
CATALYSIS

Kinetic Patterns of Condensation of Alkyl- and Cycloalkylcyclopentanones with Dihydric Alcohols in the Presence of Polyoxomolybdate Modified with Oxides of Rare-Earth Elements

Kh. M. Alimardanov^a, F. M. Velieva^{a,*}, and H. R. Dadashova^a

^aMamedaliyev Institute of Petrochemical Processes, of the National Academy of Sciences of Azerbaijan,
Baku, AZ 1025 Azerbaijan

*e-mail: firuzal@aport2000.ru

Received May 7, 2018

Abstract—The results of condensation of C₅–C₇ alkyl- and cycloalkyl-substituted cyclopentanones with diatomic vicinal alcohols in the presence of polyoxomolybdate modified with gadolinium oxide are considered. Kinetic patterns are investigated and a kinetic model of the process is proposed. It was established that alkyl- and cycloalkyl derivatives of dioxaspironone are formed directly by two parallel-consecutive routes and through the stages of the preparation of the corresponding hemiacetal. The ratio of the rate constants of these routes depends on the composition and structure of the starting ketones and diols.

Keywords: alkyl cyclopentanones, vicinal diols, kinetic model

DOI: 10.1134/S1070427218110204

The reaction of acetalization (or ketalization) of aldehydes and ketones with dihydric alcohols is widely used to protect carbonyl groups [1]. 1,3-Dioxalanes and dioxaspiroalkanes with different functional groups synthesized at the same time have independent significance and are used as fragrant and flavoring compounds in the perfume and food industry [2, 3], in the manufacture of pharmaceutical preparations [4], solvents [5], biologically active substances [6], insecticides with high biological degradability [7], etc. In the literature there is enough information about the production of 1,3-dioxolanes with the participation of homogeneous acid-type catalysts [8–11]. Recently, studies have emerged in which complexes containing Rh, Pd, Pt, Ce [12, 13] or heterogeneous catalytic systems [14, 15] have been used as condensation catalysts. These works are mainly devoted to the synthesis of 1,3-dioxolanes from aromatic or unsubstituted alicyclic aldehydes and ketones. On the synthesis of dioxaspiroalkanes based on alkyl-substituted alicyclic ketones, there are only a few works [3, 16]. The mechanism of these reactions is considered from

the generally accepted position and is not sufficiently substantiated by step-by-step kinetic studies.

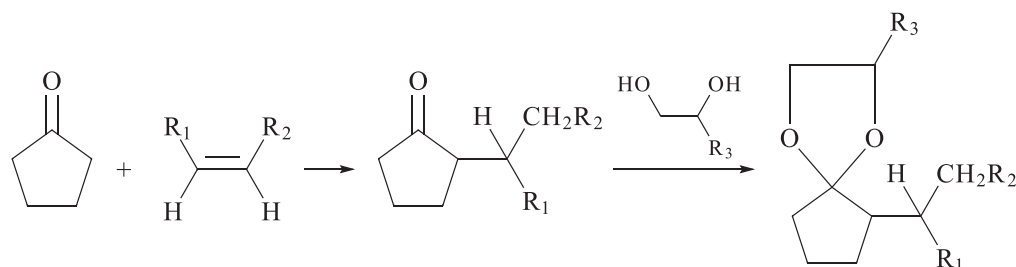
Thus, the synthesis of dioxaspiroalkanes based on C₅–C₇ alkyl- and cycloalkyl-substituted cyclopentanones used as aromatic compounds [2] and especially the study of the step-by-step kinetic pattern of these reactions are relevant both from theoretical and practical points of view.

The work is devoted to the preparation of the above compounds using polyoxomolybdate modified with neodymium or gadolinium cations, and the study of the kinetic patterns by the multi-route mechanism of this reaction.

EXPERIMENTAL

The procedures of preparation of the catalyst and the experiment performing are similar to that described earlier in [16, 17]. In the experiments, Nd- and Gd-containing samples of polyoxomolybdate were used, prepared by mixing aqueous solutions of (NH₄)₆Mo₇O₂₄, (CH₃COO)₂Nd, Gd(NO₃)₃ of chemically pure grade, 85%

Scheme 1.



where R₁ = R₃ = H, R₂ = *n*-C₃H₇ (**1**); R₁ = R₃ = H, R₂ = *n*-C₄H₉ (**2**); R₁ = R₃ = H, R₂ = *n*-C₅H₁₁ (**3**); R₁ + R₂ = C₄H₈, R₃ = H (**4**); R₁ + R₂ = C₅H₈, R₃ = H (**5**); R₁ = H, R₂ = C₅H₁₁, R₃ = CH₃ (**6**); R₁ + R₂ = C₄H₈, R₃ = CH₃ (**7**); R₁ + R₂ = C₅H₈, R₃ = CH₃ (**8**).

H₃PO₄ and carbon material obtained by the interaction of CCl₄ (chemically pure grade) and metallic Al according to the method of [17]. Stirring was continued for 8 h at a temperature of 85–90°C, followed by evaporation of the suspension and heat treatment of the dry residue at 150–180°C.

The starting compounds were ethane-1,2- and propane-1,2-diols of the chemically pure grade, cyclopentanone (Alfa Aesar Co.). Alkyl- and cycloalkylcyclopentanones were obtained according to the previously developed method [18]. A preset amount of cyclopentanone, C₅–C₇ α-olefins (or C₆–C₇ cycloolefins), and di-*tert*-butyl peroxide were loaded into a 2 L autoclave with a molar ratio of of 4 : 1 : 0.15 and kept at 140–160°C for 4–6 h. Alkyl- and cycloalkylcyclopentanones were isolated from the reaction mixture by atmospheric vacuum distillation.

Ketones and glycols were condensed in a thermostated glass reactor; the kinetic studies were performed in a 25 mL microreactor equipped with a thermometer, magnetic stirrer, reflux condenser, Dean–Stark nozzle, and sampling device. Ketone (0.0025 mol), glycol (0.03 mol), catalyst (0.05 mol Moⁿ⁺), and toluene (10 mL) as a solvent were simultaneously charged to the reactor. After reaching the set temperature, the catalyzed was analyzed every 30 min. The reaction was monitored by gas-liquid chromatography (GLC) and infrared spectroscopy (IR). In the IR spectrophotometric analysis a change in the absorption band of the carbonyl group at 1730 cm^{−1} was taken as a criterion (Fig. 1).

Effective separation of ketones and synthesized spirodioxolanes was achieved on a Tsvet-100m chromatograph with a thermal conductivity detector, helium carrier gas, 1 m × 2 mm column with a stationary phase Apiezon L deposited on Chromaton N-AW-HMDS

(15 wt %). IR spectra were recorded on an Alpha Fourier transform spectrometer in the range 400–4000 cm^{−1}.

RESULTS AND DISCUSSION

It is known that some spiroacetals, in particular 7-*tert*-butyl-1,4-dioxaspiro[4,5]decane (Kiprenal) and 2-butyl-1,4-dioxaspiro[4,4]nonane (jasmonan), are used in the composition of various perfume compositions [2].

The latter is characterized by the scent of jasmine note. The synthesized alkyl and cycloalkyl-substituted dioxaspiroalkanes according to Scheme 1 are analogues of jasmonan. Physicochemical and spectral data of these compounds are given in Table 1 and Fig. 2. The kinetic patterns of the reaction were investigated using the example of the condensation of 2-*n*-pentylcyclopentanone and ethane-1,2-diol.

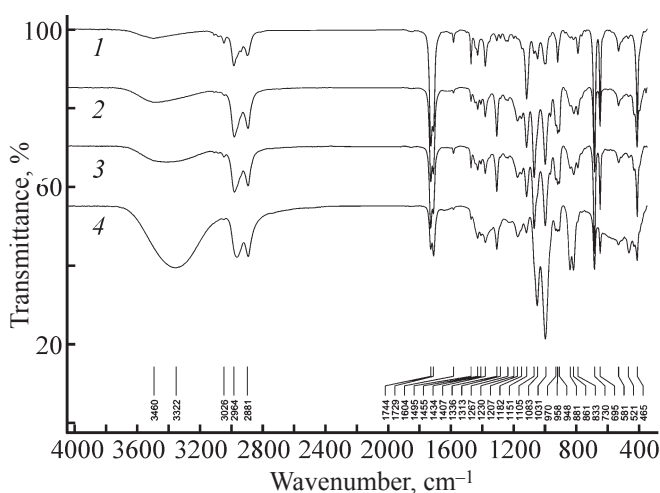


Fig. 1. Comparative description of the IR spectra corresponding to each hour of the condensation reaction of ethanediol-1,2 with 2-*n*-pentylcyclopentanone. τ (min): (1) 60, (2) 120, (3) 180, (4) 240.

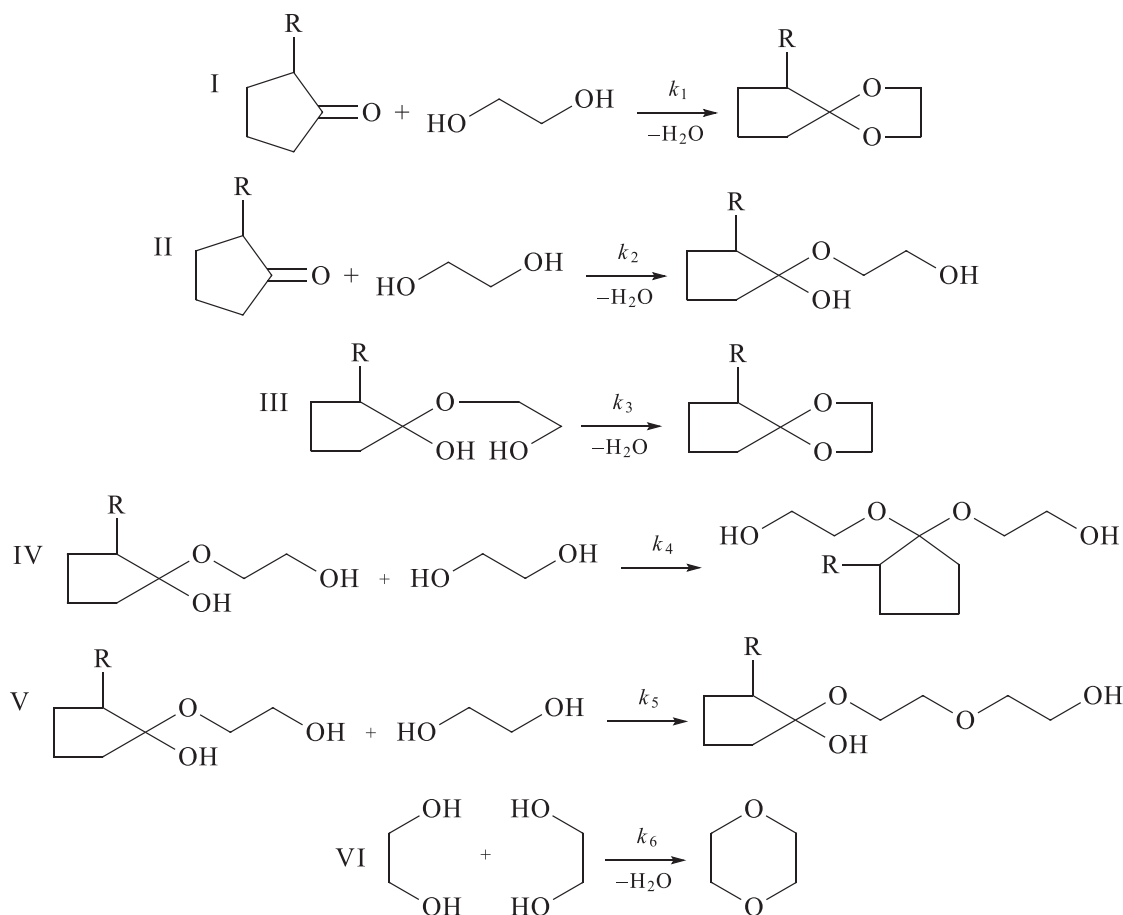
Table 1. Physicochemical properties and spectral data of the synthesized compounds

Compound	Yield, %	T_b , °C	Pressure, kPa	d_4^{20}	n_D^{20}	Found, %		Calculated, %		IR spectrum, ν , cm^{-1}	^1H NMR spectrum, δ , ppm
						C	H	C	H		
5-Pentyl-1,4-dioxaspiro[4.4]nonane	67.4	115–117	2.4	0.9610	1.4554	72.24	10.97	72.73	11.11	2925, 2859, 1460, 1319, 1203, 1152, 1116, 951, 835	0.97 t (3H, CH_3 , $J = 8.2$ Hz), 1.25–1.85 m (14H, 3CH_2 cycle and 4CH_2 Alk.), 2.13 m (1H, CH), 3.88–4.02 d (4H, $\text{H}^{2,3}$, $2\text{CH}_2\text{O}$, $J = 8.2$ Hz)
5-Hexyl-1,4-dioxaspiro[4.4]nonane	61.8	124–125	2.3	0.9615	1.4561	73.08	11.07	73.58	11.32	2925, 2860, 1460, 1325, 1205, 1165, 1120, 951, 835	0.97 t (3H, CH_3 , $J = 8.2$ Hz), 1.25–1.85 m (16H, CH_2 cycle and 5CH_2 Alk.), 2.12 m (1H, H^5), 3.88–4.02 d (4H, $\text{H}^{2,3}$, CH_2O , $J = 8.2$ Hz)
5-Heptyl-1,4-dioxaspiro[4.4]nonane	54.7	141–142	1.33	0.9525	1.4585	74.68	11.28	74.34	11.50	2938, 2855, 1460, 1320, 1220, 1165, 1140, 950, 835	0.97 t (3H, CH_3 , $J = 8.2$ Hz), 1.22–1.84 m (18H, 3CH_2 cycle and 6CH_2 Alk.), 2.13 m (1H, H^5), 3.85–3.98 d (4H, $\text{H}^{2,3}$, $2\text{CH}_2\text{O}$, $J = 8.2$ Hz)
5-Cyclohexyl-1,4-dioxaspiro[4.4]nonan	76.0	151–153	0.4	1.0451	1.4945	73.95	10.71	74.29	10.48	2860, 2845, 1460, 1340, 1220, 1175, 1150, 910, 820	0.82–1.62 m (16H, 3CH_2 spiro and 5CH_2 Hex), 1.28t (1H, H^1 , CH Hex), 2.12 m (1H, $\text{H}^{5\text{-spiro}}$), 3.86–3.94 d (4H, $\text{H}^{2,3}$, $2\text{CH}_2\text{O}$, $J = 8.2$ Hz)
5-Bicyclo[2.2.1]heptyl-1,4-dioxaspiro[4.4]nonan	72.0	96–98	0.27	1.1085	1.511	75.25	10.15	75.68	9.91	2855, 2840, 1460, 1380, 1340, 1260, 1175, 1140, 910	1.22–1.56 d (8H, 4CH_2 , $J = 7.9$ Hz, Hept), 1.36–1.83 m (6H, 3CH_2 spiro), 1.42t (1H, H^2 , CH, $J = 7.1$ Hz, Hept), 1.43–1.45 d (2H, $\text{H}^{1,4}$, 2CH , $J = 7.0$ Hz Hept), 2.14 m (1H, Hz Hept), 2.14 m (1H, $\text{H}^{5\text{-CH}}$ spiro), 3.84 3.99 d.d (4H, $\text{H}^{2,3}$, 2CH_2 , $J = 8.2$ Hz)
2-Methyl-5-heptyl-1,4-dioxaspiro[4.4]nonane	80.0	139–141	1.33	0.9420	1.4505	74.68	11.38	75.0	11.67	2950, 2845, 1460, 1380, 1340, 1215, 1165, 1165, 1152, 950, 835	0.95 t (3H, CH_3 , Hept, $J = 8.2$ Hz), 1.20 d (3H, CH_3), 3.04 m (1H, H^5 , CH), 4.05 m (1H, H^2 , CH), 3.73–3.98 m (2H, H^3 , CH_2O), 1.28–1.55 m (18H, 3CH_2 spiro and 6CH_2 Hept)
2-Methyl-5-cyclohexyl-1,4-dioxaspiro[4.4]nonane	79.0	147–149	0.27	1.0617	1.5152	74.55	10.48	75.0	10.71	2930, 2845, 1460, 1340, 1320, 1220, 1160, 1160, 1140, 950	0.82–1.62 m (10H, 5CH_2 Hex), 1.22t (3H, CH_3 , $J = 8.2$ Hz), 1.28t (1H, CH, Hex), 2.81 m (1H, H^5 , CH), 3.32t (1H, H^2 , OCH, $J = 6.8$ Hz), 3.38–3.65 m (2H, H^3 , CH_2O)
2-Methyl-5-bicyclo-[2.2.1]heptyl-1,4-dioxaspiro[4.4]nonane	68.5	143–145	0.27	1.0475	1.5051	76.58	9.91	76.27	10.17	2950, 2840, 1460, 1380, 1340, 1220, 1165, 1140, 950	1.22t (3H, CH_3 , $J = 7.9$ Hz), 1.24–1.83 m (14H, 7CH_2), 1.42t (1H, H^2 , 2CH Hept), 1.43–1.45 d (2H, $\text{H}^{1,4}$, 2CH , $J = 7.1$ Hz Hept), 2.81 m (1H, H^5 , 2CH), 3.32t (1H, H^2 , OCH, $J = 6.8$ Hz), 3.34–3.60 m (2H, Hz), 3.34–3.60 m (2H, H^3 , CH_2O)

Table 2. The observed rate of accumulation of key substances in the reaction of 2-pentylcyclopentanone and ethylene glycol at different temperatures. Catalyst $\text{GdPO}_4 \cdot (\text{MoO}_2)_{0.5} \cdot \text{PMo}_{12}\text{O}_{40}$, 0.1 g

$c_0 \times 10^{-1}$, M		Experience time, min	Conversion, %	ω , M min ⁻¹ 10 ⁻³					
ketone	diol			$-W_1$	$-W_2$	W_3	W_4	W_5	W_6
Solvent—isoctane, $T = 99^\circ\text{C}$									
7.0	7.0	60	16.4	1.92	2.26	0.203	1.71	—	0.17
7.0	7.0	120	28.0	1.64	1.84	0.110	1.53	—	0.10
7.0	7.0	180	43.1	1.675	1.88	0.111	1.485	0.08	0.10
7.0	7.0	240	54.9	1.60	1.78	0.088	1.47	0.05	0.08
7.0	7.0	300	63.4	1.48	1.64	0.068	1.38	0.03	0.08
Solvent—toluene, $T = 110^\circ\text{C}$									
7.0	7.0	60	18.7	2.18	2.53	0.14	1.95	0.092	0.18
7.0	7.0	120	40.8	2.38	2.73	0.15	2.11	0.117	0.174
7.0	7.0	180	55.1	2.14	2.47	0.15	1.95	0.045	0.164
7.0	7.0	240	56.9	1.66	1.96	0.08	1.55	0.025	0.153
7.0	7.0	300	63.3	1.48	1.78	0.08	1.38	0.015	0.153
7.0	14.0	60	44.3	5.17	5.58	0.41	4.34	0.425	0.205
7.0	14.0	120	45.8	2.67	2.98	0.175	2.36	0.139	0.155
7.0	14.0	180	51.3	2.00	2.33	0.14	1.74	0.110	0.166
7.0	14.0	240	53.7	1.57	1.895	0.11	1.43	0.025	0.165
7.0	14.0	300	60.9	1.42	1.74	0.095	1.31	0.002	0.161
7.0	28.0	60	55.4	6.47	7.08	0.683	5.46	0.327	0.307
7.0	28.0	120	63.3	3.69	4.09	0.058	3.18	0.150	0.201
7.0	28.0	180	82.0	3.19	3.59	0.340	2.14	0.149	0.196
7.0	28.0	240	91.8	2.68	3.09	0.228	2.35	0.068	0.207
14.0	7.0	60	11.4	1.326	1.767	0.067	1.25	0.01	0.175
14.0	7.0	120	25.4	1.480	1.737	0.105	1.295	0.08	0.128
14.0	7.0	180	30.6	1.191	1.424	0.075	1.079	0.037	0.117
14.0	7.0	240	36.7	1.363	1.363	0.083	0.956	0.032	0.146
Solvent—benzene, $T = 80^\circ\text{C}$									
7.0	7.0	60	12.7	1.483	2.26	0.203	1.713	—	0.173
7.0	7.0	120	17.6	1.025	1.837	0.108	1.529	—	0.100
7.0	7.0	180	21.9	1.086	1.877	0.111	1.485	0.079	0.100
7.0	7.0	240	38.3	1.118	1.776	0.088	1.467	0.046	0.088
7.0	7.0	300	45.7	1.067	1.645	0.068	1.379	0.033	0.082
Solvent— <i>m</i> -xylene, $T = 130^\circ\text{C}$									
7.0	7.0	60	41.6	4.85	5.27	0.478	4.14	0.232	0.212
7.0	7.0	120	51.4	3.00	3.32	0.250	2.64	0.115	0.160
7.0	7.0	180	64.3	2.50	2.82	0.183	2.25	0.093	0.158
7.0	7.0	240	74.6	2.175	2.48	0.114	1.95	0.111	0.152
7.0	7.0	300	82.7	1.93	2.26	0.087	1.69	0.154	0.164

Scheme 2.



The main products of the reaction in the presence of a catalytic system (polyoxomolybdate modified with gadolinium oxide) are spiroacetal, hemiacetal, and 1,4-dioxane, product of ethane-1,2-diol self-condensation.

In order to study the possible effect of the above compounds on the condensation process, special

experiments were carried out with binary mixtures. In particular, the condensation of ketone with ethylene glycol was carried out by introducing the above compounds into the system. The results of the studies indicate that no inhibition by the reaction products occurs at least to the degree of conversion of the initial ketone 30–40% (Fig. 3). According to the reported data and taking into account the results obtained, conversion curves of the process selectivity vs. the conversion of the initial ketone were constructed at various temperatures.

The selectivity of the reaction for the corresponding spiroacetal in the reaction conditions remains high, but at a conversion close to zero, determined by differentiating the corresponding curves, it differs from 100%, which indicates a parallel-sequential scheme of the ketone transformation.

Based on the experimental data in Table 2, the following independent routes can be proposed for the transformation of ketone and ethanediol-1,2 (Scheme 2).

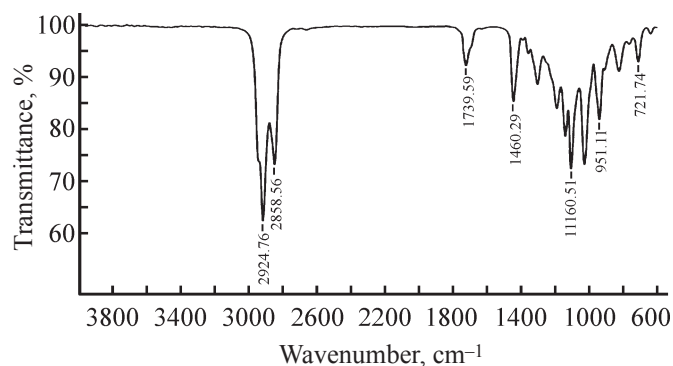


Fig. 2. IR spectrum of 5-pentyl-1,4-dioxaspiro[4.4]nonane.

In the study area (Table 2) with an increase in the initial concentration of the initial ketone, ethylene glycol, and catalyst at a constant value of the concentrations of other components of the reaction mixture, the accumulation of spiroacetal proceeds linearly, which indicates the first order of reaction for these components:

$$W = k[c_1][c_2 \times \text{cat}],$$

where W is the formal rate of accumulation of spiroacetal ($\text{M}^{-1} \text{min}^{-1}$), c_1 and c_2 are the concentrations of ketone and ethylene glycol, respectively.

Theoretically, the first product of the interaction of 2-pentylcyclopentanone and ethanediol-1,2 is hemiacetal: 1-hydroxy-1-(2-hydroxyethoxy)-2-pentylcyclopentane. The formation of ketal and hemiacetal was also indirectly proved by the reaction of cyclopentanone and ethanol in the presence of strong mineral acids (HCl , H_2SO_4). Consequently, the condensation of these compounds must proceed in a sequential pattern [9]. However, the type of graphical dependence of selectivity for hemi- and spiroacetals on ketone conversion (Fig. 3) shows that in this case the reaction proceeds according to a parallel-sequential scheme of their transformation.

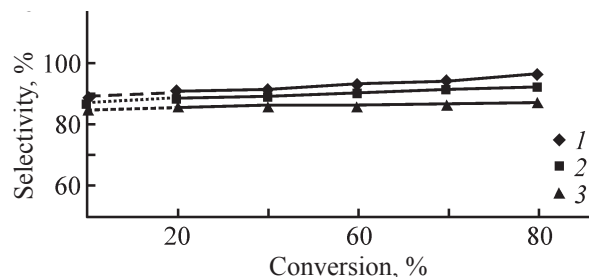


Fig. 3. Selectivity S of reaction for spiro acetal vs. conversion of 2- n -pentylcyclopentanone at different temperatures. T ($^{\circ}\text{C}$): (1) 100, (2) 120, (3) 130.

In addition to spiroacetal and hemiacetal, GLC analysis showed that the catalysate contained 1,4-dioxane and two products, presumably hydroxyesters, indicated in the reaction scheme.

The parallel-sequential scheme of the reaction is likely due to the bifunctional properties of the catalyst. According to the results of kinetic studies (Table 2), the closest convergence of the calculated and experimental data was achieved using the kinetic equations of the power type:

Table 3. Staged condensation scheme of 2-alkylcyclopentanone and ethylene glycol in the presence of a complex $\text{GdPO}_4 \cdot (\text{MoO}_2)_{0.5} \text{PMo}_{12}\text{O}_{40}$

Stage no.	Route ^a	Number of stages along stoichiometric routes					
		I	II	III	IV	V	VI
1	$\text{C}_2\text{H}_4(\text{OH})_2 + \text{ZO} \rightarrow \text{HOC}_2\text{H}_4\text{OZOH}$	1	1	0	0	0	1
2	$\text{R} = \text{O} + \text{HOC}_2\text{H}_4\text{OZOH} \rightarrow \text{HOC}_2\text{H}_4\text{OROZOH}$	1	1	0	0	0	0
3	$\text{HOC}_2\text{H}_4\text{OROZOH} \rightarrow \text{R}(\text{O})_2\text{C}_2\text{H}_4 + \text{ZO} + \text{H}_2\text{O}$	1	0	0	0	0	0
4	$\text{HOC}_2\text{H}_4\text{OROZOH} \rightarrow \text{HOROC}_2\text{H}_4\text{OH} + \text{ZO}$	0	1	1	0	0	0
5	$\text{HOROC}_2\text{H}_4\text{OH} + \text{ZO} \rightarrow \text{HOROC}_2\text{H}_4\text{OZOH}$	0	0	1	1	1	0
6	$\text{HOROC}_2\text{H}_4\text{OZOH} \rightarrow \text{R}(\text{O})_2\text{C}_2\text{H}_4 + \text{ZO} + \text{H}_2\text{O}$	0	0	1	0	0	0
7	$\text{HOROC}_2\text{H}_4\text{OZOH} + \text{R}(\text{O})_2\text{C}_2\text{H}_4 \rightarrow \text{HOC}_2\text{H}_4\text{OROC}_2\text{H}_4\text{OZOH}$	0	0	0	1	0	0
8	$\text{HOC}_2\text{H}_4\text{OROC}_2\text{H}_4\text{OZOH} \rightarrow \text{HOC}_2\text{H}_4\text{OROC}_2\text{H}_4\text{OH} + \text{ZO}$	0	0	0	1	0	0
9	$\text{HOROC}_2\text{H}_4\text{OZOH} + \text{C}_2\text{H}_4(\text{OH})_2 \rightarrow \text{HOROC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OZOH} + \text{H}_2\text{O}$	0	0	0	0	1	0
10	$\text{HOROC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OZOH} \rightarrow \text{HOROC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH} + \text{ZO}$	0	0	0	0	1	0
11	$\text{HOC}_2\text{H}_4\text{OZOH} + \text{C}_2\text{H}_4(\text{OH})_2 \rightarrow \text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OZOH} + \text{H}_2\text{O}$	0	0	0	0	0	1
12	$\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OZOH} \rightarrow \text{C}_4\text{H}_8\text{O}_2 + \text{ZO} + \text{H}_2\text{O}$	0	0	0	0	0	1

^a $\text{R} = \text{O}$ —2-pentylcyclopentanone, ZO — $\text{GdPO}_4 \cdot (\text{MoO}_2)_{0.5} \text{PMo}_{12}\text{O}_{40}$.

$$r_1 = k_1[c_1][c_2], \quad (1)$$

$$r_2 = k_2[c_1][c_2], \quad (2)$$

$$r_3 = k_3[c_3], \quad (3)$$

$$r_4 = k_4[c_2][c_3], \quad (4)$$

$$r_5 = k_5[c_2][c_3], \quad (5)$$

$$r_6 = k_6[c_2]^2, \quad (6)$$

where k_1 – k_6 are reaction rate constants along routes I–VI; r_1 – r_6 are the rates of accumulation of reaction products using the corresponding stoichiometric equations; c_1 – c_3 are the concentrations of the starting ketone, diol, and hemiacetal.

When compiling the equations, the esterification rates on the basis of additional experiments and analyzes of the reaction products were equated to zero. The rates of transformation of the initial ketone and glycol, as well as the reaction products obtained from routes I – VI, were calculated using the following equations:

$$W_1 = -r_1 - r_2, \quad (7)$$

$$W_2 = -r_1 - r_2 - r_4 - r_5 - 2r_6, \quad (8)$$

$$W_3 = r_1 - r_3 - r_4 - r_5, \quad (9)$$

$$W_4 = r_2 + r_3, \quad (10)$$

$$W_5 = r_4 + r_5, \quad (11)$$

$$W_6 = r_6. \quad (12)$$

where W_1 – W_6 are the experimentally found rates listed in Table. 2

The rate constants were calculated by a modified fourth-order Runge–Kutta method using the Matlab-6.5 program. The experimental values of the constants were found graphically and refined by minimizing the standard deviations between the observed and calculated data for Eqs. (7)–(12). Pre-exponential values of the constants and activation energy were calculated for the individual stages of the condensation reaction of 2-*n*-pentylcyclopentanone and ethanediol-1,2, having the following form:

$$k_1 = 1.65 \times 10^2 \exp(-9465/RT) \text{ M}^{-1} \text{ min}^{-1},$$

$$k_2 = 6.1 \times 10^4 \exp(-16907/RT) \text{ M}^{-1} \text{ min}^{-1},$$

$$k_3 = 7.07 \times 10^4 \exp(-22822/RT) \text{ M}^{-1} \text{ min}^{-1},$$

$$k_4 = k_5 \approx 0,$$

$$k_6 = 2.29 \times 10^2 \exp(-13451/RT) \text{ M}^{-1} \text{ min}^{-1},$$

where R is the universal gas constant, 8.3144 J mol^{−1} K^{−1}. The standard deviation for the main route I was 12.5%; for routes II–IV, 15–21%. The zero value of the constants k_4 and k_5 indicates that the main direction for the transformation of semi-acetal is route III.

Taking into account the results obtained, the process of condensation of ketone and glycol in spiroacetal can be described by the step-by-step scheme (Table 3). The stage responsible for the interaction of alkylcyclopentanone with the Gd-polyoxomolybdate diolate complex according to Scheme 2 was chosen as the limiting one.

CONCLUSIONS

(1) The conditions for the condensation of C₅–C₇-alkyl- and cycloalkyl-substituted cyclopentanone and vicinal glycols (ethane-1,2- and propane-1,2-diols) to the corresponding spiroacetals with participation of polyoxomolybdenum modified with rare-earth oxides were studied.

(2) Kinetic patterns were studied and kinetic equations and a step-by-step kinetic model were compiled describing the main reaction routes. It has been established that the corresponding spiroacetal from ketone and diol is formed both directly, in one stage, and according to a two-stage scheme, through the stages of the preparation of hemiacetal.

REFERENCES

1. Traven', V.F., *Organicheskaya khimiya* (Organic Chemistry), vol. 2, Moscow: Binom, 2013.
2. Kheyfits, L.A. and Dashunin, V.M., *Dushistyye veshchestva i drugie produkty dlya parfyumerii* (Perfumes and Other Perfumery Products), Moscow: Khimiya, 1994.
3. *Osnovy organicheskoi khimii dushistykh veshchestv dlya prikladnoi estetiki i aromaterapii* (Basics of Organic Chemistry of Fragrant Substances for Applied Aesthetics and Aromatherapy), Soldatenkov, A.T., Ed., Moscow: IKTS "Akademkniga," 2006.
4. Mashkovskii, M.D., *Lekarstvennyye sredstva* (Drugs), ch. 1, Moscow: Meditsina, 2000.
5. Nedumaran, D. and Pandurangan, A., *Micropor. Water*, 2013, vol. 169, pp. 25–34.
6. Miyake, H., Nakao, Y., and Sasaki, M., *Chem. Lett.*, 2007, vol. 36, no. 1, pp. 104–105.
7. *USSR Byull. Izobr.* 587839, 1978, no. 1; *Herbicide Composition*.
8. Shui-Jin, Y., Qiang, W., and Guo-bin, D., *J. Xuzhou Institute Technol. Natural Sci. Ed.*, 2012, vol. 3, pp. 25–28.
9. Zhang, F., Xu, D., Luo, Sh., Liu, B., and Xu, Z., *J. Chem. Ind. Eng.*, 2004, vol. 55, pp. 2047–2050.

10. Waller, D.L., Stephenson, C.R.J., and Wipf, P., *Org. Biomol. Chem.*, 2007, vol. 5, pp. 58–60.
11. Vyglazov, O.G., Chuiko, V.A., Izotova, L.V., Vintarskaya, Z.V., and Yudenko, R.Y., *Russ. J. Appl. Chem.*, 2001, vol. 74, no. 11, pp. 1888–1891].
12. Eshghi, H., Rahimzadeh, M., and Saberi, S., *Catal. Commun.*, 2008, vol. 9, pp. 2460–2466.
13. Kanai, S., Nagahara, Kita, Y., Kamata, K., and Hara, M., *Chem. Sci.*, 2017, vol. 8, pp. 3146–3153.
14. Sayama, S., *Tetrahedron Lett.*, 2006, vol. 47, no. 24, pp. 4001–4005.
15. Yang, Z., Lei, C., Zhao, X., Liu, R., Wei, H., Ma, Y., Meny, S., Cao, Q., Wei, J., Wang, X., *Chem. Select.*, 2017, vol. 2, pp. 9377–9386.
16. Alimardanov, Kh.M., Sadigov, O.A., Abbasov, M.F. Suleymanova, E.T., Jafarova, H.A., Abdullayeva, M.Y., and Abbasova, S.M., *Russ. J. Org. Chem.*, 2011, vol. 47, pp. 1136–1143.
17. Garibov, N.I., Alimardanov, Kh.M., Dadashova, N.R., Sadiqov, O.A., Almardanova, M.B., Quliyev, A.D., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 5, pp. 1025–1033.
18. Abbasov, M.F., Alimardanov, Kh.M., and Suleymanova, E.T., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 4, pp. 648–655.