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Association-Assisted Kinetics of Pentanol-1 and Heptanol-1 Oxyethylation: Kinetic Parameters of Reactions and Association Parameters of Alcohols in the Series Butanol-1–Heptanol-1

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Abstract—The kinetics of pentanol-1 and heptanol-1 oxyethylation in the absence and in the presence of solvents (dodecane, *p*-xylene, and 1,4-dioxane) is studied under the conditions of base catalysis at 80–150°C and the concentrations of the catalyst (the corresponding sodium alkoxide) and ethylene oxide in the starting mixture of ~1 and 10^{-3}–10^{-1} mol/l, respectively. The experimental results are adequately described by the rate law that takes into account the association of alcohol molecules via hydrogen bonds. A hypothesis is advanced that an associate consisting of *n* alcohol molecules acts as a kinetically independent species in this reaction. The kinetic and association parameters for alcohols in the C_4–C_7 series are compared with the published data.

In general, alcohol oxyethylation can be represented by the following scheme:

$$\mathrm{ROH} \xrightarrow[k_{0,\,\mathrm{app}}]{C_2H_4O} \mathrm{ROC_2H_4OH} \xrightarrow[k_{1,\,\mathrm{app}}]{C_2H_4O} \mathrm{RO(C_2H_4O)_2H} \xrightarrow[k_{2,\,\mathrm{app}}]{C_2H_4O} \text{etc.} \qquad \text{(I)}$$

The kinetics and mechanism of this reaction has been studied by several researchers, and these results were reviewed by Shvets and Tsivinskii [1]. They showed that, under the conditions of base catalysis at certain high alcohol concentrations, the reaction rate is described by the rate law that is first-order with respect to the concentrations of the reactants and catalyst. Deviations from this rate law are due to the dependence of the association degree of alcohol on its concentration. Shvets and Tsivinskii also presented the reaction mechanism supporting this rate law.

Earlier, we investigated the kinetics of oxyethylation of butanol-1 [2] and hexanol-1 [3] and showed that the higher the product yield in the first step of reaction (I), the lower the apparent first-order rate constant of the reaction, other conditions being the same. We also found that, if the contribution of the second step of reaction (I) to the overall rate of ethylene oxide (EO) consumption can be neglected at the concentrations and conversions studied, the experimental results are adequately described by the following equation:

$$w = k_{0,\,\mathrm{app}} C_{\mathrm{Cat}} C_{\mathrm{EO}} (C_{\mathrm{o,\,alc}} - nC_{\mathrm{I}}), \qquad (1)$$

where w is the reaction rate determined from ethylene oxide consumption; $k_{0,\,\mathrm{app}}$ is the apparent rate constant of the first reaction step; C_{Cat}, C_{EO}, and C_{I} are the concentrations of the catalyst, ethylene oxide, and the corresponding ethylene glycol monoether in the reactor, respectively; $C_{0,\,\mathrm{alc}}$ is the alcohol concentration in the starting mixture; and n is a temperature-dependent constant, which does not change in the series of experiments with nearly the same alcohol concentration but does changes when the alcohol concentration varies over wide limits.

Equation (1) is valid on the following assumptions.

1. The alcohol molecules bind into linear (noncyclic and nonbranched) associates via hydrogen bonds, and the average number of molecules in the associates is equal to n.

2. The reaction involves hydroxy groups of only terminal alcohol molecules in the associates, whose reactivity is characterized by the average rate constant $k_{0,\,n}$.

3. The molecules of the corresponding ethylene glycol monoethers formed in the reaction remain in the associates and terminate them because these molecules are less reactive [2, 4].

Statements 2 and 3 require additional comments. Statement 2 implies that the reaction involves only one of the two terminal alcohol molecules of the associate. The proton of this molecule does not participate in the formation of a hydrogen bond. Statement 3 is necessary to explain the observed deviation from the first-order kinetics with respect to alcohol. If the ether molecule were not involved in the associate or were present inside the alcohol cycle, the reaction would follow the first-order kinetics. Statement 3 is indirectly supported by the fact that, unlike alcohols, the molecules of ethylene glycol monoethers can form both intermolecular and intramolecular hydrogen bonds [5]. Therefore, the molecules of these compounds in an alcohol solution can form only one intermolecular hydrogen bond and complete the chain of alcohol molecules but cannot be inside the chain.

Table 1. Experimental data for pentanol-1 oxyethylation in the absence of solvents at 100°C

τ, min	Concentration, mol/l						$k_{0,\text{app}} \times 10^3$, l^2 mol^{-2} s^{-1}	
	$C_{\text{Cat}} \times 10^2$	$C_{0,\text{EO}}$	C_{EO}	C_{alc}	C_{I}	C_{II}	$n = 1$	$n = 13.7$
9.3	0.330	0.96	0.89	7.94	0.07	–	5.38	6.05
9.3	1.257	0.96	0.79	7.83	0.15	0.008	3.91	5.16
9.3	2.514	0.96	0.70	7.75	0.22	0.019	3.41	5.32
9.3	5.280	0.95	0.57	7.66	0.31	0.033	2.94	6.01
9.3	0.628	0.98	0.87	7.88	0.10	0.003	4.58	5.46
4.2	0.628	0.94	0.88	7.95	0.06	–	5.42	5.99
18	0.628	0.98	0.80	7.82	0.16	0.009	4.23	5.71
30	0.628	0.96	0.73	7.77	0.20	0.013	3.58	5.31
60	0.628	0.95	0.61	7.69	0.28	0.027	3.19	5.92

Note: τ is the residence time of the reaction mixture in the reactor; C_{Cat} is the catalyst concentration; $C_{0,\text{EO}}$ and C_{EO} are the initial and current ethylene oxide concentrations, respectively; and C_{alc}, C_{I}, and C_{II} are the current concentrations of alcohol, ethylene- and diethylene glycol monoethers, respectively. The initial concentration of alcohol in all the experiments was $C_{0,\text{alc}} = 7.98$–8.01 mol/l.

If the above assumptions are valid and molecular self-organization takes place, formula (1) can be interpreted as a first-order equation with respect to the associate concentration. Taking into account the low yields of the second reaction product (C_{II}), this equation takes the form

$$w = k_{0,n} C_{\text{Cat}} C_{\text{EO}} (C_{0,\text{alc}}/n - C_{\text{I}}), \qquad (2)$$

where, according to the above assumptions, the expression in parenthesis is the concentration of unreacted associates and $k_{0,n}$ is their average rate constant.

By setting $k_{0,n}/n = k_{0,\text{app}}$, we obtain an equation identical to Eq. (1). At $n = 1$ (the absence of association), $k_{0,n} = k_{0,\text{app}}$, and Eq. (2) transforms into a simple first-order equation with respect to the alcohol concentration. The application of Eq. (1) is constrained by the ranges of concentrations and conversions for which $C_{0,\text{alc}} > C_{\text{I}} n$.

Therefore, because of association, this reaction involves an associate consisting of n alcohol molecules rather than a separate alcohol molecule as a kinetically independent species, and the experimental data are adequately described by the rate law that is first-order with respect to the associate concentration rather than to the analytical concentration of alcohol. For this interpretation of the reaction mechanism, it is quite important to estimate the lifetime of the alcohol associate. Experiments [6] showed that the lifetime of the methanol associates $(CH_3OH)_n$ (where $n = 5$–20) in the gas phase is 10^{-4}–10^{-5} s. For the liquid phase, the lifetime should be one to two orders of magnitude higher and close to 10^{-3} s due to the cage effect. This estimated lifetime of the associate is long enough for the elementary chemical act to occur, and the associate can participate as a kinetically independent species in this reaction.

We applied the above approach in this work to study the oxyethylation kinetics of two other alcohols: pentanol-1 and heptanol-1. Our results for the C_5 and C_7 alcohols and the data for the C_4 and C_6 alcohols from [2, 3] were compared with the available kinetic parameters for these reactions and estimated parameters of alcohol association. The goal of this comparison was to show that Eq. (1) correctly describes the reaction kinetics and that the association parameter n has the ascribed physical sense and is not merely a fitting parameter.

Kinetic experiments were carried out in a flow reactor at an excess pressure of 1.4 MPa. The kinetics of alcohol oxyethylation was studied in the absence and in the presence of solvents (dodecane, *p*-xylene, and 1,4-dioxane) at ethylene oxide concentrations in the starting mixture of ~1 mol/l. Commercial pentanol-1, heptanol-1, and solvents used in the experiments were purified by conventional procedures. Sodium *n*-pentyl- and *n*-heptyloxides, respectively, were used as catalysts. The experimental procedure was similar to that used in [2, 3].

Table 1 exemplifies primary experimental data on pentanol-1 oxyethylation in the absence of a solvent at 100°C.

Two series of experiments were carried out in which the reaction time and the catalyst concentration were varied (these series are framed in Table 1). The conditions of all kinetic experiments were chosen so that the yield of the second reaction product C_{II} was at most 10% of the yield of the first product C_{I} and equal to about 3–5% in most experiments. This allowed us to neglect the contribution of the second step of reaction (I) to the overall rate of ethylene oxide consumption and to process experimental data using Eq. (1). Table 1 presents the results of data processing and shows that the higher the yield of the first product C_{I}, the lower the $k_{0,\text{app}}$ values calculated by Eq. (1) with $n = 1$. The statistical processing of experimental data by Eq. (1) with $n \neq 1$ indicates that the least root-mean-square deviation of

Table 2. The parameters n, $k_{0,\,app}$, and $k_{1,\,app}/k_{0,\,app}$ in (*1*) pentanol-1 and (*2*) heptanol-1 oxyethylation in the absence of solvents at 80–150°C and the corresponding values of $-\Delta H^*$, E, and ΔE

t, °C	n		$k_{0,\,app} \times 10^3$, $l^2\ mol^{-2}\ s^{-1}$		$k_{1,\,app}/k_{0,\,app}$	
	1	*2*	*1*	*2*	*1*	*2*
80	15.7	10.4	2.04	1.80	2.38 ± 0.17	2.30 ± 0.16
100	13.7	9.6	5.66	5.49	2.50 ± 0.18	2.41 ± 0.20
125	11.0	9.1	14.9	17.3	2.66 ± 0.20	2.56 ± 0.17
150	9.7	8.0	39.3	45.0	2.80 ± 0.15	2.77 ± 0.21
	$-\Delta H^*$, kJ/mol		E, kJ/mol		ΔE, kJ/mol	
	8.6 ± 1.0	4.0 ± 0.8	53 ± 5	58 ± 5	3.4 ± 0.7	4.0 ± 0.8

Table 3. Kinetic parameters for oxyethylation and association parameters for C_4–C_7 alcohols

Parameter	Alcohol					Reference
	T_{exp}, °C	C_4	C_5	C_6	C_7	
$k_{0,\,app} \times 10^3$, $l^2\ mol^{-2}\ s^{-1}$	100	8.10	5.66	4.40	5.49	Our data
	100	7.86	4.80	4.67	5.08	[1]
E_{app}, kJ/mol	–	47 ± 4	61 ± 5	50 ± 5	62 ± 5	Our data
	–	60.3 ± 1.7	55.7 ± 1.3	61.6 ± 1.3	61.6 ± 1.3	[1]
$k_{1,\,app}/k_{0,\,app}$	100	2.23 ± 0.08	2.50 ± 0.18	2.27 ± 0.06	2.41 ± 0.20	Our data
	90	2.20 ± 0.20	2.48 ± 0.06	2.49 ± 0.08	2.75 ± 0.14	[7]
n	100	16.5	13.7	10.9	9.6	Our data
	20	15	13	11	10	[8]
$-\Delta H^*$, kJ/mol	–	11.0 ± 1.3	8.6 ± 1.0	5.0 ± 1.0	4.0 ± 0.8	Our data
	–	11.3 ± 0.3	–	–	–	[8]

the rate constant and its satisfactory constancy are observed at $n = 13.7$ and $k_{0,\,app} = (5.66 \pm 0.35) \times 10^{-3}\ l^2\ mol^{-2}\ s^{-1}$.

Table 2 summarizes the association parameters and kinetic characteristics thus obtained for pentanol-1 and heptanol-1 oxyethylation in the absence of solvents at 80–150°C, as well as the values of E, ΔE, and $-\Delta H^*$ reflecting their variations with temperature. The approximate or conventional ΔH^* values were calculated by processing the $\ln n$ vs. $1/T$ plots, where T is the absolute temperature. The ΔH^* values thus calculated allow us to compare our results with the available data on the n values at various temperatures. The ratio of the rate constants of the consecutive steps of reaction (I) were calculated by the equation

$$k_{1,\,app}/k_{0,\,app} = C_{alc}C_{II}/C_I(C_I + C_{II}). \qquad (3)$$

The kinetic parameters for the oxyethylation of the C_5 and C_7, as well as for the C_4 and C_6 alcohols [2, 3], agree well with the available kinetic parameters for these reactions. This is supported by the data of Table 3.

Note that the kinetics of alcohol oxyethylation was investigated in [1] at much (~3 times) lower initial concentration of ethylene oxide and, hence, lower yields of the product C_I without any deviations from the first-order kinetics in this case.

The ratio of the rate constants of the consecutive steps, listed in Tables 2 and 3, ranges from 2.2 to 2.8. This is consistent with the above assumption (statement 3) concerning the lower reactivity of monoether compared to that of the corresponding alcohol. This ratio is apparent [2, 4] because it was obtained without considering alcohol molecule association. To consider association, one should substitute the alcohol concentration (C_{alc}) by the associate concentration (C_{alc}/n) in Eq. (3). The effective ratio of the rate constants thus determined is 10–15 times lower, which agrees with the assumption made in statement 3.

Figures 1 and 2 illustrate how the association parameter and the apparent rate constant depend on the alcohol concentration in dodecane at 100°C. Figure 1 shows that the parameter n monotonously decreases on passing from butanol-1 to heptanol-1, and the corresponding curves for all of the alcohols are similar. Taking into account that the parameter n correlates with the activity coefficients for the C_4 and C_6 alcohols, we might expect [9] similar correlations for the C_5 and C_7 alcohols. The curves illustrating the dependence of the

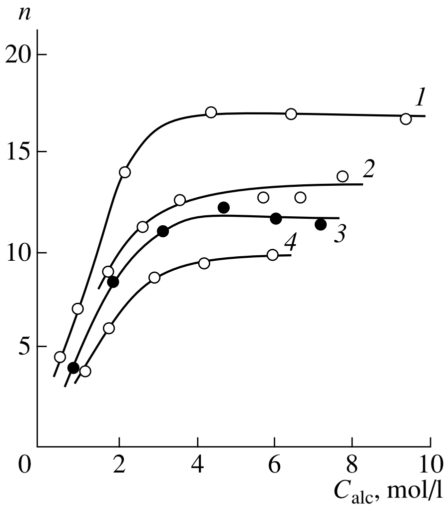

Fig. 1. The parameter n as a function of the average alcohol concentration in dodecane at 100°C: (*1*) butanol-1 [2], (*2*) pentanol-1, (*3*) hexanol-1 [3], and (*4*) heptanol-1.

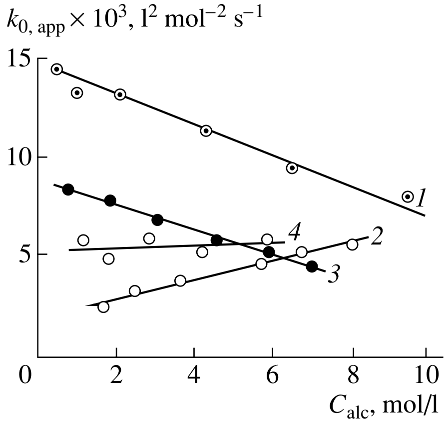

Fig. 2. The $k_{0,\,app}$ parameter as a function of the average alcohol concentration in dodecane (the designations are the same as in Fig. 1).

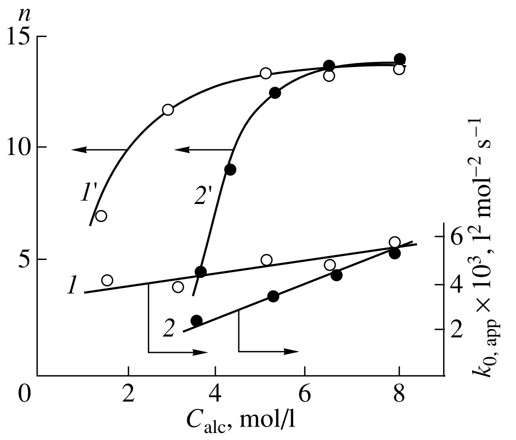

Fig. 3. The parameters $k_{0,\,app}$ and n vs. the average concentration of pentanol-1 in (*1*, *1*′) *p*-xylene and (*2*, *2*′) 1,4-dioxane at 100°C.

$k_{0,\,app}$ value on the alcohol concentration in dodecane for the C_5 and C_7 alcohols given in Fig. 2 substantially differ from the relevant curves for the C_4 and C_6 alcohols. The strong dilution of the two latter alcohols causes an approximately twofold increase in the rate constant compared to that for pure alcohol, whereas for the C_7 alcohol the rate constant remains almost unchanged and for the C_5 alcohol it nearly halves. We still cannot explain this fact and relate it to the even or odd number of carbon atoms in the alcohol molecule.

Figure 3 shows how the parameters $k_{0,\,app}$ and n vary with the pentanol-1 concentration in two other solvents, *p*-xylene and dioxane. The curves for these parameters obtained for xylene are very close to the relevant curves for pentanol-1 in dodecane (Figs. 1, 2). In dioxane solutions, a dramatic decrease in the association degree at $C_{alc} \le 5$ mol/l and a more drastic decrease in the $k_{0,\,app}$ value are observed upon alcohol dilution.

Our results on the effect of solvent on the association degree of pentanol-1 agree with the solvent classification suggested in [10]. According to this classification, dodecane is referred to as a solvent favoring association, xylene is an inert solvent, and dioxane is an associate-destroying solvent.

Note that the dependence of the $k_{0,\,app}$ value on the pentanol-1 concentration in dioxane is quite similar to that in solutions of ethylene oxide [1] used both as a solvent and as a reactant. This coincidence is not surprising because ethylene oxide and dioxane have very similar structures.

It is interesting to compare our association parameters for alcohols with those estimated earlier. The X-ray scattering data for alcohol solutions suggest that n = 100–200 [11]. The average association degree of alcohols is estimated in [12] to be n = 10–100. Our values (Table 3) belong to this interval. Note that the available average association degrees for alcohols were obtained for room temperature, whereas our values correspond to 100°C. The extrapolation of our values of n to room temperature using ΔH^* put them nearly in the middle of the interval suggested in [12].

Table 3 presents the average association degrees for the C_4–C_7 alcohols obtained in the study of their solutions by dielectric and acoustic spectroscopy at 20°C [8]. These results almost coincide with our values at 100°C. In this case, the ΔH^* values for butanol-1 are also identical. The coincidence of the ΔH^* values for other alcohols suggests that the same physical parameter is measured in both cases, but with different calibration coefficients.

Our findings suggest that our values of the average association degrees for the C_4–C_7 alcohols agree well with their available estimates.

Thus, the main conclusion of this work concerns the applicability of the proposed rate law, which considers the association of alcohols, correctly describes the kinetics of their oxyethylation, and provides information on the microheterogeneous structure of the liquid phase.

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