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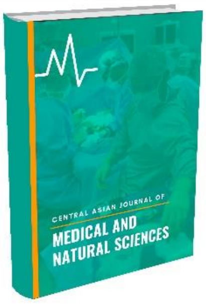

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SELECTION OF THE KINETIC EQUATION FOR THE SYNTHESIS OF PENTADECYLONITRILE AND DETERMINATION OF ITS CONSTANTS

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ABSTRACT: The kinetic and macro kinetic regularities of the synthesis of pentodecylonitrile from the corresponding alcohols and ammonia were studied, the kinetic equation for the synthesis of pentadecylonitrile was chosen, the kinetic constants were determined for various temperatures, the activation energy of the reaction and the values of the heats of adsorption of alcohol and water were calculated using kinetic constants, it was found that the equation more adequately describes the regularities deep degrees of transformation.

KEYWORDS: pentadecylonitrile, alcohol, ammonia, catalyst, kinetic equation, kinetic constants, water vapor, adsorption constant.

INTRODUCTION

In recent years, substances that were previously difficult to obtain, now one of the main tasks in the world is to study the physical and chemical properties of new substances obtained and on their basis introduce them in various sectors of the national economy. In recent years, technologies for producing various polymers containing the nitrile group have been rapidly developing.

Many countries have developed various effective methods for producing NITRILES. In particular, NaN_3 aldehydes as a result of the Schmidt reaction in the presence of triflic acid (CF_3SO_3H) [1], in the presence of the solvent dimethyl sulfoxide (DMSO) as a result of the reaction of aldehydes with hydroxylamine [2], from the corresponding alcohol and ammonia [3], aliphatic, aromatic, heteroaromatic, allylic and propargyl alcohols in interaction with the source NITRILES were synthesized in the presence of tertiary butyl HYPOCHLORITE, dioxide, and 3-diode 5,5-dimethyl hydantoin (DCM) [5,6,7]. Not all developed methods can be used in the industrial production of nitrile, and there are good reasons for this. In this regard, the development of new methods for the synthesis of NITRILES, the selection of highly effective catalysts, and the study of thermodynamic, macro kinetic, and kinetic regularities of the processes are urgent tasks of our time [8,9].

When comparing the kinetics of aliphatic and aromatic alcohols in the presence of iron sulfide and the NTC-4 catalyst, as well as the results of our experiments on cyanidation of high aliphatic alcohols, we can see the following generality: when the partial pressure of alcohol changes from 0.007 to 0.019 MPa in the studied range of temperature and volume velocity, the degree of conversion of alcohol into nitrile decreases. At the same time, at a constant value of the volume velocity, the graph of the degree of conversion of alcohol to nitrile and its dependence on the partial pressure passes through the maximum. Besides, in the studied range of partial pressures, the partial pressures of ammonia, hydrogen, and nitrile do not affect the rate of the nitrile formation reaction[10]. Increasing the partial pressure of water vapor dramatically reduces the reaction rate. From this, we can conclude that, despite the differences in the structure of the initial alcohols and the composition of the catalysts used, the mechanism of formation of high-molecular NITRILES is exactly similar to the mechanism of formation of aliphatic and aromatic NITRILES. Therefore, the mechanism of the formation of high-molecular NITRILES can be expressed using the following equations:

1. $R\text{-}CH_2OH + Z \leftrightarrow R\text{-}CH_2OHZ$
2. $NH_3 + Z \leftrightarrow NH_3Z$
3. $R\text{-}CH_2OHZ + Z \rightarrow R\text{-}CHOZ + H_2\,Z$
4. $R\text{-}CHOZ + NH_3Z \leftrightarrow R\text{-}CH{=}NHZ + H_2OZ$
5. $R\text{-}CH{=}NHZ + Z \leftrightarrow R\text{-}CNZ + H_2\,Z$
6. $R\text{-}CNZ \leftrightarrow R\text{-}CN + Z$
7. $H_2OZ \leftrightarrow H_2O + Z$
8. $H_2\,Z \leftrightarrow H_2 + Z$

where R –$C_{14}H_{29}$, Z- active center of the catalyst.

Here, as also recognized by previous authors, the reaction of dehydrogenation of the initial alcohol in the presence of two active centers of the catalyst proceeded as the slowest stage of the process. The following kinetic equation corresponds to the above regularities,

$$W = \frac{k\ \ K_{RCH_2\,OH}P_{RCH_2\,OH}}{(1 + K_{RCH_2OH}P_{RCH_2\,OH} + K_{H_2O}P_{H_2O})^2}\,, \qquad (1)$$

where W - is the reaction rate of nitrile formation, mol/kg cat. h; k-is the reaction rate constant, mol/kg cat. h; $K_{RCH_2\,OH}$- coefficient of adsorption; $P_{RCH_2\,OH}$- the partial pressure of alcohol, МПа$^{-1}$, МПа; $K_{H_2O}P_{H_2O}$ - is the coefficient of adsorption and $P_{RCH_2\,OH}$ - partial pressure of water, МПа$^{-1}$, МПа.

We need to determine whether this equation corresponds to the experimental values obtained under differential reactor conditions. To do this, we can reduce equation-1 to the following straight-line equation:

$$\sqrt{\frac{P_{RCH_2\,OH}}{W}} = \frac{1}{\sqrt{k \cdot K_{RCH_2\,OH}}} + \sqrt{\frac{K_{RCH_2\,OH}}{k}} * P_{RCH_2\,OH} \qquad (2)$$

Equation 2 for the case when an additional amount of water is added to the reaction zone is as follows:

$$\sqrt{\frac{P_{RCH_2\,OH}}{W}} = \frac{1 + K_{RCH_2\,OH}P_{RCH_2\,OH}}{\sqrt{k \cdot K_{RCH_2\,OH}}} + \frac{K_{H_2O}}{\sqrt{k \cdot K_{RCH_2\,OH}}} * P^0_{H_2O}(3)$$

If the kinetic equations 2 and 3 fair to describe experimental data, in the coordinates $\sqrt{\frac{P_{RCH_2\,OH}}{W}} - P_{RCH_2\,OH}$ and $\sqrt{\frac{P_{RCH_2\,OH}}{W}} - P^0_{H_2O}$ straight lines must be formed. Figures 1 and 2 show the processing results in a graphical state. As seen in Fig. 2 and 3 in the studied range of parameters (temperature, the partial pressure of alcohol and water), the experimental results fit satisfactorily on straight lines, which indicates the applicability of equations 2 and 3 to describe the kinetic laws of the reaction under study.

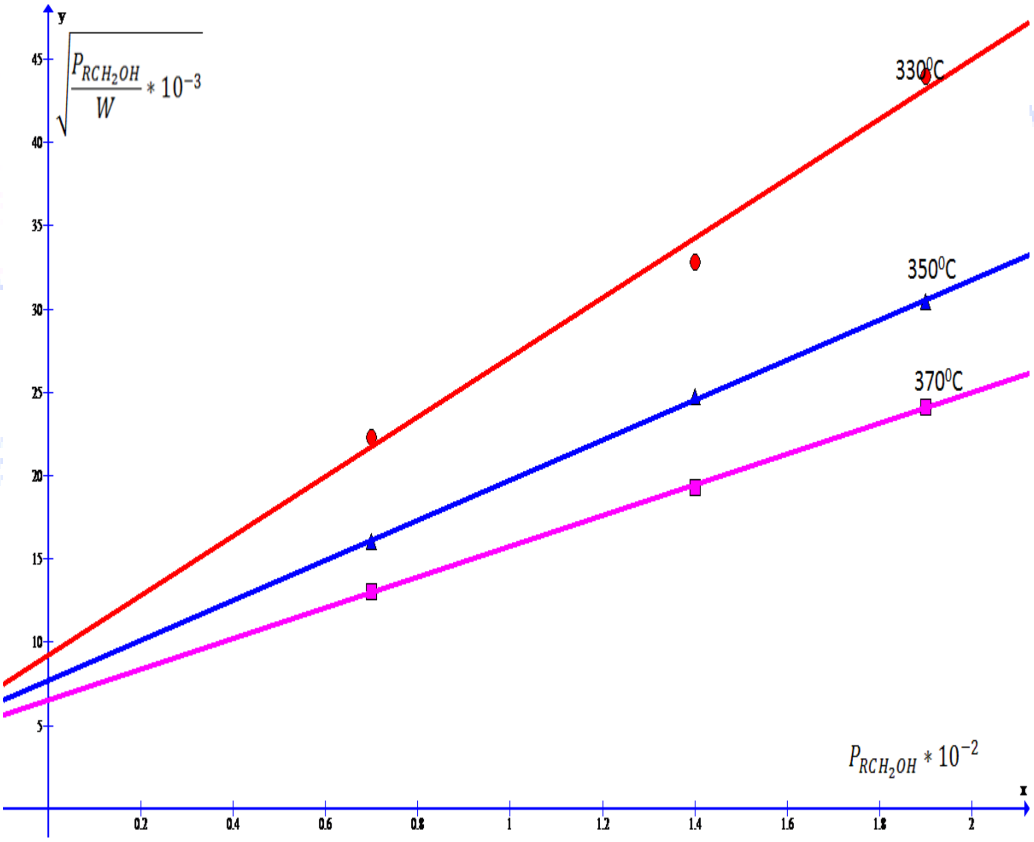

Figure-1. Processing of experimental data in the coordinates of equation 2

Using values in the temperature range 330-370^0 C From figures 1-2, the adsorption coefficients of alcohol and water and the rate constants of the cyanidation reaction of pentadactyl alcohol were calculated. The results are presented in Table 1.

Table 1. Values of kinetic constants for different temperatures

№	Temperature, ^{0}C	*k* ±5, mol/kg cat. hour	K_{RCH_2OH}±5, MPa^{-1}	K_{H_2O}±5, MPa^{-1}
1.	330	58,0	185,0	220,0
2.	350	108,0	170,0	195,0
3.	370	170,0	160,0	174,0

Using the values given in table 1, the activation energy of the reaction (63.0 ± 2 kJ / mol) and the heat of adsorption of alcohol (10.0 ± 0.4 kJ / mol) and water (14.5 ± 0.4 kJ / mol) were calculated.

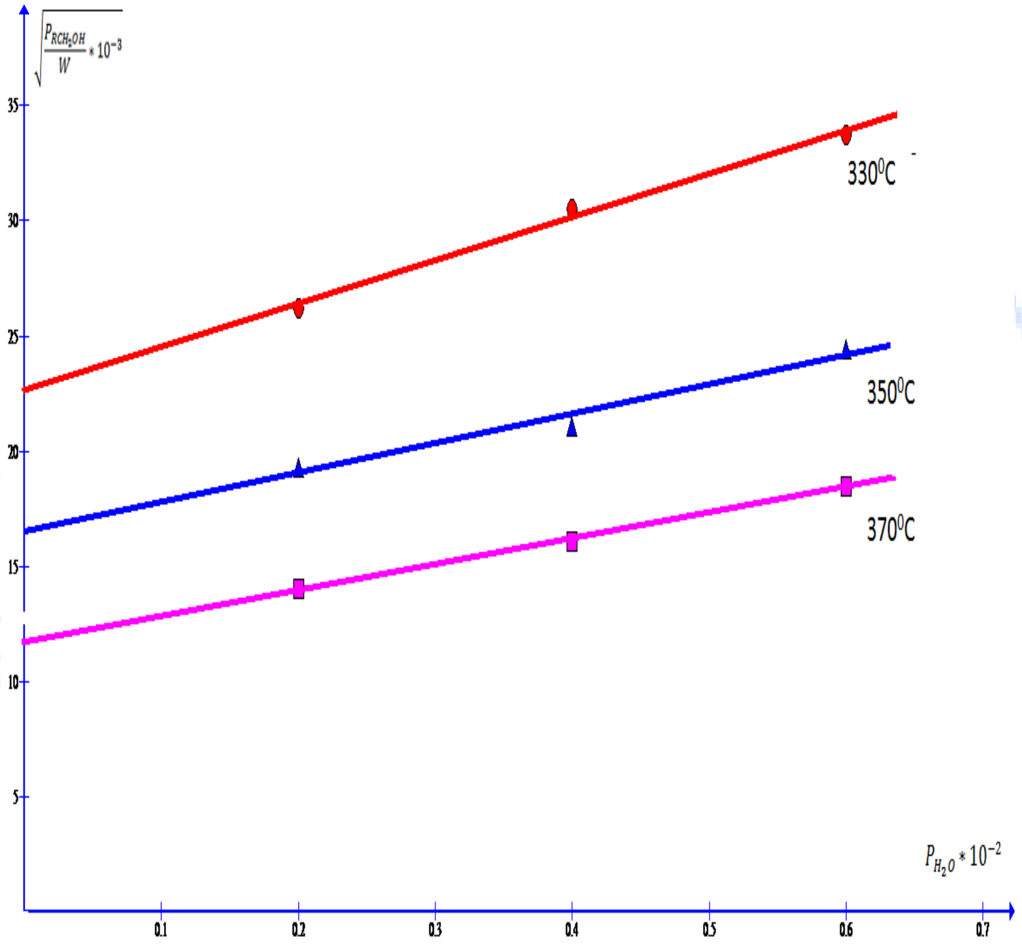

Figure 2. Processing of experimental data in the coordinates of equation 3.

It was necessary to additionally check the applicability of the obtained equation (1) to describe the kinetics of the cyanidation reaction of pentadactyl alcohol with ammonia for deeper degrees of transformation.

Equation (1), taking into account the degree of conversion of the initial alcohol, can be presented in the following form:

$$W = \frac{k\,K_{RCH_2OH}P_0(1-x)}{[1+K_{RCH_2OH}P_0(1-x)+K_{H_2O}P_0x]^2}\;(4)$$

where, $P_0 -$ is the initial partial pressure of the alcohol, MPa.
$x -$ the degree of conversion of alcohol.
After integrating equation (1), we have:

$$\tau = \frac{1}{v} = \frac{1}{k\,K_{RCH_2OH}}\left\{\begin{matrix}\dfrac{(1+P_0K_{H_2O})^2}{P_0}\ln\dfrac{1}{1-x} - \left(K_{H_2O}-K_{RCH_2OH}\right) * \\ * \left(2+K_{H_2O}P_0+K_{RCH_2OH}P_0\right)x - 0{,}5P_0x^2\left(K_{H_2O}-K_{RCH_2OH}\right)^2\end{matrix}\right\}(5)$$

Using the values of the reaction rate constants and the adsorption coefficients of pentadactyl alcohol and water shown in table 1, the conditional contact time was calculated using equation (5) for temperatures 330, 350, and 370^{0}C.

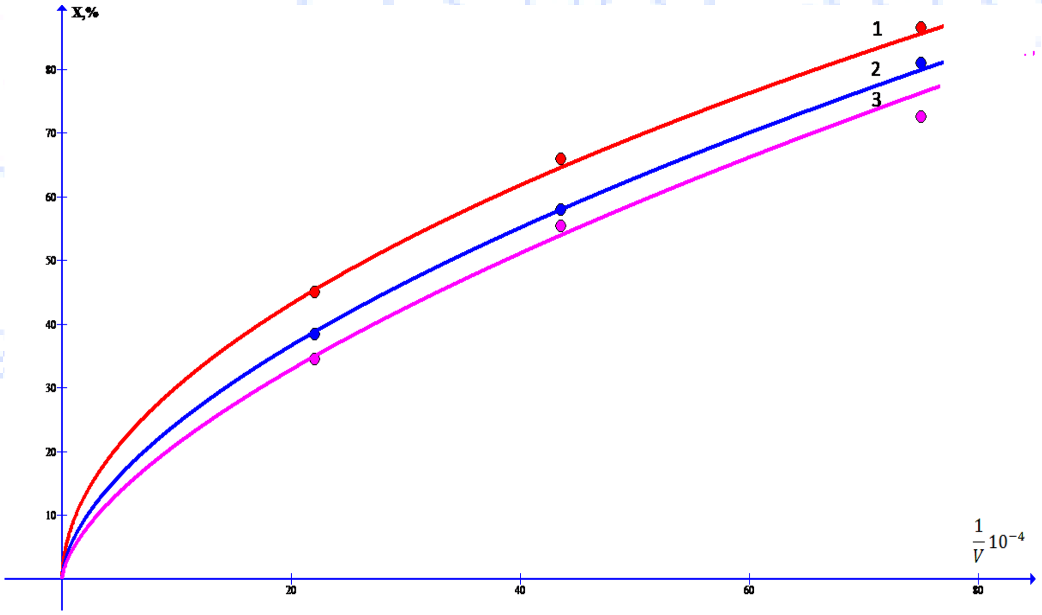

Figure 3. Comparison of calculated and experimental data on the effect of the partial pressure of pentadactyl alcohol on the degree of its conversion to pentadactylonitrile (t=350^{0}C, $P_{general}$-0,1 MPa, P_{NH_3} –0,078 MPa). 1- P_{RCH_2OH}=0,007 MPa , 2- P_{RCH_2OH}=0,014 MPa, 3- P_{RCH_2OH}=0,019 MPa

As an illustration, figure 3 shows a comparison of calculated and experimental data on the effect of the partial pressure of alcohol on the degree of its conversion to nitrile for a temperature of 350^{0}C. As can be seen from figure 3, these values are in good agreement with each other (the value of the standard deviation is 12.3%), which indicates the possibility of applying the integral form of equation (1) for deep degrees of the transformation of the initial alcohol.

CONCLUSIONS

1. The selected kinetic equation for the synthesis of pentadecanolide, which is described by the equation:

$$W = \frac{k \cdot K_{RCH_2\,OH} P_{RCH_2\,OH}}{(1 + K_{RCH_2 OH} P_{RCH_2\,OH} + K_{H_2O} P_{H_2O})^2}.$$

2. Kinetic constants were determined for different temperatures.
3. Using the found values of kinetic constants, the activation energy of the reaction (63.0±2 kJ/mol) and the values of the heat of adsorption of alcohol (10.0±0.4 kJ/mol) and water (14.5±0.4 kJ/mol) are calculated.

It is Established that the equation adequately describes the regularities in the deeper degrees of transformation (30-100%).

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