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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetics of Alcoholysis of Valeric Anhydride by Cyclohexanol in the Presence of Formic Acid

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Abstract—Kinetics of the reaction proceeding at the industrial process of cyclohexane oxidation are studied by the model reaction of the alcoholysis of valeric anhydride by cyclohexanol in the presence of formic acid.

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The reactions of the alcoholysis of mixed anhydrides of carboxylic acids by cyclohexanol are a main way of formation of cyclohexyl esters of mono- and dicarboxylic acids in the industrial process of cyclohexane oxidation [1–4]. It was assumed that the mixed anhydrides are produced as a result of transacylation of adipic anhydride by free acids and they contain the residues of all the carboxylic acids present in the reaction medium [2, 3] including the formic acid. High relative yield of cyclohexyl formate in the course of oxidation of the cyclohexane was understood through the features of the alcoholysis reaction of the mixed anhydrides with formyl group [5].

For revealing pathways of the formation and alcoholysis of the mixed anhydrides containing the residue of formic acid the kinetics of all stages of these reactions should be studied. At the same time the presence in real processes (e.g., at cyclohexane oxidation [5]) of more than ten compounds with carboxyl groups and also the presence of reactive water essentially complicated the study of the kinetics of the whole complex of series-parallel reactions producing esters. Under these conditions an employment of the model reactions for the study of the ester formation is reasonable.

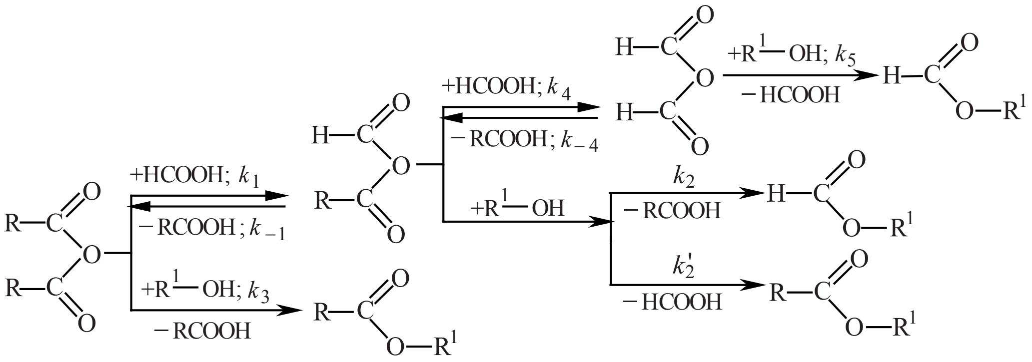
A target of this paper is the study of the kinetics of the reactions proceeding at the alcoholysis of valeric anhydride by cyclohexanol in the presence of formic acid. Mixture of anhydrides formed in situ contains formic-valeric anhydride including the residues of two important acids of the oxidized cyclohexane.

EXPERIMENTAL

Formic acid (85%, pure for analysis) was maintained over anhydrous $MgSO_4$ for dehydration and then it was sublimated in a water-jet pump vacuum. For additional drying a working solution of formic acid in *o*-dichlorobenzene was maintained over the anhydrous $MgSO_4$ for 24 hours. A content of the main substance in the used working solution determined by gas-liquid chromatography (GLC) (after transferring in benzyl ether according to [6]) was 99.3 ± 0.4% ($n = 10$, $P = 0.95$). Technical grade cyclohexanol was purified from ethers and cyclohexanone according to [7]. The content of the main substance in the used material by GLC data was 99.5 ± 0.1%. Valeric anhydride was obtained by a treatment of the anhydrous sodium valerate by acid chloride of valeric acid [8]. The product was treated by diazomethane and subjected to rectification in a vacuum in an argon flow for removing valeric acid. The content of the main substance in the used material by GLC data was 99.5 ± 0.1%. A solvent (*o*-dichlorobenzene) was of pure gtrade and it was rectified [7].

The experiments on an interaction of the valeric anhydride and cyclohexanol in the presence of formic acid in the solution of *o*-dichlorobenzene were conducted in a thermostated sealed ampoule. The temperature maintained with an accuracyin of ±0.2°C. In the previous experiments we established that the starting rate of the reaction depended on an order of the reagent mixing. The reproducible result was reached by mixing of solutions of valeric anhydride

Scheme 1.



in *o*-dichlorobenzene and a mixture of cyclohexanol with formic acid in equipment operating according to a principle of a stopped stream.

The reaction products, esters, were determined by GLC. A decomposition of unreacted anhydrides by an excess of methanol–pyridine mixture added just after a sampling preceded the determination of cyclohexyl formate and cyclohexyl valerate. Analysis of the reaction products was performed in a column of 2000 × 3 mm with a nozzle that was 5% silicone XE-60, on Khromaton N-AW 0.20–0.25 mm. An internal standard is hexadecane.

We calculated the 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 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 the pre-exponential factor [9].

We used software Hyperchem 8.04 for quantum chemical computations and also semi-empirical method MINDO3.

According to the assigned task we studied the interaction of valeric anhydride (0.31 M) with cyclohexanol (0.332 M) in the presence of formic acid (0.21 M) in the solution of *o*-dichlorobenzene in a temperature range of 60–100°C.

Obstacles caused by difficulties of the formic anhydride presence arose in the course of development of kinetic schemes required for a solution of an inverse kinetic problem.

Transformations may be presented by a scheme assuming the formation of formic anhydride on the basis of existing concepts about mechanisms of the transacylation of anhydrides by carboxylic acids and of the alcoholysis of anhydrides by alcohols [1–4].

However a majority of sources rejects the possibility of existence of the formic anhydride probably due to its instability [10, 11]. Thus a simplified scheme that excluded formation of formic anhydride was considered as alternative.

In the case of realization of Scheme 1 the kinetics of the reaction product accumulation and the initial compound consumption may be described by a set of differential equations:

$$\frac{\mathrm{d[HC(O)OC(O)R]}}{\mathrm{d}t} = k_1\mathrm{[RC(O)OC(O)R][HCOOH]} - k_{-1}\mathrm{[HC(O)OC(O)R][RCOOH]}$$
$$- (k_2 + k_2')\mathrm{[HC(O)OC(O)R][R^1OH]} - k_4\mathrm{[HC(O)OC(O)R][HCOOH]}$$
$$+ k_{-4}\mathrm{[HC(O)OC(O)H][RCOOH]}, \qquad (1)$$

$$\frac{\mathrm{d[RC(O)OC(O)R]}}{\mathrm{d}t} = k_1\mathrm{[RC(O)OC(O)R][HCOOH]} - k_{-1}\mathrm{[HC(O)OC(O)R][RCOOH]}$$
$$+k_3\mathrm{[RC(O)OC(O)R][R^1OH]}, \qquad (2)$$

$$\frac{\mathrm{d[HCOOR^1]}}{\mathrm{d}t} = k_2\mathrm{[HC(O)OC(O)R][R^1OH]} + k_5\mathrm{[HC(O)OCOH][R^1OH]}\,, \qquad (3)$$

$$\frac{d[\mathrm{RCOOR^1}]}{dt} = k_2'[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}], \tag{4}$$

$$\frac{d[\mathrm{RCOOH}]}{dt} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$+ k_2[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}] + k_4[\mathrm{HC(O)OC(O)R}]$$
$$\times [\mathrm{HCOOH}] - k_{-4}[\mathrm{HC(O)OC(O)H}][\mathrm{RCOOH}], \tag{5}$$

$$-\frac{d[\mathrm{HCOOH}]}{dt} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$- k_2'[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_4[\mathrm{HC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-4}[\mathrm{HC(O)OC(O)H}]$$
$$\times [\mathrm{RCOOH}] - k_5[\mathrm{HC(O)OC(O)H}][\mathrm{R^1OH}], \tag{6}$$

$$\frac{d[\mathrm{HC(O)OC(O)H}]}{dt} = k_4[\mathrm{HC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-4}[\mathrm{HC(O)OC(O)H}][\mathrm{RCOOH}]$$
$$- k_5[\mathrm{HC(O)OC(O)H}][\mathrm{R^1OH}], \tag{7}$$

$$-\frac{d[\mathrm{R^1OH}]}{dt} = (k_2 + k_2')[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}]$$
$$+ k_5[\mathrm{HC(O)OC(O)H}][\mathrm{R^1OH}], \tag{8}$$

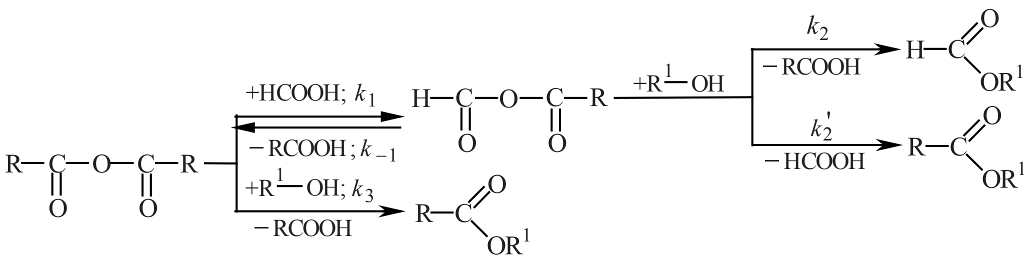
where k_1, k_{-1}, k_4, k_{-4} are the rate constants of the direct and the inverse reactions of the formation of formic-valeric anhydride, and formic anhydride; k_2, k_2 are rate constants of reaction of cyclohexyl formate and ciclohexyl valerate formation according to alcoholysis of mixed anhydride by an alcohol, respectively; k_3, k_5 are rate constants of cyclohexyl valerate and cyclohexyl formate formation according to alcoholysis of appropriate anhydride by cyclohexanol.

In the case of realization of Scheme 2 kinetics of the reaction product accumulation and the initial compound consumption may be described by a set of equations

$$\frac{d[\mathrm{HC(O)OC(O)R}]}{dt} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$- (k_2 + k_2')[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}], \tag{9}$$

$$-\frac{d[\mathrm{RC(O)OC(O)R}]}{dt} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$+ k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}], \tag{10}$$

Scheme 2.



$$\frac{\mathrm{d}[\mathrm{HCOOR^1}]}{\mathrm{d}t} = k_2[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}], \tag{11}$$

$$\frac{\mathrm{d}[\mathrm{RCOOR^1}]}{\mathrm{d}t} = k_2'[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}], \tag{12}$$

$$\frac{\mathrm{d}[\mathrm{RCOOH}]}{\mathrm{d}t} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$+k_2[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(O)R}][\mathrm{R^1OH}], \tag{13}$$

$$-\frac{\mathrm{d}[\mathrm{HCOOH}]}{\mathrm{d}t} = k_1[\mathrm{RC(O)OC(O)R}][\mathrm{HCOOH}] - k_{-1}[\mathrm{HC(O)OC(O)R}][\mathrm{RCOOH}]$$
$$- k_2'[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}], \tag{14}$$

$$-\frac{\mathrm{d}[\mathrm{R^1OH}]}{\mathrm{d}t} = (k_2 + k_2')[\mathrm{HC(O)OC(O)R}][\mathrm{R^1OH}] + k_3[\mathrm{RC(O)OC(OO)R}][\mathrm{R^1OH}]. \tag{15}$$

Considering the experiments at *j*th temperature the values of the appropriate rate constants may be expressed by the following equation:

$$\ln k_j = \ln k_i + \frac{E}{R}\left(\frac{1}{T_i} - \frac{1}{T_j}\right). \tag{16}$$

Although according to data of [12] valeric acid does not influence the rate of alcoholysis of valeric anhydride by cyclohexanol it can be assumed that the stronger formic acid possesses ability for influencing some stage of the kinetic schemes 1, 2. Hence we suggested that effective constants of the stages of Scheme 1, 2 depend linearly on the formic acid concentration.

A preliminary treatment of the experimental data using both equations (1)–(8), (16) and equations (9)–(16) showed that in all cases a sum of constants k_2 and k_{-2} was essentially higher then k_{-1}, i.e. under conditions of the experiment the reaction of formic-valeric anhydride formation from a symmetric anhydride and formic acid was become practically irreversible and that led to diminishing accuracy at computation of k_{-1}. In specific experiments an equilibrium constant for the reaction of formic-valeric anhydride formation (ratio k_1/k_{-1}) was determined to increase the reliability of computation of k_{-1}.

Valeric acid concentrations in equilibrium mixture at the interaction of formic acid (0.21 M) and valeric anhydride (0.169 M) in the solution of *o*-dichlorobenzene in the temperature range of 90–150°C are presented in Table 1.

With the help of obtained values of equilibrium concentrations for valeric acid $[\mathrm{RCOOH}]_\mathrm{p}$, and the starting concentrations of valeric anhydride $[\mathrm{RC(O)OC(O)R}]_0$, and formic acid $[\mathrm{HCOOH}]_0$ by the following formula:

$$K_\mathrm{p} = \frac{[\mathrm{RCOOH}]_n^2}{([\mathrm{RC(O)OC(O)R}]_0 - [\mathrm{RCOOH}]_\mathrm{p})} \times \frac{[\mathrm{RCOOH}]_n^2}{([\mathrm{HCOOH}]_0 - [\mathrm{RCOOH}]_\mathrm{p})} \tag{17}$$

the values of the eqiuilibrium constants for reaction of formic-valeric anhydride formation from valeric anhydride and formic acid in the case of Scheme 2 realization were determined (Table 1).

The temperature dependence of this constant was computed on the basis of data presented in Table 1.

$$\ln K = \ln(15773.35 \pm 0.01) - \frac{22411 \pm 3\ \mathrm{kJ\ mol^{-1}}}{RT}. \tag{18}$$

Naturally the equilibrium constants of the kinetic scheme 1 cannot be computed by equation (18) but it can be used in calculation as the first approximation. The values of the effective rate constants, activation energies, and pre-exponential factors for the stages of the kinetic scheme 1, 2 (Table 2) were calculated by solution of the inverse problem taking into account equation (18). The calculation showed that formic acid practically did not influence the effective rate constants of the stages both of Scheme 1 and Scheme 2.

Computed accumulation curves of cyclohexyl formate and cyclohexyl valerate corresponding to obtained sets of

Table 1. Effects of the temperature on the equilibrium concentrations of the valeric acid and on the equilibrium constants of the interaction reactions of the valeric anhydride and formic acid

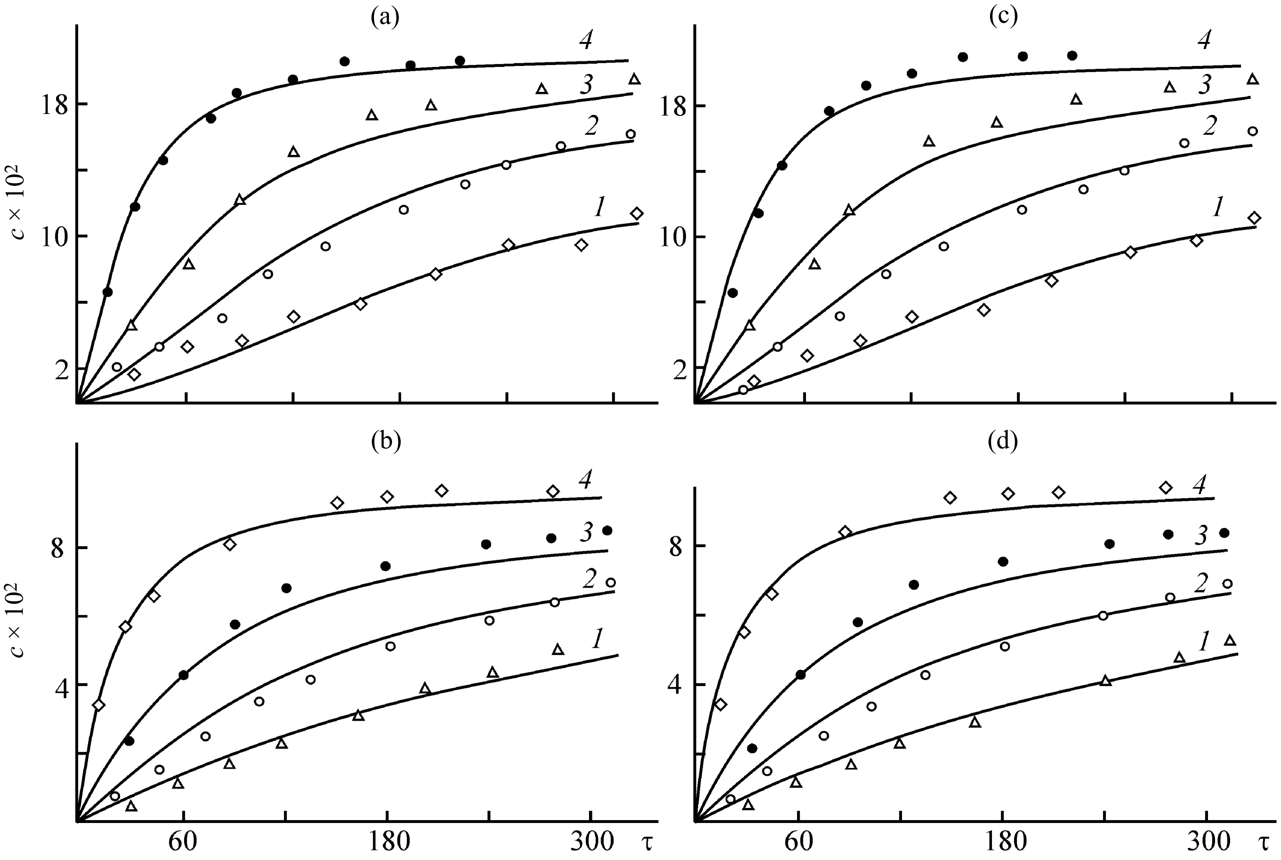
T, °C	c_{eq}, M	K_{eq}
90	0.140	9.40
100	0.143	11.46
110	0.146	13.85
130	0.150	19.64
150	0.154	26.94

the constants quite closely describe experi-mental values of these ester concentrations both for kinetic scheme 1 and for kinetic scheme 2 (see the figure). Smaller value of the sum of squared deviations for Scheme 1 can not be governing factor at selection from two alternative schemes since a scheme with larger number of parameters as a rule better describes an experiment. Data of Table 2 show that in the case of Scheme 1 activation energy of the stages at alcoholysis of valeric anhydride producing cyclohexyl formate (111.23 ± 0.03 kJ mol^{-1}) and cyclohexyl valerate (117.36 ± 0.35 kJ mol^{-1}) are essentially higher than activation energy of alcoholysis of valeric anhydride (61.5 kJ mol^{-1}) [9]. Moreover at calculation by kinetic scheme 1 activation energy for transacylation of formic-valeric anhydride by formic acid (136.74 ± 0.21 kJ mol^{-1}) appears almost twice higher than activation energy for transacylation of valeric anhydride by formic acid. Hence from the point of view of physical sense some preference can be given to kinetic scheme 2

Data of Table 2 confirm existing ideas concepts prevailing formation of formates in alcoholysis of mixed anhydrides including the residue of formic acid [5]. Apparently that is understood by a character of an electron density distribution on a functional group of mixed anhydride that governs capability of this group to a nucleophilic attack. Values of atomic charges in molecules of (a) formic, (b) formic-valeric, and (c) valeric anhydrides are presented on Scheme 3.

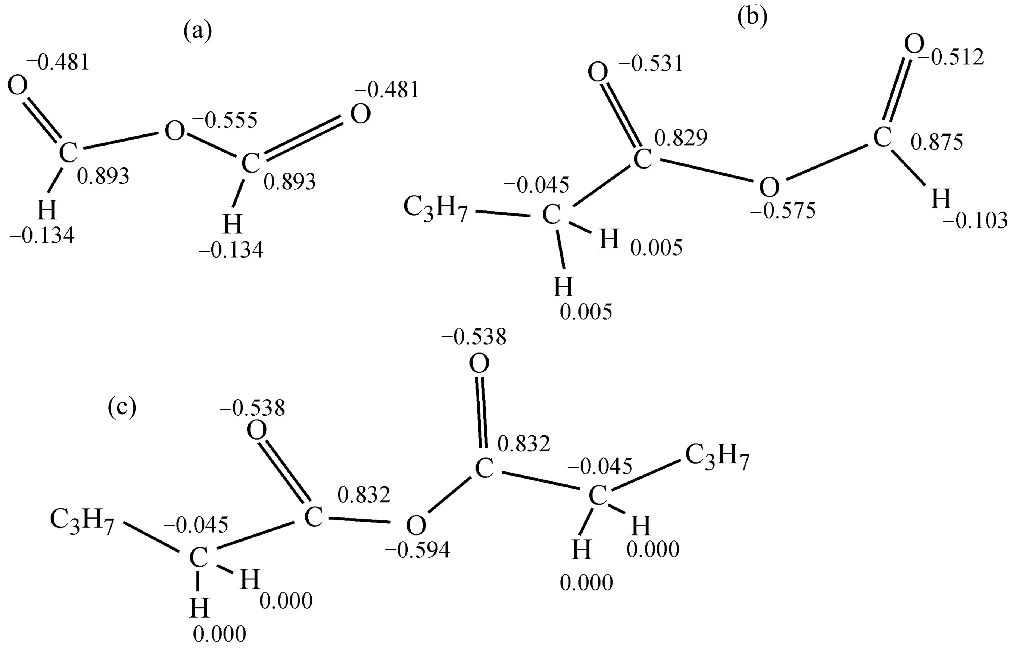
Table 2. Results of the calculation of the rate constants, activation energies, and pre-exponential factors of the stages in the kinetic schemes 1 and 2

k	$k_i \times 10^3$, l s^{-1}·mol^{-1}, at temperature, °C				E, kJ·mol^{-1}	A
	60	70	80	100		
Kinetic scheme (1)						
k_1	0.89	1.88	3.83	14.2	71.54 ± 0.04	18.81 ± 0.11
k_{-1}	0.26	0.31	0.51	1.24	41.88 ± 1.71	6.74 ± 4.90
k_2	0.47	1.51	4.56	34.9	111.23 ± 0.03	32.51 ± 0.09
k_2'	0.11	0.40	1.26	10.5	117.36 ± 0.35	33.30 ± 1.01
k_3	0.03	0.06	0.11	0.35	63.22 ± 0.17	12.43 ± 0.49
k_4	6.01	25.4	98.8	1203	136.74 ± 0.21	44.30 ± 0.82
k_{-4}	4.25	6.86	10.8	24.8	45.55 ± 0.01	10.99 ± 0.02
k_5	0.12	0.15	0.20	0.44	33.99±1.30	3.16 ± 3.68
Sum of squared deviations σ					1.76 × 10^{-3}	
Kinetic scheme (2)						
k_1	0.78	1.24	1.93	4.34	44.43 ± 0.02	8.86 ± 0.06
k_{-1}	0.16	0.20	0.25	0.38	22.39 ± 0.09	−0.65 ± 0.27
k_2	0.34	0.87	2.12	10.8	89.30 ± 0.02	24.27 ± 0.07
k_2'	0.033	0.067	0.13	0.45	67.44 ± 0.06	14.04 ± 0.18
k_3	0.052	0.11	0.21	0.75	68.65 ± 0.22	14.94 ± 0.62
Sum of squared deviations σ					4.04 ×10^{-3}	



Experimental values of the concentrations *c* (M) and calculated curves of cyclohexyl formate accumulation (a, c) and cyclohexyl valerate (b, d) at various temperature. (τ) time (min); *T* (°C): (*1*) 60, (*2*) 70, (*3*) 80, (*4*) 100. (a, b) Scheme 1, (c, d) Scheme 2.

Scheme 3.



Quantum chemical calculation for the molecules of formic, valeric, and formic-valeric anhydrides evidences the correlation between the value of the positive charge on the carboxylic carbon and a relative yield of the appropriate ester. It is important that formic acid forming simultaneously with cyclohexyl valerate at alcoholysis of formic-valeric anhydride by cyclohexanol is involved in the reaction cycle of transformations till the complete exhaustion of it or anhydrides.

It may be assumed that the obtained temperature dependencies of the rate constants for the stages of alcoholysis of mixed anhydrides are useful for ester formation simulation both of cyclohexane oxidation and of other industrial processes of a liquid-phase oxidation by molecular oxygen.

CONCLUSIONS

1. The temperature dependences of the rate constants for the stage of alcoholysis of valeric anhydrides by cyclohexanol in the presence of formic acid were calculated by the solution of the inverse kinetic problem.
2. Prevailing formation of formates at alcoholysis of anhydrides in the presence of formic acid is understood through the features of alcoholysis of mixed anhydrides including formyl group and correlates with charge on carbonyl atoms of anhydride carbon.

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