KINETICS OF OXIDATION OF HEPTADECANE AND MIXTURE OF HEPTADECANE WITH ITS OXIDATE RESIDUE BY ATMOSPHERIC OXYGEN IN THE PRESENCE OF A CATALYST*

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Abstract

Certain kinetic rate constants were determined for the formation of monobasic carboxylic acids and esters as a result of the oxidation reaction of heptadecane with its oxidate residue by atmospheric oxygen in the presence of a catalyst.

Kinetic analyses showed that the rate of formation of monobasic carboxylic acids and esters as a result of the oxidation reaction of heptadecane with its oxidate residue (mass ratio 1:1) is 2,8 times higher than that of heptadecane.

Keywords: reaction order, reaction molecularity, reaction rate, Van't Hoff's differential method, oxidation, cobalt stearate, homogeneous catalysis, kinetic curves.

Concentrates of n-paraffin hydrocarbons used to produce monobasic carboxylic acids are formed as by-product in the production of lubricants obtained from Turkmen oil. These monobasic carboxylic acids serve as intermediate raw material in the production of surfactants necessary for various industries in our country, such as plastic, extreme pressure additives for lubricating oils that increase abrasion resistance, enriching substances for local mineral raw materials, especially oil dehydrators, anti-corrosion additives for oil pipelines, plasticizers and stabilizers of synthetic polymers. This in turn creates conditions for the development of scientific foundations for the technology of production of monobasic carboxylic acids from accessible and cheap local raw materials. In this regard, studying the composition of local raw materials and researching possibility of obtaining monobasic carboxylic acids by oxidation in the presence of a catalyst, as well as developing a method for their preparation is an important scientific task.

On the example of n-paraffin hydrocarbons, the optimal conditions for the oxidation of heptadecane with atmospheric oxygen in the presence of a catalyst were established, and the possibility of obtaining monobasic carboxylic acids from the concentrates of n-paraffin hydrocarbons in the oil fraction of oil was studied (O. Hallyýewa, K. Poladow, 2015). An in-depth study of oxidation kinetics contributes to the development of the scientific basis for effective process control. Kinetic analyzes were carried out according to the values of change ($\omega=\Delta C/\Delta \tau$) in the concentration of formed products (C) depending on the duration of interaction (τ) (Ya.D. Samuilov, E.N. Cherezova, 2003).

The kinetic constants (k) of the rate of transformation reactions were determined graphically. The order of the catalytic reaction (**n**) of hydrocarbons with oxygen was determined by converting the equation $\lg\omega=\lg k+n\cdot\lg C$ according to the Van't Hoff's differential method.

Kinetics of heptadecane oxidation

The kinetic constants (k_k) of the rate of formation of monobasic carboxylic acids as a result of heptadecane oxidation, calculated depending on the duration of interaction (τ) are shown in table 1.

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The studied process proceeds through 3 different stages, characterized by different rate values.

Table 1

The values of the kinetic constant (k_k) of the rate of formation of carboxylic acids during the oxidation of heptadecane in different time limits (τ)

τ, time	1	2	3	4	5	6	7	8	9	10	11	12
n	1		0									
k_k·10-3	23,10	23,14	21,84	21,66						20,0	16,66	13,33
Unit	[min^{-1}]		[$mol \cdot l^{-1} \cdot min^{-1}$]									
$kk \cdot 10^{-3}_{av.}$	23,12		21.84	20,83							15,0	

The **first stage** lasts 2 hours from the beginning of the reaction, and the formation of carboxylic acids occurs according to the rules of the 1st order reaction. At this stage, the average value of its kinetic rate constant is $23{,}12 \cdot 10^{-3} min^{-1}$.

At the **second stage**, during the 3rd hour after the start of the oxidation reaction, the reaction rate begins to decrease ($k_k=21{,}84 \cdot 10^{-3} min^{-1}$). During 4-10 hours of the reaction, the formation of carboxylic acids as a result of transformations is carried out according to the rules of interactions of the 0th order. At this stage, the value of the kinetic rate constant of interactions is constant during each hour and is $20{,}83 \cdot 10^{-3} mol \cdot l^{-1} \cdot min^{-1}$ on the average.

At the **third stage**, that is, during 11-12 hours of interaction, the reaction rate is strongly reduced, and the average value of the kinetic reaction rate constant is $15{,}0 \cdot 10^{-3} mol \cdot l^{-1} \cdot min^{-1}$.

In general, by the end of the reaction, the kinetic rate constants of the formation of carboxylic acids gradually decrease from $23{,}12 \cdot 10^{-3} min^{-1}$ to $15{,}0 \cdot 10^{-3} mol \cdot l^{-1}\ min^{-1}$.

In the process of heptadecane oxidation, esters are formed in three consecutive stages parallelly (table 2).

Table 2

The values of the kinetic constant (k_e) of the rate of ester formation during the oxidation of heptadecane in different time limits (τ)

τ, time	1	2	3	4	5	6	7	8	9	10	11	12	13
n	1												2
$k_e \cdot 10^{-3}$	23,1	3,31	2,76	2,60	2,43	2,61	2,60	2,55	2,46	2,28	2,28	2,27	2,63
Unit	[min^{-1}]												$mol^{-1} \cdot min^{-1}$
$k_e \cdot 10^{-3}_{av.}$	23,1	2,56											2,63

Transformations occurring within 12 hours from the beginning of the reaction are going on in accordance with the rules of interaction of the 1st order. At this stage, the value of the kinetic rate constant for the formation of esters in the 1st hour of interaction is $23{,}1 \cdot 10^{-3} min^{-1}$. The average value of the kinetic rate constant for the formation of esters within 2-12 hours from the start of the reaction was $2{,}56 \cdot 10^{-3} min^{-1}$. After that, at the 13th hour of the reaction, the transformation occurs according to the rules of interaction of the 2nd order, and the value of its kinetic rate constant increases to $2{,}63 \cdot 10^{-3} mol^{-1} \cdot min^{-1}$.

Oxidation Kinetics of a Heptadecane Mixture with Its Oxidate Residue

The formation of monobasic carboxylic acids in this sample during 12 hours of the oxidation process proceeds in 2 stages characterized by different rates (Table 3).

Table 3

The value of the kinetic constant (k_k) of the rate of formation of carboxylic acids during the oxidation of a mixture of heptadecane with its oxidate residue in different time intervals (τ)

τ, time	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
n	1	0										
$k_k \cdot 10^{-3}$	23,12	75,0	71,6	68,3	66,6	65,0	63,3	61,6	58,3	53,3	51,6	48,3
Unit	[min^{-1}]	[mol·l^{-1}· min^{-1}]										
$k_k \cdot 10^{-3}_{ort.}$	23,12	60,83										

The **first stage** lasts 1 hour from the beginning of the reaction and the formation of carboxylic acids is going on according to the rules of the 1st order reaction. At this stage, its kinetic rate constant is 23,12·10^{-3}min^{-1}.

At the **second stage**, the formation of carboxylic acids occurs according to the rule of 0th order reactions, the rate of which gradually decreases with an increase in the duration of the reaction, that is, from the 2nd to the 12th hour it decreases, respectively, from 75,0·10^{-3}mol·l^{-1} min^{-1} to 48,3·10^{-3}mol·l^{-1}·min^{-1}. During this period, the average kinetic rate constant of the reaction is 60,83·10^{-3}mol·l^{-1}·min^{-1}.

The transformations associated with the formation of esters as a result of the oxidation of this sample proceed according to the rules of 1st order reactions in two successive stages (Table 4).

The **first stage** lasts 1 hour from the beginning of the reaction and the kinetic rate constant of ester formation is 28.1·10^{-3}min^{-1}.

At the **second stage**, i.e. within 2-12 hours of interaction, the kinetic rate constants of the formation of esters gradually decrease from 2.72·10^{-3}min^{-1} to 1.30·10-3 min^{-1}, respectively (almost twice), and the average value of the kinetic interaction constant was 1,59·10^{-3} min^{-1}.

Table 4

The values of the kinetic constant (k_e) of the rate of ester formation during the oxidation of a mixture of heptadecane with its oxidate residue at different time intervals (τ)

τ, time	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
n	1											
$k_e \cdot 10^{-3}$	28,1	2,72	2,24	1,42	1,46	1,40	1,42	1,42	1,42	1,38	1,35	1,30
Unit	[min^{-1}]											
$k_e 10^{-3}_{av.}$	28,1	1,59										

Thus, it has been shown that, the kinetic rate constant of the formation of monobasic carboxylic acids increases by 2.8 times, and the kinetic constant of the formation of esters decreases by 1.6 times as compared to the oxidation of heptadecane, during the oxidation of a mixture of heptadecane with its oxidate residue.

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