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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Assessment of Formation Channels of Cyclohexyl Mono- and Dicarboxylates in Oxidation of Cyclohexane

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Abstract—Temperature dependences of the rate constants of the esterification reactions of the main carboxylic acids contained in oxidized cyclohexane (adipic, caproic, and formic) by cyclohexanol in a nonpolar medium were determined by solving the inverse kinetic problem.

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Esters of carboxylic acids and secondary alcohols are among the main by-products in oxidation of saturated hydrocarbons and their oxygen derivatives [1–4]. It was assumed in the early stages of development of the theory of liquid-phase oxidation of organic compounds by molecular oxygen that the main source of formation of these products is the reaction of esterification of carboxylic acids by alcohols [1, 5]. Later, the significance of the acid pathway to esters was questioned [6–8] and it was shown that reactions of alcoholysis of carboxylic acid anhydrides by alcohols serve as the main channel in which the esters are formed [4, 9–12]. In [12], the kinetics of stages of the reaction of alcoholysis of valeric anhydride by cyclohexanol in the presence of formic acid was studied, and this enabled estimation of the formation rate of cyclohexyl esters via the pathway involving carboxylic acid anhydrides. To evaluate the role of the esterification reaction in the process of ester formation, it is necessary to obtain additional data on the kinetics of interaction of cyclohexanol with carboxylic acids under the conditions close to those of oxidation.

The aim of the present study was to analyze the kinetics of interaction between cyclohexanol and the main types of mono- and dicarboxylic acids contained in oxidized cyclohexane and to estimate the relative contributions of the above-mentioned main channels to ester formation in industrial oxidation of cyclohexane to cyclohexanol and cyclohexanone.

EXPERIMENTAL

Methods for purification of formic acid, cyclohexanol, and o-dichlorobenzene were described in [12]. Caproic acid of pure grade was dried over anhydrous $MgSO_4$ and distilled in a vacuum in a flow of argon. Adipic acid of chemically pure grade was used without additional purification.

The esterification of carboxylic acids with cyclohexanol in an o-dichlorobenzene solution was performed by the ampule method. Samples of oxidized cyclohexane (150–155°C, 0.04% cobalt naphthenate, pressure 0.8 MPa) were obtained from the caprolactam oxidation shop of Azot Open Joint-Stock Company, Kemerovo.

Products of the esterification reactions, esters, were determined by gas-liquid chromatography (GLC). Prior to determination by GLC, reaction mixtures containing monocyclohexyl adipate were treated with diazomethane. The reaction products were analyzed on a 2000×3 mm column packed with 5% XE-60 silicone on N-AW 0.20–0.25 mm Chromaton. Hexadecane served as internal standard. Water in samples of oxidized cyclohexane was determined by the Fischer method [13]. Methods for determination of other products in oxidized cyclohexane were described in [11].

We calculated the sought-for parameters of kinetic equations by using software implementing the least-squares method in the Delphi 5.5 environment. The system of

differential equations was solved in each step by the Euler or Runge-Kutta method. The calculation was performed over the entire body of data for the object under study. This made it possible to improve the accuracy of determination of the activation energy and pre-exponential factor [14].

In accordance with the task formulated, we chose caproic, adipic, and formic acids as objects of study for examining the esterification reaction. The first two acids are the most important representatives of mono- and dicarboxylic acids of oxidized cyclohexane [1], and the last of these imparts specific properties to the esterification process in oxidation of cyclohexane [11, 12].

In the absence of acid catalysts, the esterification of caproic and formic acid by cyclohexanol occurs by the reversible reaction

$$R^1C(=O)-OH + C_6H_{11}OH \underset{k_-}{\overset{k_+}{\rightleftharpoons}} R^1C(=O)-OC_6H_{11} + H_2O, \quad (1)$$

R^1–H, C_5H_{11}

and the accumulation kinetics of the corresponding ester is described by the differential equation

$$\frac{d[R^1COOR]}{dt} = k_{i+}[R^1COOH][ROH] - k_{i-}[R^1COOR][H_2O], \quad (2)$$

where [ROH], [H_2O], [R^1COOH], and [R^1COOR] are the running concentrations of cyclohexanol, water, and the corresponding carboxylic acid and ester; k_{i+} and k_{i-} are the rate constants of reaction (1) at ith temperature.

On passing to experiments at jth temperature, values of the corresponding rate constants can be expressed by the reaction

$$\ln k_j = \ln k_i + \frac{E}{R}\left(\frac{1}{T_i} - \frac{1}{T_j}\right) \quad (3)$$

Experiments on interaction of formic acid (0.14 M) with cyclohexanol (1.77 M) were carried out in the temperature range 150–180°C in a solution of o-dichlorobenzene. The values obtained for the cyclohexyl formate concentrations are presented in the figure. The rate constants of the stages of reaction (1), activation energies, and pre-exponential factor were calculated by solving the inverse kinetic reaction with the use of Eqs. (2) and (3) (Table 1). The fact that the experimental points obtained by varying the initial concentrations of formic acid or cyclohexanol can also be described by equations of the type (2), with the same values of the constants, confirms the validity of the chosen kinetic scheme. Even the strongest of unsaturated aliphatic monocarboxylic acids, formic acid, has nearly no effect of the rate of the esterification reaction.

In a similar way, we obtained the rate constants of the stages, activation energies, and pre-exponential factors for the reaction of esterification of caproic acid (0.14 M) by cyclohexanol (1.77 M), carried out in the temperature range 160–190°C (see figure, Table 1).

In the reaction of adipic acid with cyclohexanol, dicyclohexyl adipate is formed in two successive reversible stages:

$$HO-C(=O)(CH_2)_4C(=O)-OH \underset{-H_2O;\ k_{-1}}{\overset{+ROH;\ k_{+1}}{\rightleftharpoons}} HO-C(=O)(CH_2)_4C(=O)-OR \underset{-H_2O;\ k_{-2}}{\overset{+ROH;\ k_{+2}}{\rightleftharpoons}} RO-C(=O)(CH_2)_4C(=O)-OR. \quad (4)$$

In this case, the kinetics of accumulation of mono- and dicyclohexyl adipate at ith temperature can be described by a system of differential equations

$$\frac{d[HOOC(CH_2)_4COOR]}{dt} = k_{+1}[HOOC(CH_2)_4COOH] \times [ROH] - k_{-1}[HOOC(CH_2)_4COOR][H_2O] - k_{+2}[HOOC(CH_2)_4COOR][ROH] + k_{-2} \times [ROOC(CH_2)_4COOR][H_2O], \quad (5)$$

$$\frac{d[ROOC(CH_2)_4COOR]}{dt} = k_{+2}[HOOC(CH_2)_4COOR] \times [ROH] - k_{-2}[ROOC(CH_2)_4COOR][H_2O], \quad (6)$$

where [$HOOC(CH_2)_4COOH$], [$HOOC(CH_2)_4COOR$], and [$ROOC(CH_2)_4COOR$] are the running concentrations of adipic acid and mono- and dicyclohexyl adipates, respectively.

The reaction of esterification of adipic acid (0.075 M) by cyclohexanol (1.86 M) was studied in the temperature

Table 1. Results of calculation of rate constants, activation energy, and pre-exponential factor for esterification of formic, caproic, and adipic acids by cyclohexanol

Constant	$k \times 10^5$, s^{-1}, M^{-1}, at indicated temperature, °C				E, kJ mol^{-1}	A
	150	160	170	180		
Formic acid						
k_+	3.8	7.2	13.2	23.8	97.46 ± 0.27	17.54 ± 0.07
k_-	1.7	3.6	7.4	14.9	116.5 ± 0.1	22.14 ± 0.03
Sum of squared deviations					1.3×10^{-4}	
Caproic acid						
k_+	0.27	0.39	0.54	0.75	56.16 ± 0.43	2.80 ± 0.11
k_-	3.03	3.43	3.88	4.35	20.07 ± 0.48	–4.83 ± 0.13
Sum of squared deviations					1.1×10^{-4}	
Adipic acid						
k_{+1}	0.73	1.07	1.55	2.22	61.68 ± 0.16	5.32 ± 0.04
k_{-1}	7.36	11.2	16.6	24.3	66.3 ± 0.01	8.91 ± 0.004
k_{+2}	0.28	0.4	0.56	0.76	54.64 ± 0.24	2.42 ± 0.06
k_{-2}	4.47	5.64	7.04	8.7	36.93 ± 0.004	0.25 ± 0.001
Sum of squared deviations					6.16×10^{-5}	

range 160–190°C. The experimental data were used to calculate by Eqs. (3), (5), and (6) the corresponding rate constants of the stages, pre-exponential factors, and activation energies of this reaction (Table 1). The resulting calculated curves of ester accumulation rather well describe the experimental values of the concentrations of mono- and dicyclohexyl adipates (see figure).

It can be seen from the data in Table 1 that the formation rate constant of cyclohexyl formate substantially exceeds that of other esters. These results are in good agreement with the data of [15], according to which the reactivity of formic acid in the reaction with cyclohexanol is 30 times that of other aliphatic carboxylic acids.

The kinetic dependences obtained and the data on the composition of products in industrial samples of oxidized cyclohexane (Table 2) enabled us to calculate the formation rates of cyclohexyl formate and cyclohexyl caproate in the esterification reaction by Eq. (7) and those of mono- and dicyclohexyl adipates, by Eqs. (8) and (9), respectively:

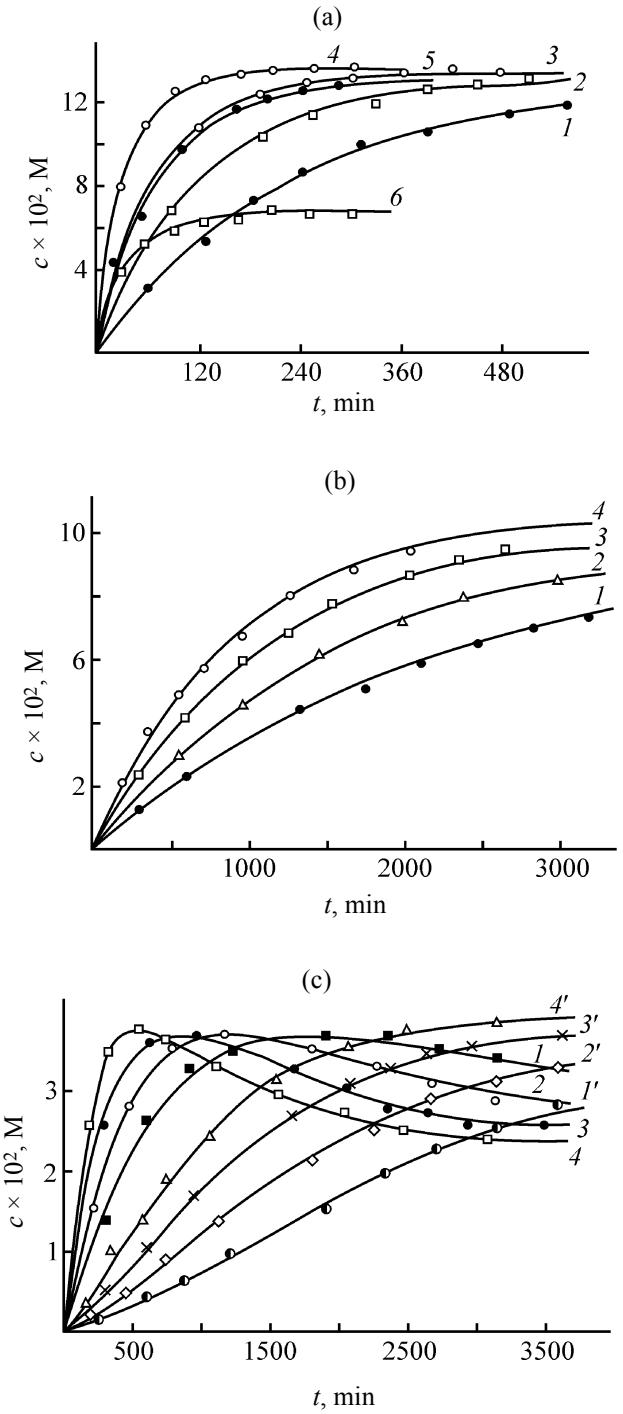
$$W_{\text{est}} = k_+[\text{R}^1\text{COOH}][\text{ROH}] - k_-[\text{R}^1\text{COOR}][\text{H}_2\text{O}], \quad (7)$$

$$W_{\text{est}} = k_{+1}[\text{HOOC(CH}_2)_4\text{COOH}][\text{ROH}] - k_{-1} \times [\text{HOOC(CH}_2)_4\text{COOR}][\text{ROH}] + k_{-2} \times [\text{ROOC(CH}_2)_4\text{COOR}][\text{H}_2\text{O}] + k_{-2} \times [\text{ROOC(CH}_2)_4\text{COOR}][\text{H}_2\text{O}] \quad (8)$$

$$W_{\text{est}} = k_{+2}[\text{HOOC(CH}_2)_4\text{COOR}][\text{ROH}] - k_{-2}[\text{ROOH(CH}_2)_4\text{COOR}][\text{H}_2\text{O}]. \quad (9)$$

According to Table 1, the rate constants of the forward and reverse reactions at 150°C are as follows (s^{-1} M^{-1}): $k_+ = 3.8 \times 10^{-5}$ and $k_- = 1.7 \times 10^{-5}$ for formic acid; $k_+ = 1.85 \times 10^{-6}$ and $k_- = 2.65 \times 10^{-5}$ for caproic acid; and $k_{+1} = 4.87 \times 10^{-6}$, $k_{-1} = 4.76 \times 10^{-5}$ and $k_{+2} = 2.03 \times 10^{-6}$, $k_{-2} = 3.51 \times 10^{-5}$ for adipic acid. The calculated formation rates of cyclohexyl formate, caproate, and adipate in samples of oxidized cyclohexane are listed in Table 3.

As already noted, an alternative to the esterification reaction pathway to cyclohexyl esters is the alcoholysis of anhydrides by cyclohexanol. To evaluate the relative importance of these two channels, it is necessary to calculate the rate of the alcoholysis reactions. The difficulty is in that oxidized cyclohexane contains more than ten products of acid nature [1, 11]. Naturally, mixed and



Experimental values of the concentrations c and the calculated curves of accumulation of esters in the interaction of (a) formic, (b) caproic, and (c) adipic acids with cyclohexanol at various temperatures. (*t*) Time. *T* (°C): (a) (*1*) 150, (*2*) 160, (*3*) 170, (*4*) 180, and (*5*) 180 at c^0_{HCOOH} = 0.14 M and c^0_{ROH} = 0.88 M, (6) 180 at c^0_{HCOH} = 0.067 M and c^0_{ROH} = 1.77 M; (b) (*1*) 160, (*2*) 170, (*3*) 180, and (*4*) 190; (c) (*1, 1′*) 160, (*2, 2′*) 170, (*3, 3′*) 180, and (*4, 4′*) 190; (*1–4*) cyclohexyl adipate and (*1′–4′*) dicyclohexyl adipate.

symmetric anhydrides will be formed in considerably greater amounts and there is no way of determining their individual composition by the existing methods. It is possible, however, to use the circumstance that, according to the results of [10, 11], the ratios between the yields of carboxylic acids and their cyclohexyl esters are close for all mono- and dicarboxylic acids (except formic acid). If we assume that mixed anhydrides containing acyls of all carboxylic acids found in oxidized cyclohexane (except formic acid) must have reactivities close to those of the corresponding anhydrides containing the acyl of valeric acid, then the rate of the alcoholysis reaction can be estimated using temperature dependences reported in [12] for the rate constants of the stages of the reaction between valeric anhydride and cyclohexanol in the presence of formic acid.

The analytically determined sum of carboxylic acid anhydrides ($\Sigma[R_iC(O)OC(O)R_j]$) in oxidized cyclohexane includes anhydrides with different reactivities, with formic acid {Σ[HC(O)OC(O)R']} and without it {Σ[R'C(O)OC(O)R']}:

$$\sum[R^iC(O)OC(O)R^j] = \sum[HC(O)OC(O)R'] + \sum[R'C(O)OC(O)R']. \quad (10)$$

The ratio between these groups of anhydrides is determined by the equation for the equilibrium constant [12]:

$$K = \frac{\sum[HC(O)OC(O)R']\sum[R'COOH]_i}{\sum[R'C(O)OC(O)R'][HCOOH]}, \quad (11)$$

where *K* is the equilibrium constant ($K = k_1/k_{-1}$ = 26.94) [12]; [HCOOH], concentration of formic acid; and Σ[R'COOH]I, total content of carboxylic groups without formic acid.

It is possible to derive from Eq. (11), using Eq. (10), an expression for calculating the total concentration of mixed anhydrides including the formic acid residue:

$$\sum[HC(O)OC(O)R'] = \frac{\sum[R^iC(O)OC(O)R^j]}{1+\sum[R'COOH]/([HCOOH])} \quad (12)$$

The formation rate of cyclohexyl formate is determined by the equation

$$W_{est} = k\sum[HC(O)OC(O)R'][ROH], \quad (13)$$

Table 2. Effect of the degree of hydrocarbon conversion on the content of some products in samples of cyclohexane oxidized at 150°C

Conversion, %	Cyclohexanol, M	$c \times 10^3$, M, of indicated acid			Sum of carboxyl-containing substances $c \times 10^3$	Anhydrides $c \times 10^3$	Water
		formic	caproic	adipic	M		
1.9	0.153	0.12	2.49	6.34	31.17	3.62	0.026
3.2	0.245	0.14	6.14	16.36	65.23	6.55	0.047
4.8	0.302	0.20	7.93	17.56	70.32	7.81	0.041

where k is the rate constant of alcoholysis of a mixed anhydride, including the acyl of formic acid, into cyclohexyl formate, and [ROH] is the cyclohexanol concentration.

According to the results of [12], the temperature dependence of the formation rate constant of cyclohexyl formate by the reaction of alcoholysis of a mixed anhydride, including the acyl of formic acid, by cyclohexanol has the form

$$\ln k = (24.27 \pm 0.07) - \frac{89.30 \pm 0.02 \text{ kJ mol}^{-1}}{RT}. \quad (14)$$

Hence we find the formation rate constant of cyclohexyl formate, $k = 32.2 \times 10^{-2}$ s^{-1} M^{-1} at 150°C. The calculated formation rates of cyclohexyl formate in samples of oxidized cyclohexane are listed in Table 4.

In contrast to that of cyclohexyl formate, the formation rate W of cyclohexyl caproate is equal to the sum of alcoholysis rates of formic-caproic anhydride, W', and of other mixed anhydrides including the acyl of caproic acid, W'':

$$W = W' + W'' = k'[HC(O)OC(O)C_5H_{11}][ROH] + 0.5k''\sum[R'C(O)OC(O)C_5H_{11}][ROH], \quad (15)$$

where k' is the rate constant of alcoholysis of formic-caproic anhydride into cyclohexyl caproate; k'', rate constant of alcoholysis of a mixed anhydride, including the acyls of caproic and another carboxylic acid, into cyclohexyl caproate; $[HC(O)OC(O)C_5H_{11}]$, concentration of formic-caproic anhydride; $\Sigma[R'C(O)OC(O)C_5H_{11}]$, total concentration of other mixed anhydrides including the acyl of caproic acid; and 0.5, coefficient that accounts for the fact that, in alcoholysis of a mixed anhydride of caproic and another carboxylic acid, the formation of cyclohexyl ester of the latter acid is equiprobable.

The equation necessary for calculating the concentrations of formic-caproic anhydride can be derived from expression (12) on the assumption that the concentration of mixed anhydrides of a carboxylic acid is proportional to the concentration of its carboxylic groups:

$$[HC(O)OC(O)C_5H_{11}] = \frac{\sum[R^iC(O)OC(O)R^j]}{1 + \sum[R'COOH]_i^2/(K[HCOOH][C_5H_{11}COOH])}, \quad (16)$$

and $\Sigma[R'C(O)OC(O)C_5H_{11}]$ can be calculated by the equation

$$\sum[R'C(O)OC(O)C_5H_{11}] = \frac{\sum[R^iC(O)OC(O)R^j] - \sum[HC(O)OC(O)R']}{\sum[R'COOH]_i} \times [C_5H_{11}COOH]. \quad (17)$$

According to [12], the temperature dependence of the rate constant of cyclohexyl caproate formation by the reaction of alcoholysis of a mixed anhydride, including the acyl of formic acid, by cyclohexanol has the form

$$\ln k' = (14.04 \pm 0.18) - \frac{67.44 \pm 0.06 \text{ kJ mol}^{-1}}{RT}. \quad (18)$$

Table 3. Effect of the degree of cyclohexane conversion on the calculated rates of formation of cyclohexyl esters of carboxylic acids by the reaction of esterification in samples of cyclohexane oxidized at 150°C

Conversion, %	$W_{est} \times 10^9$, M s^{-1}			
	cyclohexyl formate	cyclohexyl caproate	monocyclohexyl adipate	dicyclohexyl adipate
1.9	0.631	0.007	2.23	0.246
3.2	1.11	–0.577	6.56	0.86
4.8	2.01	0.278	11.68	1.77

Table 4. Effect of the degree of conversion on the calculated rates of formation of cyclohexyl esters of carboxylic acids by the reactions of alcoholysis of anhydrides by cyclohexanol in samples of cyclohexane oxidized at 150°C

Conversion, %	$W \times 10^6$, M s^{-1}									
	cyclohexyl formate	cyclohexyl caproate			monocyclohexyl adipate			dicyclohexyl adipate		
		W'	W''	W	W'	W''	W	W'	W''	W
1.9	17.0	0.03	0.21	0.24	0.07	1.06	1.13	0.02	0.31	0.33
3.2	28.7	0.05	0.75	0.80	0.14	3.95	4.09	0.05	1.31	1.36
4.8	54.9	0.12	1.29	1.41	0.26	5.69	5.95	0.10	2.05	2.15

Table 5. Equilibrium concentrations c_{eq} and the ratio of the observed concentrations c_{obs} to the equilibrium concentrations of cyclohexyl formate, caproate, and adipate in samples of cyclohexane oxidized at 150°C

Conversion, %	Cyclohexyl formate		Cyclohexyl caproate		Monocyclohexyl adipate		Dicyclohexyl adipate	
	$c_{eq} \times 10^{-3}$, M	c_{obs}/c_{eq} 100, %	$c_{eq} \times 10^{-3}$, M	c_{obs}/c_{eq} 100, %	$c_{eq} \times 10^{-3}$, M	c_{obs}/c_{eq} 100, %	$c_{eq} \times 10^{-3}$, M	c_{obs}/c_{eq} 100, %
1.9	1.58	9.5	1.03	98.1	3.82	47.6	2.16	16.2
3.2	1.63	14.7	2.24	120.5	8.72	62.0	4.93	22.5
4.8	3.29	12.5	4.09	93.2	13.2	47.9	7.47	19.7

Hence we find the rate constant of cyclohexyl caproate formation, $k' = 5.89 \times 10^{-3}$ s^{-1} M^{-1} at 150°C.

The temperature dependence of the rate constant of cyclohexyl caproate formation by the reaction of alcoholysis of a mixed anhydride, containing the acyl of another carboxylic acid, by cyclohexanol has the form [12]

$$\ln k'' = (14.94 \pm 0.62) - \frac{68.65 \pm 0.22 \text{ kJ mol}^{-1}}{RT}. \qquad (19)$$

Hence we find the rate constant of cyclohexyl caproate formation, $k'' = 1.02 \times 10^{-2}$ s^{-1} M^{-1} at 150°C.

Using the values obtained for the rate constants and taking into account the assumptions of their applicability to other mixed anhydrides of oxidized cyclohexane, we calculated W' and W'' by Eqs. (16) and (17) and then, using Eq. (16), also W for cyclohexyl caproate and mono- and dicyclohexyl adipates. The results of the calculation are listed in Table 4.

The data in Table 4 indicate that the rate at which cyclohexyl formate is formed by the reactions of alcoholysis of mixed anhydrides substantially exceeds that at which cyclohexyl caproate and mono-and dicyclohexyl adipates are produced at all degrees of cyclohexane conversion. The main contribution to the formation of these three esters is made by alcoholysis of mixed anhydrides that do not contain the acyl of formic acid (Table 4). Comparison of the formation rates of cyclohexyl esters of these acids by the reactions of esterification and alcoholysis of anhydrides (Tables 3 and 4) shows that formation rate of all the cyclohexyl esters in the industrial process of cyclohexane oxidation by the esterification reactions is negligible as compared with the alcoholysis rate of mixed anhydrides. For example, for cyclohexyl formate, this rate is more than 25 thousand times lower than the rate of its formation by the reaction of alcoholysis of mixed anhydrides including a formic acid residue. For mono- and dicyclohexyl adipates, the importance of the esterification reaction somewhat exceeds that for the formate, but in this case too, its contribution does not exceed 0.2%. It can also be seen from the data in Tables 3 and 4 that, for these esters, the ratio between the rates of esterification and alcoholysis of the anhydrides by cyclohexanol is almost independent of the degree of cyclohexane conversion. For cyclohexyl caproate, this ratio varies. This possibly occurs because

the esterification reaction is close to equilibrium in this case and, as a result, the calculation accuracy of the rate becomes poorer. In particular, this is indicated by the negative value of the formation rate of cyclohexyl caproate (occurrence of hydrolysis) at a cyclohexane conversion of 3.2% (Table 3).

In contrast to the reaction with an anhydride, the reaction of esterification of an alcohol by an acid is reversible and, under certain conditions, can make lower the content of cyclohexyl esters formed by the reaction of alcoholysis of carboxylic acid anhydrides by alcohols.

Using the running concentrations of cyclohexanol, water, and the corresponding carboxylic acids in oxidized cyclohexane (Table 2), we calculated by the formula

$$[\mathrm{R'COOR}]_i = \frac{k_+[\mathrm{ROH}][\mathrm{R'COOH}]}{k_-[\mathrm{H_2O}]} \qquad (20)$$

the equilibrium concentrations of cyclohexyl formate, caproate, and adipate under the industrial conditions of cyclohexane oxidation (Table 5).

It can be seen from Table 5 that the concentrations of cyclohexyl caproate in the samples studied are indeed close to the equilibrium concentrations. At the same time, the concentrations observed for cyclohexyl formate and dicyclohexyl adipate are substantially lower than their equilibrium values (on average, 12.2 and 19.5%, respectively).

Nevertheless, the results we obtained demonstrate that, similarly to the esterification reaction, hydrolysis of esters presumably cannot noticeably affect the ester formation in liquid-phase oxidation processes, because its rate is substantially lower than that of the reaction of alcoholysis of anhydrides by alcohols. Therefore, a significant decrease in the yield of esters and secondary alcohols can be achieved by using catalysts making less important the oxidative destruction pathway leading to carboxylic acid anhydrides [3, 16, 17].

CONCLUSIONS

(1) Formic, caproic, and adipic acids do not affect the effective rate constants of stages of the reactions of esterification of these carboxylic acids by cyclohexanol in a solution of o-dichlorobenzene. The reactivity of formic acid in the esterification reaction markedly exceeds that of caproic and adipic acids.

(2) The contribution of the reaction of esterification of mono- and dicarboxylic acids by cyclohexanol to the formation of cyclohexyl esters in the oxidation of cyclohexane is less than 0.2% relative to that from the main channel of their accumulation: alcoholysis of mixed carboxylic acid anhydrides by cyclohexanol.

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REFERENCES

1. Berezin, I.V., Denisov, E.T., and Emanuel, N.M., *Okislenie tsiklogeksana* (Oxidation of Cyclohexane), Moscow: Mosk. Gos. Univ., 1962.
2. Denisov, E.T., Mitskevich, N.I., and Agabekov, V.E., *Mekhanizm zhidkofaznogo okisleniya kislorod-soderzhashchikh soedinenii* (Mechanism of Liquid-Phase Oxidation of Oxygen-containing Compounds), Minsk: Nauka i tekhnika, 1975.
3. Perkel, A.L., Voronina, S.G., and Freidin, B.G., *Usp. Khim.*, 1994, vol. 63, no. 9, pp. 793–796.
4. Perkel, A.L., Buneeva, E.I., and Voronina, S.G., *Oxid. Commun.*, 2000, vol. 23, no. 1, pp. 12–28.
5 Berezin, I.V. and Ragimova, A.N., *Zh. Fiz. Khim.*, 1961, vol. 35, no. 4, pp. 842–847.
6. Berezin, I.V., Ragimova, A.N., and Emanuel, N.M., *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1959, no. 10, pp. 1734–1739.
7. Freidin, B.G., Zh. Prikl. Khim., 1963, vol. 36, no. 5, pp. 1101–1106.
8. Manakov, M.P. and Farkhf, F.Kh., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1970, vol. 13, no. 5, pp. 705–708.
9. Freidin, B.G. and Perkel, A.L., *Zh. Prikl. Khim.*, 1980, vol. 53, no. 4, pp. 861–866.
10. Perkel, A.L., Freidin, B.G., Neginskaya, R.V., et al., *Zh. Prikl. Khim.*, 1985, vol. 58, no. 7, pp. 1572–1577.
11. Kotel'nikova, T.S., Voronina, S.G., and Perkel, A.L., *Zh.*

Prikl. Khim., 2006, vol. 79, no. 3, pp. 424–428.

12. Kotel'nikova, T.S., Revkov, O.A., Voronina, S.G., and Perkel, A.L., *Zh. Prikl. Khim*., 2008, vol. 44.
13. Klimova, V.A., *Osnovnye mikrometody analiza organicheskikh soedinenii* (Basic Microscopic Methods for Analysis of Organic Compounds), Moscow: Khimiya, 1975.
14. Kotel'nikova, T.S., Revkov, O.A., Voronina, S.G., and Perkel, A.L., *Vestn. Kuz. Gos. Tekhn. Univ.*, 2006, no. 5, pp. 105–107.
15. Faiclough, R.A. and Hinshelwood, C.N., *J. Chem. Soc.*, 1939, vol. 593, pp. 539–600.
16. Freidin, B.G. and Perkel, A.L., *Zh. Prikl. Khim.*, 1981, vol. 54, no. 12, pp. 2733–2739.
17. Freidin, B.G., Perkel, A.L., and Borodina, O.V., *Zh. Prikl. Khim.*, 1985, vol. 58, no. 12, pp. 2689–2693.