increase in temperature does the latter increase slightly (Fig. 4). The rate of d-ChMA formation at an initial  $\text{CO}_2$  concentration of up to  $5.36 \cdot 10^{-3}$  mol/l reaches a maximum. With an increase in temperature after 713 K, it decreases slightly. The rate of deep oxidation at initial oxygen concentrations is low and increases with an increase in  $\text{CO}_2$ , reaching its maximum at a value of  $\text{CO}_2 = 0.858 \cdot 10^{-3}$  mol/l, and then decreases slightly and becomes constant with a further increase in  $\text{CO}_2$ . However, with an increase in temperature, the rate of formation of freely cleaved chlorine increases. Comparison of the rates of the d-ChMA formation reaction and the deep oxidation reaction showed that when the reaction is carried out in a fixed catalyst bed, the  $w_{\text{CO}_2}/w_{\text{d-ChMA}}$  ratio changes more sharply than in the case of a fluidized bed (Fig. 4). With increasing temperature and with changing  $\text{CO}_2$ , this ratio increases [5, 7]. The reaction mechanism describes the step-by-step process of transforming reagents into products. For oxidation reactions involving chlorine-containing hydrocarbons and vanadium-phosphorus catalysts, the mechanism may include stages of oxygen activation on the catalyst surface, its interaction with the hydrocarbon, and the formation of intermediate products.

One of the main decisive and central places in the development of mathematical models of the process, which is important for the design and management of chemical technological processes, is occupied by the kinetic model of processes. The development of the kinetic model of processes, in turn, proceeds from the reaction mechanisms based on the experimental results of the study of the kinetic regularities of chemical reactions. Based on the proposed mechanisms of heterogeneous catalytic oxidation reactions of hydrocarbons and their chlorinated derivatives and the results of the oxidation reactions of chlorobutenes, we will consider a number of their stage mechanisms based on the results of the oxidation reactions of trichlorobutenes, which we studied. It should be noted that the discrimination of kinetic equations based on the proposed mechanisms and the calculation of the parameters of the kinetic model are based on known methods.

It is assumed that all active centers on the surface of the catalyst are in an oxidized state and modified by reaction products. Also, the process is quasi-stationary, the initial TXBs and the oxidation reaction occur according to the oxidation-reduction mechanism, and the main and by-products of the reaction are obtained according to the sequential-parallel reaction scheme. The oxidation reaction of TXB, which occurs in the "hot" layer of the catalyst, is more complex and occurs in more than 30 stages. Since solving the kinetic equation of this step-by-step reaction requires too much computer time and memory, and since it is necessary to solve a complex kinetic equation, it is possible to propose a relatively simplified mechanism that includes the main stages. Such a step-by-step mechanism can be written as follows:



where ZO — is the means adsorbed oxygen on the surface of the active centers of the catalyst.

Based on this mechanism, we can write the kinetic equations of individual stages as follows:

$$W_1 = K_1 C_{\text{ZO}} P_{\text{TXB}} - K_{-1} C_{\text{ZOTXB}}$$

$$W_2 = K_2 C_{\text{ZOTXB}} P_{\text{O}_2}$$

$$W_3 = K_3 C_{\text{ZOH}_2\text{O}} P_{\text{TXB}} - K_{-3} C_{\text{ZOH}_2\text{OTXB}}$$

$$W_4 = K_4 C_{\text{ZOH}_2\text{OTXB}} P_{\text{O}_2}$$

$$W_5 = K_5 C_{\text{ZOXA}} P_{\text{O}_2}$$

$$W_6 = K_6 C_{\text{ZOXA}} P_{\text{TXB}}$$

$$W_7 = K_7 C_{\text{ZOH}_2\text{O}} P_{\text{XA}} - K_{-7} C_{\text{ZOH}_2\text{OXA}}$$

$$W_8 = K_8 C_{\text{ZOH}_2\text{OXA}} P_{\text{TXB}} - K_{-8} C_{\text{ZOH}_2\text{OTXB}}$$

$$W_9 = K_9 C_{\text{ZOH}_2\text{OXATXB}} P_{\text{O}_2}$$

$$W_{10} = K_{10} C_{\text{ZOH}_2\text{O}} P_{\text{O}_2} - K_{-10} C_{\text{ZOH}_2\text{OCI}}$$

$$W_{11} = K_{11} C_{\text{ZOH}_2\text{OCI}} P_{\text{TXB}} - K_{-11} C_{\text{ZOH}_2\text{OCITXB}}$$

$$W_{12} = K_{12} C_{\text{ZOH}_2\text{OCITXB}} P_{\text{O}_2}.$$

The results of the calculations showed that the kinetic model that more accurately reflects the experimental results is the one based on the mechanism put forward in the hypothesis. Based on the kinetic model, we found the parameters of the kinetic equations for three temperatures (693, 713 and 733 K) with the “OptimMe” software application [24, 25]. Here the experimental and calculated values coincided. The calculated values of stiffness’s were found from that system of equations by the Kutta-Meyerson and Runge-Kutta method, and the values of the obtained parameters were initially taken for function minimization.

$$F = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{Y_{ij}^t - Y_{ij}^N}{Y_{ij}} \right)^2;$$

$$F(K_1, \dots, K_{12}) = \sum_{k=1}^{12} [C_{ip}(K_1, \dots, K_{12}) - C_{ip}]^2.$$

Here,  $C_{ip}(K_1, \dots, K_{12})$   $i = 1 \div 2$  minimization was carried out based on Powell's method, and the values of  $\ln K_0$  and activation energy were calculated by substituting the obtained rate constants in the Arrhenius equation. It should be noted that the experimental results accurately corresponded with the calculated values (10–15 %) of the concentrations obtained as a result of minimization, which indicates that the mechanisms of the oxidation reactions of TCHbutenes were correctly deduced.

Table 2

Parameters and rate constants of the kinetic model of the oxidation process of 1,2,4-TXButene-2 to m-ChMA

$k_i$	Temperature, K			$\ln K_0$	$E$ , kC/mol
	693 K	713 K	733 K		
$K_1$	0.3861	0.3712	0.3142	–6.4731	32.45
$K_{-1}$	$0.6742 \cdot 10^{-10}$	$0.6240 \cdot 10^{-9}$	$0.5036 \cdot 10^{-8}$	–5.4873	28.06
$K_2$	5.4623	5.8751	7.0221	14.3221	96.34
$K_3$	74.2702	68.7254	64.3104	1.0436	27.02
$K_{-3}$	$0.4823 \cdot 10^{-9}$	$0.4062 \cdot 10^{-8}$	$0.26 \cdot 10^{-7}$	–3.1435	36.78
$K_4$	1.5245	1.6113	2.1402	4.3768	58.43
$K_5$	$0.1024 \cdot 10^{-4}$	$0.56 \cdot 10^{-4}$	$0.632 \cdot 10^{-4}$	2.89	70.19
$K_6$	$0.091 \cdot 10^{-7}$	$0.041 \cdot 10^{-7}$	$0.018 \cdot 10^{-7}$	–14.41	23.54
$K_7$	71.2024	65.423	61.671	–3.172	19.22
$K_{-7}$	$0.23 \cdot 10^{-10}$	$0.56 \cdot 10^{-9}$	$0.12 \cdot 10^{-8}$	–2.01	20.46
$K_8$	$62.136 \cdot 10^{-8}$	$58.712 \cdot 10^{-8}$	$56.4 \cdot 10^{-8}$	–2.45	21.36
$K_{-8}$	$10.21 \cdot 10^{-9}$	$9.43 \cdot 10^{-9}$	$7.45 \cdot 10^{-6}$	–4.02	20.71
$K_{-9}$	33.56	38.42	41.76	13.84	80.68
$K_{10}$	$4.1 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	4.25	26.93
$K_{11}$	52.12	46.38	41.82	–5.32	24.02
$K_{-11}$	54.21	57.01	62.36	–1.21	15.27
$K_{-12}$	29.37	42.38	68.70	+11.20	68.74



Based on the obtained model, rate constants and parameters of the model were calculated for the kinetic equations of the mechanism of oxidation reactions in the hot bed of 1,2,3-TXB-1; 2,3,3-TXB-1; 1,2,3-TXB-2 and PXB V–P–O/SiO<sub>2</sub> catalysts. The obtained results are shown in Table 2.

### Conclusions

Thus, the study of the kinetic regularities of the oxidation reactions of tri- and pentachloro-containing non-limiting hydrocarbons C<sub>4</sub> on vanadium-phosphorus catalysts showed that they have the same character. The comparison of the rates of formation of products of selective and deep oxidation indicates the presence of parallel-consequential pathways of their formation, and the presence of an additional path of formation of CO<sub>2</sub> from chlorine-containing target compounds. It is shown that the amount, as well as the location of chlorine atoms and the double bond, have an effect on the direction of the oxidation reaction. The comparison of the rates of formation of the target products confirms the correctness of the choice of the fluidized bed of the catalyst for the implementation of selective oxidation. It is also shown that the initial end products of the reaction do not have an inhibitory effect on the rate of oxidation reactions. On the basis of kinetic conditions, a staged mechanism, kinetic model and oxidation reaction of chlorine-containing hydrocarbons were compiled and the parameters of this model were calculated.

### Author Information\*

*\*The authors' names are presented in the following order: First Name, Middle Name and Last Name*

**Irada Hasan Melikova** (*corresponding author*) — Leading Researcher, Associate Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev of Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [iradam@rambler.ru](mailto:iradam@rambler.ru); <https://orcid.org/0000-0002-7906-1556>

**Arif Javanshir Efendi** — Doctor of Chemical Sciences, Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev, Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [efendi-arif@mail.ru](mailto:efendi-arif@mail.ru); <https://orcid.org/0000-0002-5529-980X>

**Manaf Rizvan Manafov** — Leading Researcher, Associate Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev, Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [mmanafov@gmail.com](mailto:mmanafov@gmail.com); <https://orcid.org/0000-0002-9965-4850>

**Natavan Fakhraddin Aykan** — Senior Researcher, Assistant Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev, Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [ntvn\\_78@hotmail.com](mailto:ntvn_78@hotmail.com); <https://orcid.org/0000-0003-2245-7047>

**Guseyn Mammad Faradjev** — Leading Researcher, Associate Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev, Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [huseynfaracov13@gmail.com](mailto:huseynfaracov13@gmail.com)

**Ceyran Teymur Rustamova** — Senior Researcher, Assistant Professor, Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev of Ministry of Science and Education of Republic of Azerbaijan, H. Javid Ave. 113, Az-1143, Baku, Azerbaijan; e-mail: [rustamovac63@gmail.com](mailto:rustamovac63@gmail.com); <https://orcid.org/0000-0003-2300-8120>

**Nizami Ismail Shikhaliyev** — PhD, Assistant Professor, Azerbaijan Technical University, Ministry of Education of the Republic of Azerbaijan, G. Javid Ave. 25, Az-1073, Baku, Azerbaijan; e-mail: [nizamishihaliyev54@gmail.com](mailto:nizamishihaliyev54@gmail.com); <https://orcid.org/0009-0008-0381-8912>

### Conflicts of Interest

The authors declare no conflict of interest.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Irada Hasan Melikova** conceptualization, data curation, methodology; writing — review and editing; **Arif Javanshir Efendi** writing — original draft, writing-review and editing, investigation, data curation; **Manaf Rizvan Manafov** data curation, writing — review and editing; **Nata-van Fakhreddin Aykan** and **Nizami Ismail Shikhaliyev** investigation, resources; **Guseyn Mammad Farad-jov** and **Jeyran Teymur Rustamova** investigation.

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