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## Isothermal Kinetics of Titanium-oxo-alkoxy Clusters Formation

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### Abstract:

*In this article, the influences of titanium tetraisopropoxide  $Ti(OR)_4$  ( $R = Pr^i$ ) concentration, molar ratio,  $h = [H_2O]/[Ti(OR)_4]$ , and temperature, on the formation kinetics of the titanium-oxo-alkoxy clusters (TOAC), were studied. The TOAC formation isothermal kinetics was monitored by measuring absorbance changes versus time in the reaction mixture at predefined wavelength  $\lambda = 350$  nm. It was determined that the isothermal rate of clusters formation is a power law function of titanium tetraisopropoxide concentration and the molar concentration of water ( $c_w$ ). The kinetic parameters  $\alpha$  and  $\beta$  were calculated. The apparent activation energy  $E_a$  values in the clusters formation reaction has been calculated and correlated with the change of titanium tetraisopropoxide concentration and molar ratio. The model for mechanism of TOAC formation is proposed.*

**Keywords:** Titanium tetraisopropoxide, Isothermal kinetics, Hydrolysis, Titanium-oxo-alkoxy clusters formation.

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## 1. Introduction

Titania powders are widely used in industrial applications as pigments, opacifiers, catalysts, photocatalysts, fillers, cell separations and environmental remediation. The key application properties of  $TiO_2$  are defined by the size and shape of particles and also by the particle size distribution [1-5]. To create a  $TiO_2$  with the predefined functional characteristics it is extremely important to know the mechanism and kinetics of  $TiO_2$  particle formation in the initial phase of particle growth [6].

The kinetics of the sol-gel process based on titanium metal alkoxides has been studied in a number of papers [7-11]. It is generally assumed, that in the first stage of the sol-gel process, hydrolyzed monomers are created and accumulated [9,12-13]. The induction time corresponds to the moment when the concentration of these monomers reaches the level of critical supersaturation. As a result of nucleation, primary particles are formed. They then grow by monomer addition and aggregation [10].

Barringer et al. [7] studied the production of spherical, monodispersed  $TiO_2$  with a controlled hydrolysis of diluted ethanolic solution of titanium tetraethoxide -  $Ti(OC_2H_5)_4$ , at room temperature, at a molar ratio of water to tetraethoxide ( $h$ ) always greater than 2.5. They

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found that the nucleation process is homogenous and that the rate of nucleation follows the stoichiometry of the reaction.

The kinetics of nucleation, when generating a monodisperse  $\text{TiO}_2$  by the hydrolysis of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  in ethanolic solution, (with different titanium tetraethoxide concentrations  $c = 0.075\text{--}0.2$  M, molar ratios of water to tetraethoxide  $h = 5\text{--}13$  and temperature  $T = 298$  K) was investigated in the paper of Jean et al. [8]. It was found that the induction time (I) can be described with the following equation:

$$I = 0,33[\text{Ti}(\text{OC}_2\text{H}_5)_4]^2 \cdot [\text{H}_2\text{O}]^4. \quad (1)$$

Golubko et al. [11] investigated the hydrolysis of  $\text{Ti}(\text{OR})_4$  ( $R = \text{Et}$ ,  $^i\text{Pr}$ ,  $^n\text{Bu}$ ) in alcoholic solutions, with different titanium alkoxides concentrations ( $c = 0.19\text{--}0.67$  M), and different molar ratios  $h = 0.5\text{--}20$ , at room temperature. It was concluded that the induction time can be described with the same equation as in the paper of Jean et al. [8] and also suggested that the addition of water to perform hydrolysis of  $\text{Ti}(\text{O}^i\text{Bu})_4$ , should be in two steps, which enables the decrease in rate of the solid precipitate formation, to regulate particles morphology in a wide range.

A spectroscopic study of the initial stage of the  $\text{Ti}(\text{OPr}^i)_4$  sol-gel process in 2-propanol ( $c = 0.1$  M and  $h = 0.1\text{--}3$ ) was presented out in the paper of Soloviev et al. [14]. It was concluded that the hydrolysis-condensation reaction takes place during the mixing of reagents and that it is complete at low  $h \leq 1$ . The molar ratio  $h > 1$  is needed for particle growth.

The kinetics of hydrolysis and condensation of  $\text{Ti}(\text{OPr}^i)_4$  in isopropanol, under neutral conditions ( $c = 0.08\text{--}0.28$  M,  $h = 1.5\text{--}7$  and  $T = 298$  K), was investigated in the paper of Soloviev et al. [6]. It was found that the kinetics of the process is complex in nature and that it includes different processes: hydrolysis, condensation and aggregation of primary particles. The formation of primary particles (nucleation) takes place for a short time, after the initial hydrolysis and condensation.

The rate of individual particles mass growth ( $r$ ) can be described with a power law equation:

$$r = k \cdot c^{\alpha+\beta} \cdot (h - 1.45)^\beta, \quad (2)$$

where  $k$  is the constant of the reaction rate,  $h$  is the molar ratio and  $\alpha$  and  $\beta$  are kinetic parameters.

The effect of mixing on the  $\text{Ti}(\text{OPr}^i)_4$  sol-gel process in isopropyl alcohol ( $c = 0.5\text{--}1$  M,  $h = 2\text{--}4$ ,  $T = 298$  K) was investigated in the paper of Marchisio et al. [15]. It was found that, processes of hydrolysis and condensation are much faster than mixing and that they have the decisive influence on kinetics and characteristics of the  $\text{TiO}_2$  formation.

Azouani et al. [16] investigated nucleation and growth of titanium-oxo-alkoxy  $\text{Ti}_x\text{O}_y(\text{O}^i\text{Pr})_z$  clusters which were created in the  $\text{Ti}(\text{OPr}^i)_4$  sol-gel process in 2-propanol, at the hydrolysis ratio,  $h$ , between 1.0 and 2.6. Four different domains of the cluster/nanoparticle stability and growth kinetics were identified:  $h < 1.45$  (I),  $1.45 \leq h \leq 1.75$  (II),  $1.75 < h \leq 2.0$  (III) and  $h > 2.0$  (IV). In the fourth domain, the equation was derived, describing the induction kinetics:

$$t_{\text{ind}} \propto c_{\text{Ti}}^{-6} (h - h^*)^{-5}, \quad (3)$$

where  $c_{\text{Ti}}$  is the initial Ti-atom concentration,  $h^* = 1.45$  and  $t_{\text{ind}}$  is the induction time.

Azouani et al. [17] synthesized pure and doped  $\text{TiO}_2$  nanoparticles in the sol-gel reactor with turbulent micromixing of two reactive fluids, containing titanium

tetraisopropoxide and water, in T-mixer. It has been found that mixing, at the nucleation stage, has a strong impact on the nanoparticles polydispersity and mean size of the created TiO<sub>2</sub>.

Taking into account the complexity of all these processes, in this article, the influences of *c*, *h*, *T* parameters on TOAC formation kinetics have been investigated.

## 2. Experimental procedure

The kinetic study of the TOAC formation was carried out by measuring absorbance changes versus time in the reaction mixture, composed of titanium tetraisopropoxide, Ti(OPr<sup>*i*</sup>)<sub>4</sub>, (98 + % Acros Organics), n-propanol provided by Lachner, 0.1% maximum water content and distilled water.

In each individual experiment, the molar concentration of titanium tetraisopropoxide (*c* - ranging from 0.04–0.07 M) was fixed, as was the temperature at one of three different values (298 K, 308 K and 318 K), and the molar ratio *h* varied between 11 and 20 (*h* = 11, 14, 17, 20).

In the beaker-type reactor filled with 100 ml of the n-propanol solution, preliminarily heated to predetermined temperatures, a precalculated amount of titanium tetraisopropoxide was added in order to obtain an appropriate value of *c*. The temperature of each individual experiment was kept constant, within ± 1 K. The reaction mixture was homogenized by stirring with a magnetic stirrer (450 rpm) and the required amount of distilled water was added drop-wise into the titanium alkoxide solutions in order to achieve a predetermined molar ratio of water to titanium tetraisopropoxide. Immediately afterwards, an immersion quartz Suprasil probe (Hellma, 661.500-QX, optical path length 10<sup>-2</sup> m) was inserted in the beaker-type reactor for the measurement of absorbance changes versus time, at predefined time intervals. The optical probe is connected to the spectrometer through the standard fiber-optic cable (Hellma, 041.002-UV). Absorbance changes versus time were recorded on GBC Cintra 10e UV–Visible Spectrometer at predetermined wavelength λ = 350 nm.

The time of clusters formation (*t<sub>f</sub>*), was determined by the graphical method, as the section of extrapolation of the absorbance's linear time dependence with time axis.

The rate of clusters formation (*v<sub>f</sub>*) was calculated by using the equation:

$$v_f = 1/t_f . \quad (4)$$

The apparent activation energy of the clusters formation reaction (*E<sub>a</sub>*) was determined by the Arrhenius equation:

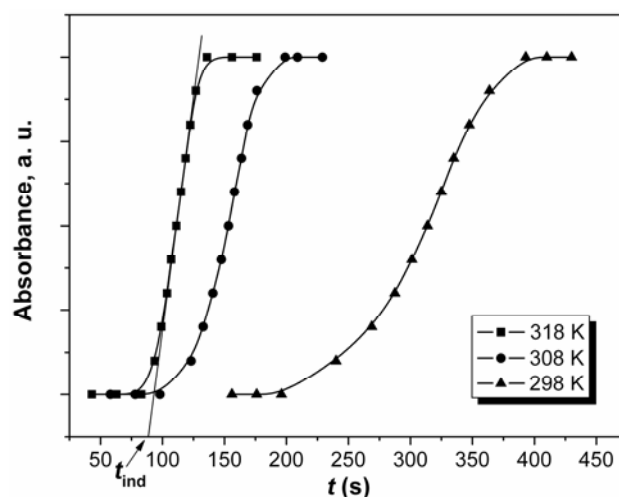
$$\ln v_f = \ln A - \frac{E_a}{RT} . \quad (5)$$

where *A* is the pre-exponential factor, *R* is the gas constant and *T* is the temperature.

## 3. Results and discussion

The typical kinetic curves of the TOAC formation, produced in the reaction between Ti(OR)<sub>4</sub> and H<sub>2</sub>O in n-propanol solution, at different operating temperatures, are presented in Fig. 1. Three distinctive regions of absorbance changes over reaction time are clearly observed at all experimental temperatures, each of them corresponding to a different stage of the reaction. In the beginning of the reaction, the reaction system is completely transparent.

At this stage, the formation and growth of titanium-oxo-alkoxy clusters up to their critical size  $d_c$  [18] occurs. As a result, absorbance doesn't grow as reaction time increases. In the second stage of TOAC formation, further cluster growth occurs, which results in rapid increase of absorbance value during this stage. In the third stage, the reaction system is completely turbid and the value of absorbance reaches its maximum value. During this stage there is a deceleration of clusters growth and their mutual repelling, overlapping and aggregating.



**Fig. 1.** The TOAC formation isothermal kinetic curves, produced in the reaction between  $Ti(OR)_4$  and  $H_2O$ , in n-propanol solution, at  $c = 0.07$  M and  $h = 17$ .

Assuming that the formation rate of clusters ( $v_f$ ) and their growth up to a critical size  $d_c$ , is the inverse value of the time of clusters formation ( $t_f$ ), the effects of  $c$ ,  $h$  and experimental temperature  $T$  on  $v_f$  were examined. The effects of  $c$ ,  $h$  and  $T$  on  $t_f$  and  $v_f$  are shown in Tab. I and Tab. II respectively.

**Tab. I** The effects of  $c$ ,  $h$  and  $T$  on the time of clusters formation.

T (K)	298			308			318		
c (M)	0.04	0.05	0.07	0.04	0.05	0.07	0.04	0.05	0.07
h	$t_f$ (s)								
11	20000	7127	566	7800	3356	355	2100	2223	202
14	10697	1713	268	3201	1106	187	1782	960	147
17	3360	1057	196	1482	972	98	1130	584	83
20	1099	552	77	600	474	54	492	169	9

Analysis of the obtained results, in all the investigated cases, leads to the conclusion that the clusters formation rate increases as: a)  $h$  values increase, with  $c = \text{const.}$  and  $T = \text{const.}$ , b)  $c$  values increase, with  $h = \text{const.}$  and  $T = \text{const.}$  and c)  $T$  values increase, with  $c = \text{const.}$  and  $h = \text{const.}$  Assuming that the rate of cluster formation is a power law function of  $c$  and  $c_w$  [6], in these investigations we proposed a new equation for the clusters formation rate ( $v_f$ ):

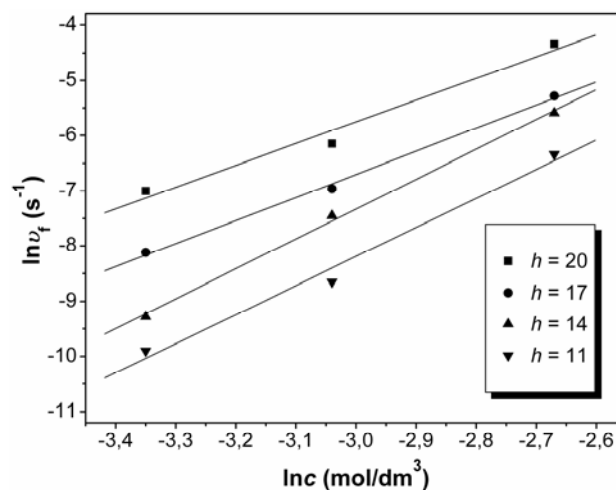
$$v_f = k \cdot c^\alpha \cdot c_w^\beta \quad (6)$$

where  $k$  is reaction rate constant,  $c$  is titanium tetraisopropoxide concentration,  $c_w$  is a molar concentration of water and  $\alpha$  and  $\beta$  are kinetic parameters for the cluster formation process.

**Tab. II** The effects of  $c$ ,  $h$  and  $T$  on the rate of titanium-oxo-alkoxy clusters formation.

T (K)	298			308			318		
$c$ (M)	0.04	0.05	0.07	0.04	0.05	0.07	0.04	0.05	0.07
$h$	$v_f$ ( $s^{-1}$ )								
11	$5.0 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$	$4.3 \cdot 10^{-3}$
14	$9.4 \cdot 10^{-5}$	$5.8 \cdot 10^{-4}$	$3.7 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$	$5.4 \cdot 10^{-3}$	$5.6 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$
17	$3.0 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$	$5.1 \cdot 10^{-3}$	$6.8 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$8.8 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$
20	$9.1 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-1}$

According to Eq. 6, it is possible to determine the value of kinetic parameter  $\alpha$  for the clusters formation process. Namely, the dependence  $\ln v_f$  vs.  $\ln c$  for  $h = \text{const.}$  and  $T = \text{const.}$  is linear and its plot is a straight line whose slope can be used for the kinetic parameter  $\alpha$  calculation.

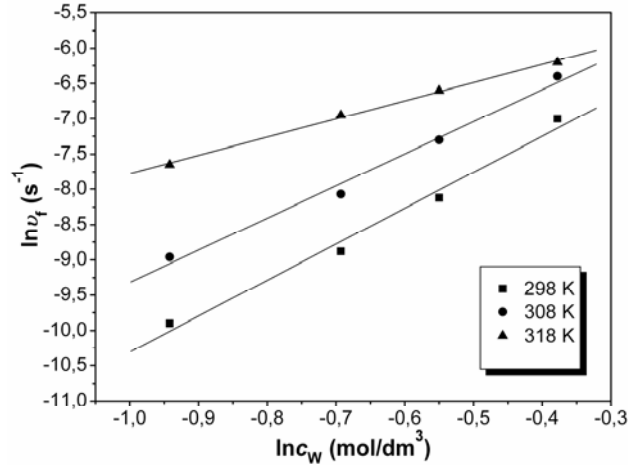
**Fig. 2.** The plot of  $\ln v_f$  vs.  $\ln c$  dependence at temperature of 298 K.

The plot of  $\ln v_f$  vs.  $\ln c$  dependence, at temperature of 298 K and  $h$  ranging from 11–20, is presented in Fig. 2. In Tab. III the effects of experimental temperature  $T$  and  $h$  on the value of kinetic parameter  $\alpha$ , for the clusters formation process, are displayed.

**Tab. III** The temperature  $T$  and  $h$  effects on the value of kinetic parameter  $\alpha$ .

h	$\alpha$							
	11		14		17		20	
T (K)		$R^2$		$R^2$		$R^2$		$R^2$
298	7.0	1.000	5.0	0.996	4.0	0.996	4.0	0.953
308	6.0	0.958	4.0	0.990	4.0	0.893	4.0	0.854
318	6.0	1.000	4.0	0.947	4.0	0.949	4.0	0.956

We have established that at temperatures  $T = 298\text{ K}$  and  $T = 308\text{ K}$   $\alpha$  decreases, as  $h$  increases, while further increase of  $T$  leads to the  $\alpha$  reduction if  $h \geq 14$ , or parameter  $\alpha$  remains constant if  $h \geq 17$ .



**Fig. 3.** The plot of  $\ln v_f$  vs.  $\ln c_w$  dependence for titanium tetraisopropoxide concentration of 0.04 M.

In order to determine the kinetic parameter  $\beta$  the dependences  $\ln v_f$  vs.  $\ln c_w$  for  $c = \text{const.}$  and  $T = \text{const.}$  are presented. The plot of  $\ln v_f$  vs.  $\ln c_w$  dependence for  $c = 0.04\text{ M}$  and temperature  $T$  ranging from 298–318 K is presented in Fig. 3. In Tab. IV, the effects of experimental temperature  $T$  and  $c$  on kinetic parameter  $\beta$  are displayed.

**Tab. IV** The temperature  $T$  and  $c$  effects on kinetic parameter  $\beta$ .

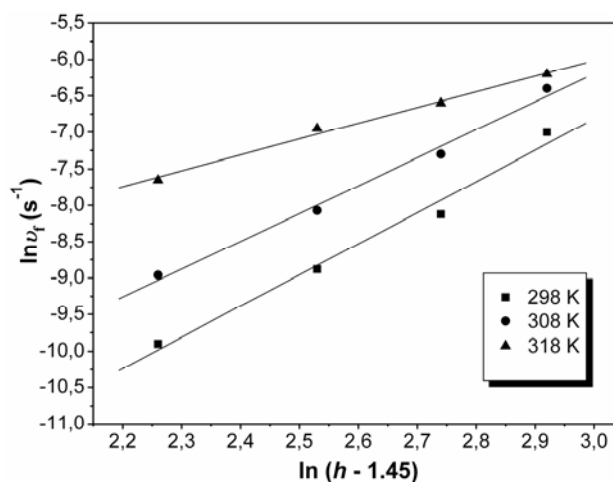
		$\beta$				
$c$ (M)		0.04	0.05	0.07		
$T$ (K)		$R^2$	$R^2$	$R^2$	$R^2$	$R^2$
298	7.0	0.996	4.0	0.960	4.0	0.953
308	5.0	1.000	4.0	0.960	4.0	0.994
318	4.0	0.988	4.0	0.941	4.0	0.986

We have noticed that as the concentration of titanium tetraisopropoxide increases in the reaction mixture at  $T = 298\text{ K}$ , while the kinetic parameter  $\beta$  decreases from 7 to 4. Contrary to that, at temperatures  $T = 308\text{ K}$  and  $T = 318\text{ K}$ , for  $c \geq 0.05$ , the kinetic parameter  $\beta$  is independent of  $c$  and equals 4 ( $\beta = 4$ ).

Assuming that the initial hydrolysis reaction is very fast compared to the whole induction period, and that in order to describe correctly the kinetics of this process, instead of the amount of water put initially in the system, the amount of water remaining after the nucleation must be used, Soloviev obtained the following kinetic equation [6]:

$$r = k \cdot c^{\alpha^* + \beta^*} \cdot (h - 1.45)^{\beta^*}, \quad (7)$$

where  $\alpha^*$  and  $\beta^*$  are Soloviev's kinetic parameters.



**Fig. 4.** The dependence  $\ln v_f$  on  $\ln (h - 1.45)$  for  $c = 0.04$  M.

In order to validate the Soloviev's kinetic model, the dependence  $\ln v_f$  on  $\ln (h - 1.45)$  was examined within the tested ranges of  $c$ ,  $h$  and  $T$ . On Fig. 4, as an example, the dependence  $\ln v_f$  on  $\ln (h - 1.45)$  is shown, for  $c = 0.04$  M.

**Tab. V** The values of kinetic parameter  $\beta^*$ , obtained by applying Soloviev's model, with different values of  $c$  and  $T$ .

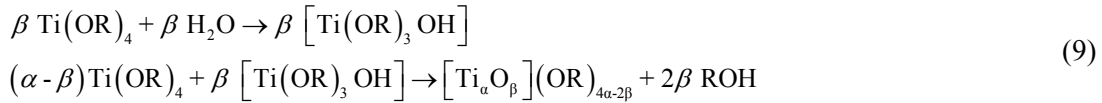
		$\beta^*$				
$c$ (M)	0.04	0.05	0.07			
$T$ (K)	$R^2$		$R^2$		$R^2$	
298	4.41	0.955	3.78	0.974	2.85	0.953
308	3.83	0.990	2.77	0.941	2.85	0.994
318	2.12	0.854	3.70	0.949	4.31	0.762

In Tab. V, the values of kinetic parameter  $\beta^*$ , obtained by applying Soloviev's model with different values of  $c$  and  $T$ , are shown. It can be noticed that kinetic parameters  $\beta^*$  are nonintegers and vary complexly with  $c$  and  $T$ . Based on the values of  $\alpha$  and  $\beta^*$ , the value of Soloviev's model kinetic parameter  $\alpha^*$  was determined. In Tab. VI, as an example, the values of kinetic parameter  $\alpha^*$  are shown, for different values of  $c$  and  $h$  at  $T = 298$  K. It should be noticed that kinetic parameters  $\alpha^*$  are also nonintegers. In a series of examined examples, values of  $\alpha^*$  were less than 1 or negative, which directly indicates that Soloviev's kinetic model isn't applicable for observing kinetics of TOAC formation. If we carefully analyze values of kinetic parameters  $\alpha$  and  $\beta$ , shown in Tab. III and Tab. IV, it can be easily concluded that values of  $\alpha$  are a)  $\alpha = \beta$ , b)  $\alpha > \beta$  or c)  $\alpha < \beta$ . Bearing this in mind and accepting that the rate of hydrolysis is greater than the rate of cluster formation and also that the basic product of hydrolysis reaction is  $\text{Ti}(\text{OR})_3\text{OH}$  [19,20], it is possible to obtain the following kinetic models of TOAC formation:

a) In case of  $\alpha = \beta$ ,



b) In case of  $\alpha > \beta$ ,



c) In case of  $\alpha < \beta$ , during the hydrolysis, not only  $\text{Ti(OR)}_3\text{OH}$  is formed, but also some more complex, higher level products of hydrolysis, such as  $\text{Ti(OR)}_2(\text{OH})_2$  or  $\text{Ti(OR)(OH)}_3$ , which consequently interact and create  $[\text{Ti}_\alpha\text{O}_\beta](\text{OR})_{4\alpha-2\beta}$ .

**Tab. VI** The values of kinetic parameter  $\alpha^*$  for different values of c and h at T = 298 K.

$\alpha^*$				
h	11	14	17	20
c (M)				
0.04	2.6	0.6	-0.4	-0.4
0.05	3.2	1.2	0.2	0.2
0.07	3.3	2.2	1.2	1.2

In according to Day et al. [22], the titanium-oxo core structural formulas and degrees of condensation (DC =  $\alpha/\beta$ ) are shown in Tab. VII.

**Tab. VII** The titanium-oxo core structural formulas and degrees of condensation (DC), with different values of c and T, for h = 11 and h ranging from 14 – 20.

		$[\text{Ti}_\alpha\text{O}_\beta]$			DC		
h = 11							
T (K)		298	308	318	298	308	318
c (M)							
0.04		$\text{Ti}_7\text{O}_7$	$\text{Ti}_6\text{O}_7$	$\text{Ti}_6\text{O}_7$	1	1.17	1.17
0.05		$\text{Ti}_7\text{O}_4$	$\text{Ti}_6\text{O}_4$	–	0.57	0.66	0.66
0.07		$\text{Ti}_7\text{O}_4$	$\text{Ti}_6\text{O}_4$	–	0.57	0.60	0.66
h = 14 – 20							
T (K)		298	308	318	298	308	318
c (M)							
0.04		$\text{Ti}_5\text{O}_7$	$\text{Ti}_4\text{O}_5$	$\text{Ti}_4\text{O}_5$	1.4	1.25	1.25
0.05		$\text{Ti}_5\text{O}_4$	$\text{Ti}_4\text{O}_4$	$\text{Ti}_4\text{O}_4$	0.8	1	1
0.07		$\text{Ti}_5\text{O}_4$	$\text{Ti}_4\text{O}_4$	$\text{Ti}_4\text{O}_4$	0.8	1	1

It can be noticed that for h = 11 at 298 K,  $[\text{Ti}_7\text{O}_7]$  clusters are formed, and for h = 14 – 20,  $[\text{Ti}_5\text{O}_7]$  clusters are formed. The increase of  $\text{Ti(OR)}_4$  concentration leads to  $[\text{Ti}_7\text{O}_4]$  or  $[\text{Ti}_5\text{O}_4]$  clusters formation and therefore to decrease of DC values.

Also, it has been observed that at 308 K and 318 K, for c = 0.04 M,  $[\text{Ti}_6\text{O}_7]$  clusters are formed at h = 11, and  $[\text{Ti}_4\text{O}_5]$  clusters are formed at h = 14 – 20. Further more, the increase of  $\text{Ti(OR)}_4$  concentration leads to the decrease of DC values and  $[\text{Ti}_4\text{O}_4]$  clusters are formed.

Established structural formulas  $[\text{Ti}_7\text{O}_4]$ , at c = 0.05 M and c = 0.07 M, for h = 11 and T = 298 K, are in agreement with the results of the X-ray diffraction and NMR spectroscopy



analysis of trititanates which were isolated from the reaction of  $Ti(OPr^i)_4$  with water and methanol in the isopropanol solution [21].

Therefore, TOAC formation in the reaction of  $Ti(OR)_4$  with  $H_2O$  in n-propanol solution is a complex kinetic reaction whose elementary stages are  $Ti(OR)_4$  fast hydrolysis to  $Ti(OR)_3OH$  or  $Ti(OR)_nOH_{4-2n}$  and the formation of titanium-oxo-alkoxy clusters through the alcoxolation reaction.

**Tab. VIII** The h and c influences on apparent activation energy  $E_a$  in the clusters formation reaction.

c (M)	0.04			0.05			0.07		
	$E_a$ (kJ/mol)	$\ln A$ ( $s^{-1}$ )	$R^2$	$E_a$ (kJ/mol)	$\ln A$ ( $s^{-1}$ )	$R^2$	$E_a$ (kJ/mol)	$\ln A$ ( $s^{-1}$ )	$R^2$
11	(87.7±0.1)	24.70	0.978	(46.05±0.04)	9.76	0.978	(34.92±0.01)	7.76	0.998
14	(70.78±0.08)	19.37	0.968	(34.53±0.04)	6.05	0.929	(34.65±0.02)	7.97	0.986
17	(43.17±0.07)	9.38	0.931	(23.35±0.06)	2.39	0.843	(34.09±0.07)	8.56	0.920
20	(31.07±0.06)	5.86	0.920	(16.2±0.1)	1.18	0.828	(33.9±0.2)	9.29	0.950

Since the increase of  $v_f$  as T increases is exponential, at all investigated c ( $h = \text{const.}$ ), the apparent value of energy  $E_a$  in the clusters formation reaction was determined, by applying the Arrhenius equation. Tab. VIII shows the dependence of apparent activation energy  $E_a$  on h and c. Based on the results given in Tab. VIII, it has been concluded that apparent activation energy  $E_a$  decreases as the  $Ti(OPr^i)_4$  concentration in the reaction mixture increases. The relatively low values of the apparent activation energy  $E_a$  in the clusters formation reaction, which ranged from 16.2 kJ/mol to 87.7 kJ/mol, confirm the above given reaction mechanism. It also indicates that the energy barrier of the reaction is linked to the process of a transition complex formation.

#### 4. Conclusions

In this article titanium-oxo-alkoxy clusters formation kinetics has been investigated. TOAC clusters formation is a reaction with complex kinetics whose elementary stages are hydrolysis  $Ti(OR)_4$  to  $Ti(OR)_3OH$  and the formation of titanium-oxo-alkoxy clusters  $[Ti_\alpha O_\beta](OR)_{4\alpha-2\beta}$  through the alcoxolation reaction. New equation for isothermal rate of TOAC clusters formation has been established and correlated with Soloviev's kinetic equation. Processing parameters c, h, T were determined and apparent activation energy  $E_a$  has been calculated and correlated with the change of c and h. Kinetic parameters  $\alpha$  and  $\beta$  have been determined as well. It has been established that the values of kinetic parameters  $\alpha$  and  $\beta$  change complexly as molar ratio h, titanium tetraisopropoxide concentration c and temperature T change.

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**Садржај:** У овом раду испитивани су утицаји концентрације, титан изопроксида  $Ti(OR)_4$  ( $R = Pr^j$ ), молског односа,  $h = [H_2O]/[Ti(OR)_4]$ , и температуре, на кинетику формирања титан оксо-алкокси кластера (ТОАС). Изотермна кинетика формирања ТОАС праћена је снимањем промене апсорбансе са временом у реакционој смеши, на предефинисаној таласној дужини  $\lambda = 350$  nm. Утврђено је да је брзина изотермног формирања кластера степена функција концентрације титан изопроксида и моларне концентрације воде ( $c_w$ ). Кинетички параметри  $\alpha$  и  $\beta$  су израчунати. Вредности привидне енергије активације  $E_a$  у реакцији формирања кластера су израчунате и повезане са променама концентрације титан изопроксида и молског односа  $h$ . Предложен је модел механизма формирања ТОАС.

**Кључне речи:** титан тетраизопропоксид, изотермна кинетика, хидролиза, формирање титан оксо-алкокси кластера.

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