Physical Chemistry

The Kinetics of Tri-Isobutylarsenite Transesterification in Presence of Decane

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ABSTRACT. Choosing the direction of a kinetic experiment, the reaction between tri-isobutylarsenite and ethylene glycol has been studied under nonisothermal conditions. The reaction mixture contained ethylene glycol in excess and decane was used as a diluent. The observation of process development was accomplished by volumetric method, distilling the by-product (isobutyl alcohol). The values of reaction rate were determined by means of graphical differentiation of kinetic curve. Statistical analysis of experimental results has shown that the most likely value for the activation energy of reaction under mentioned conditions is 10800 J•mol^{-1}. The kinetic equation used describes the experimental results with satisfactory precision on the initial stages of reaction when, essentially, a partial transesterification of arsenite by dialcohol takes place. © *2015 Bull. Georg. Natl. Acad. Sci.*

Key words: *chemical kinetics, tri-isobutylarsenite, transesterification, kinetic equation, Euler method, graphical differentiation.*

From all arsenic containing organic compounds trialkylarsenites $As(OR)_3$ are of the most practical usage. They are easily subjected to purification with physical methods; at the same time, the products of their transformation are characterized with high purity. Therefore, trialkylarsenites are successfully used in production of arsenic compounds with high purity [1]. For choosing of optimum conditions of preparation it is necessary to estimate physical and chemical characteristics of esters of arsenious acid including kinetic parameters. The solution of this problem was the major goal of the present work.

Kinetics of transformation of arsenic containing chemical compounds is not yet sufficiently studied [2-8]. In the previous work [9] the kinetics of transesterification of some trialkylarsenites with ethylene glycol was studied. It has been found that under the conditions of arsenites excess the order of reaction to glycol is 2, while numerical values of activation energy are within the range of 34–44 kJ·mol^{-1}. Under the conditions of glycol excess the kinetic order to arsenites is 1, while activation energy is too low and does not exceed 12 kJ·mol^{-1}.
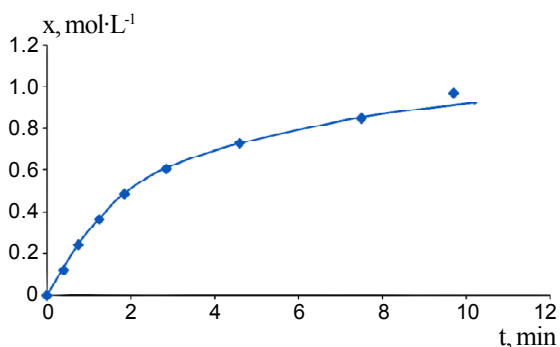
The purpose of the present work was to study

Fig.1. Dependence of the depth of chemical conversion on time (experimental data).
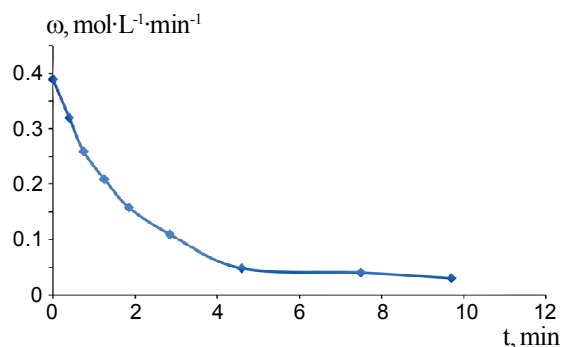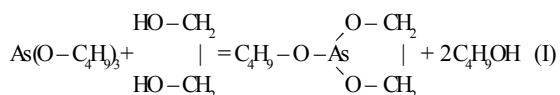

Fig.2. Kinetic curve of the reaction rate variation (experimental data).

kinetics of partial transesterification of tri-isobutyl arsenite with ethylene glycol under condition of glycol excess (6:1). In such a case, during the first several minutes the reaction mainly proceeds according to the following stoichiometric equation [9]:

$$As(O-C_4H_9)_3 + \begin{matrix} HO-CH_2 \\ | \\ HO-CH_2 \end{matrix} = C_4H_9-O-As\begin{matrix} O-CH_2 \\ | \\ O-CH_2 \end{matrix} + 2C_4H_9OH \quad (I)$$

In order to observe the reaction course the by-product (isobutyl alcohol) distillation method was used. The continuous increase of reaction temperature became necessary that enabled to evaluate activation energy of the reaction. Decane was used as an inert diluent of reaction mixture.

Preparation of starting trialkylarsenite was performed by reaction of isobutyl alcohol with arsenic trioxide (at this time high purity ester was produced). As to by-product of reaction (I) the evaluation of its purity was performed by methods of refractometric and chromatographic analysis ("RPL-3" and "Chrom-5" devices were used). It was shown that decane content in this product did not exceed 8-9%.

Chemical composition of initial reaction mixture was:

$$[As(OC_4H_9)_3]_0 = 0.82 \text{ M}; \quad [C_2H_4(OH)_2]_0 = 4.96 \text{ M};$$
$$[C_{10}H_{22}] = 2.63 \text{ M}.$$

The above mentioned mixture was placed in distillation flask inserted in electric heater connected to calibrated receiver; the latter was equipped with Dyna-Stark packing and reflex condenser [10]. The observation of reaction course in time was performed based

on the quantity of condensate (mainly isobutyl alcohol) flowing into receiver. In the course of the process the temperature of reaction mixture increased from 397K to 434K; at the same time the volume of liquid mixture in flask remained almost unchanged (45 ml).

The results obtained are presented in Fig. 1, where the experimental curve shows the variation of x depth of chemical transformation in time t. Quantity x was calculated based on the following expression [9]:

$$x = \rho v / 2 M V, \quad (1)$$

where ρ and M represent density and molar mass of isobutyl alcohol (as by-product), v is the volume of alcohol accumulated in the receiver and V is the volume of reaction mixture.

By means of graphical differentiation of experimental curve in Fig. 1 numerical values of the rate of investigated reaction (ω) for different moments of time were determined. The results obtained are shown in Fig. 2. It is seen that for 5 minutes from the beginning of the process the reaction rate decreases considerably, while on the next stages the change of rate is insignificant. Such results should indicate specific change of reaction mechanism after 5-6 minutes. Therefore, the experimental results were processed only for time interval $0 \leq t < 5$ min.

Reaction rate as the function of chemical transformation depth and temperature may be represented as follows [11]:

$$\omega = dx/dt = k(C_0 - x)^m, \quad (2)$$

where

$$k = A \cdot e^{-E/RT}. \quad (3)$$
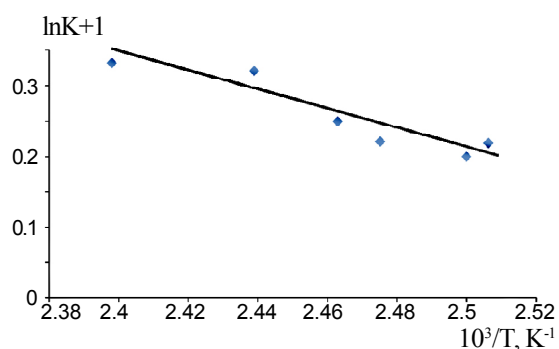
In this expressions k represents the rate constant

Fig. 3. A plot of *lnk* versus *1/T*.

Fig. 4. Dependence of the depth of chemical conversion on time (calculated data).

of reaction, *m* is overall order of the process, *E* is activation energy and *A* is preexponent factor.

From our previous investigations it is known that, under the conditions of ethylene glycol excess, a kinetic order of partial transesterification of tri-alkylarsenites is equal to 1 [9]. If one considers the value m = 1 in equation (2), then on the basis of experimental data obtained, it will be possible to determine the numerical values of rate constant of the reaction at different temperatures. Equation (3) may be rewritten in the following form:

$$ln\ k = ln\ A - E\ /\ RT. \qquad (4)$$

Hence, with the help of equation (2) numerical values of *k* were calculated and the results are presented in *Arrhenius* coordinates in the form of Fig. 3 according to expression (4).

These results were processed using the "least-squares technique" [12] and the coefficient of linear correlation *r*, as well as the values of preexponent factor, activation energy and its standard deviation were evaluated:

$$r = -0.9334, \quad A = 12.5\ min^{-1}, \quad E = 10.8\ kJ \cdot mol^{-1};$$
$$S(E) = 2.1\ kJ \cdot mol^{-1}.$$

The values of rate constant *k* and those values of the same constant that had been obtained by us earlier were compared in the absence of decane [9]
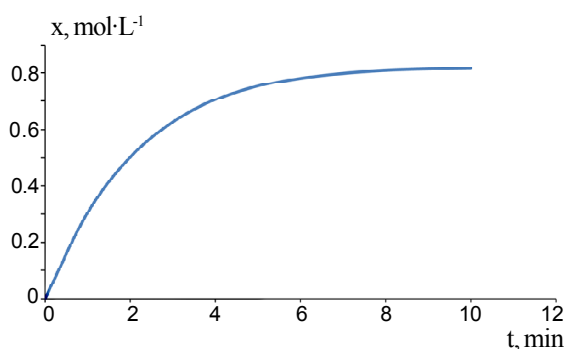
within a temperature interval $397 - 434K$. As a result, in case of the presence of diluent the rate constant is approximately $2 - 4$ times higher than in its absence. Such a result must be explained by a viscosity reduction in the reaction system in case of the presence of decane.

The numerical solution of differential equation (2) was also performed with consideration of the mentioned values of *m, A* and *E* parameters and non-isothermal conditions of the experiment using *Euler* method [13]. Integration step (Δt) made 0.1 min. while initial condition was as follows: when *t* = 0, then *x* = 0. When calculating, *T(t)* function was approximately presented in the form of the following empirical expression (obtained on the basis of statistical treatment of experimental data): $T(t) = 397 + 5.1 \cdot t^{0.89}$.

Results of calculations are presented in Fig. 4. It is seen that within 5 minutes after the beginning of the reaction the calculated curve runs quite near to experimental points presented in Fig. 1: root-mean-square value of relative deviation between calculated and experimental quantities of *x* for the above mentioned interval of time is approximately 5.3%.

ფიზიკური ქიმია

ტრი-იზობუტილარსენიტის გადაეთერების კინეტიკა დეკანის თანაობისას

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ექსპერიმენტულად შესწავლილია ტრი-იზობუტილარსენიტსა და ეთილენგლიკოლს შორის არაიზოთერმულ პირობებში მიმდინარე რეაქციის კინეტიკა. პროცესის მიმდინარეობაზე დაკვირვება ხორციელდებოდა ვოლუმეტრული მეთოდით, თანაური პროდუქტის (იზობუტილის სპირტის) გადადენის გზით. რეაქციის სიჩქარის მნიშვნელობათა განსაზღვრა ხდებოდა კინეტიკური მრუდის გრაფიკული დიფერენცირებით. შედეგების ანალიზმა აჩვენა, რომ რეაქციის აქტივაციის ენერგიის მნიშვნელობა აღნიშნულ პირობებში არის 10,8 კჯოული•მოლი⁻¹. ჩატერილი კინეტიკური განტოლება დამაკმაყოფილებელი სიზუსტით აღწერს ექსპერიმენტის შედეგებს რეაქციის საწყისი ეტაპებისათვის, როდესაც ძირითადად მიმდინარეობს არსენიტის ნაწილობრივი გადაეთერება ორატომიანი სპირტით.

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