

On the Ratio of the rate Constants of Successive Stages in the Reaction Oxyethylation of Alcohols

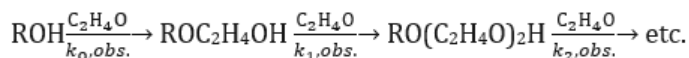
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Received: April 11, 2022; Published: April 19, 2022

The reaction of oxyethylation of alcohols in general can be represented by the following scheme



This is an irreversible reaction consistent with alcohol, which can have many stages, but in this case we are talking about the first two stages of this reaction.

The kinetics of this reaction is investigated in /1/. In this work, it is shown that under the conditions of basic catalysis at the initial site, the reaction rate has the first orders of magnitude in terms of the concentration of the catalyst and ethylene oxide. The expected first order of alcohol concentration is not observed, but some kind of incomprehensible dependence is observed. All the authors who have studied the kinetics of this reaction agree that the difficulties associated with describing the kinetics of this reaction depending on the concentration of alcohol are explained by the association of alcohol molecules due to the formation of hydrogen bonds.

In works /2-4/, the kinetics of the oxyethylation reaction of primary alcohols of the normal structure of the composition C1-C7 and C10 was studied. It is established that in a flow reactor of ideal mixing, the reaction rate at the initial site is described by equation (1), which takes into account the association

$$W = (C_o^\circ - C_o) / \tau = k_{o,obs.} \cdot C_k \cdot C_o \cdot (C_c^\circ - nC_1) \quad (1)$$

Where W is the reaction rate determined by the decrease of ethylene oxide (OE) ; C_o° and C_o are the concentrations of OE in the initial mixture and in the reactor, respectively; τ - is the residence time of the reaction mixture in the reactor; $k_{o,obs.}$ - the observed rate constant of the first reaction stage; C_k and C_1 are the concentrations in the reactor of the catalyst and the first reaction product, respectively; C_c° is the concentration of alcohol in the initial mixture; n is a constant depending on temperature and alcohol concentration, which will be interpreted later as the average number of alcohol molecules in a linear chain alcohol associate /2-4/. With the right side of equation (1), identical transformations can be performed by dividing and multiplying it by n. We obtain equation (2)

$$W = (C_o^\circ - C_o) / \tau = k_{o,obs.} \cdot n \cdot C_k \cdot C_o \cdot (C_c^\circ / n - C_1) = k_{o,n} \cdot C_k \cdot C_o \cdot C_{Ass}. \quad (2)$$

Where the expression in parentheses indicates the first order of concentration of linear chain alcohol associates - C_{Ass} . Thus, the description of the kinetics of the reaction of oxyethylation of alcohols is possible according to equation (1) with $k_{o,obs.}$ and according to equation (2) with $k_{o,n} = k_{o,obs.} \cdot n$. Which description is more correct. Equation (2) with a constant that includes n should be more correct. But how to prove it.

Since the yield of the second reaction product did not exceed 9%, and in the vast majority of experiments 5-6% of the yield of the first reaction product /2-4/, this was neglected in equation (1) $k_{1,obs.}$ not included. However, there is always a second reaction product in the primary experimental data. This allows us to find the ratio of velocity constants.

The ratio of the rate constants of successive stages for constants related to the gross alcohol concentration is calculated by the formula

$$k_{1,obs.}/k_{o,obs.} = C_c C_2 / (\Delta C_1 + C_2) C_1 \quad (3)$$

Where $\Delta = C_1 - C_1^0$; C_c - alcohol concentration in the reactor; C_{1o} - concentration of the first product at the reactor inlet; C_2 - concentration of the second product in the reactor. For n-butanol at 100°C $k_{o, obs.} = 8 \times 10^{-3} \text{ L}^2/\text{mol}^2 \text{ s}$; $k_{1, obs.}/k_{o, obs.} = 2.25 / 2$. Therefore, the rate constant of the oxyethylation reaction of ethylene glycol monobutyl ether should be equal to $k_{1, obs.} = 1.8 \times 10^{-2} \text{ L}^2 / \text{mol}^2 \text{ s}$. In fact, it turns out to be nine times smaller than $k_{1, obs.} = 2.0 \times 10^{-3} \text{ L}^2 / \text{mol}^2 \text{ s}$. We got this result with constants that do not take into account the value of the parameter n. If we go to the constants $k_{o,n}$ and considering that for butyl alcohol $n = 16.5$ and for ethylene glycol monobutyl ether $n \approx 1 / 2$ we get $k_{1,n}/k_{o,n} = 0.136$. This leads to a value of $k_{1,n} = 1.1 \times 10^{-3} \text{ L}^2 / \text{mol}^2 \text{ s}$, which is only ~ 2 times less than the expected value. This result is obtained at $n \approx 1$ for ethylene glycol

monobutyl ether. If we take $n = 1,4$, which is quite possible, we get an absolute match experimental and calculated constant. This is proof that constants that do not contain the parameter n are apparent and do not reflect the true reactivity of these compounds.

The same conclusion can be reached by considering the ratio of the constants of successive stages during the reaction in a solvent.

Table 1 shows the ratio of the rate constants of successive stages for the oxyethylation reaction of butanol and hexanol in dodecane, calculated based on the constants related to the gross concentration of alcohol and the constants related to the concentration of associates.

Table 1. The ratio of the rate constants of the butanol and hexanol oxyethylation reaction in dodecane, calculated based on the constants related to the gross alcohol concentration and the constants related to the concentration of associates.

| BUTANOL | | | | | | |
|-------------------------|------|------|------|------|------|------|
| C_c mol/L | 0,63 | 1,0 | 2,16 | 4,39 | 6,44 | 9,44 |
| $k_{1,obs.}/k_{o,obs.}$ | 0,67 | 0,92 | 1,79 | 2,33 | 2,06 | 2,23 |
| n | 4,4 | 7,5 | 16,7 | 17,0 | 16,6 | 16,5 |
| $k_{1,n}/k_{o,n}$ | 0,14 | 0,13 | 0,13 | 0,14 | 0,12 | 0,13 |
| HEXANOL | | | | | | |
| C_c mol/L | 0,89 | 1,95 | 3,12 | 4,67 | 6,05 | 7,21 |
| $k_{1,obs.}/k_{o,obs.}$ | 0,95 | 1,45 | 2,20 | 2,16 | 2,23 | 2,27 |
| n | 4,5 | 8,5 | 11,0 | 12,0 | 10,6 | 10,8 |
| $k_{1,n}/k_{o,n}$ | 0,21 | 0,17 | 0,20 | 0,18 | 0,21 | 0,21 |

As can be seen from the table, the ratio $k_{1,obs.}/k_{o,obs.}$ depends on n, and the ratio $k_{1,n}/k_{o,n}$ shows satisfactory constancy regardless of n.

This once again confirms the previously made conclusion that the observed rate constants attributed to the gross alcohol concentration do not reflect the real reactivity of these compounds, and the constants attributed to the concentration of alcohol associates do.

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