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Calorimetric analysis of the ethanolysis of 1,2-epoxybutane[1]

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Abstract

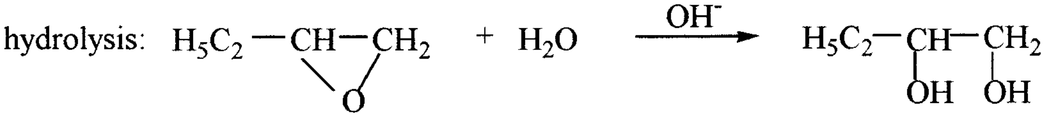
Polyethers, which are produced by alcoholysis of oxiranes, are often used as solvents in chemical plants. The spectra of the products can be influenced by the choice of the catalyst (acid or base). The results of the base-catalyzed ethanolysis of 1,2-epoxybutane are displayed. The reaction was investigated calorimetrically by varying the molar ratio between ethanol and 1,2-epoxybutane, the starting temperature and the concentration of the catalyst sodium hydroxide. Additionally, the influence of the used alcohol will be shown in one example. To determine the activation parameters, the experiments were evaluated by the nonlinear software package TA-kin v3.3. © 1998 Elsevier Science B.V.

Keywords: 1,2-epoxybutane; Alcoholysis; Calorimetry; Nonlinear kinetic evaluation

1. Introduction

Polyglycoles and polyglycolethers are solvents widely used in chemical synthesis. These compounds are formed by hydrolysis (polyethers) or by alcoholysis (polyglycolethers) of oxiranes, mainly ethylene oxide and propylene oxide.

It is remarkable, that the non-catalytic process can be realized only under extreme conditions, e.g. high pressure. Therefore, catalysts have to be employed. Its kind, acid or base, determines the product spectra. In contrast to the acid catalysis, the base type gives a well-defined reaction. Due to this fact, many papers were published on this topic. A lot of investigation deals with the catalyzed hydrolysis as well as alcoholysis. Not so many results could be obtained by the non-catalyzed processes. One example for this is the



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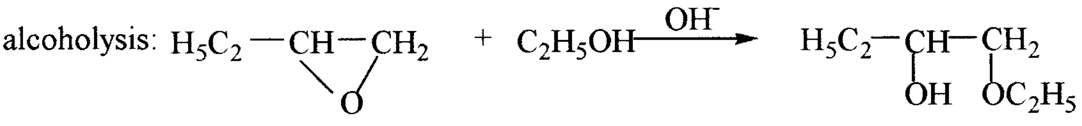

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paper by Pritchard and Siddiqui [1], where the activation parameters and the mechanism of the acid-catalyzed hydrolysis of oxiranes is investigated. It can be shown, that the first reaction step is a ring opening reaction, followed by the addition of a water molecule. The non-catalytic, acid-catalyzed and base-catalyzed reactions of propylene oxide with ethanol were investigated by Chitwood and Freure [2]. A well-defined reaction mixture has been obtained only in the case of a base catalyst. The reaction products have been separated by distillation. It is noteworthy that temperatures of about 245°C are necessary for the non-catalytic process.

Ethylene oxide or propylene oxide were not applicable because we wanted to measure in the liquid phase, under normal pressure. Therefore, the following results are related to the conversion of ethanol with 1,2-epoxybutane. As a catalyst, sodium hydroxide was chosen and ethanol was used in molar surplus. Under these conditions, the monoglycolether is mainly formed, following Eq. (2). This is important for the kinetic evaluation of this reaction below.

2. Experimental

For the investigation of the alcoholysis of 1,2-epoxybutane, a modified isoperibolic calorimeter was used [3]. Since the calorimeter was constructed of stainless steel, the transition of the temperature between the content of the reactor and the calorimeter was improved. For measuring and recording of the temperature data, the hard- and software of the ACTRON-calorimeter [4] have been employed.

The reaction was carried out without a solvent, so that an endothermic mixing peak of about 6 K could not be avoided. This temperature decreased whilst the mixing process became nearly independent of the reaction conditions. The reaction volume was about 60 ml. The starting temperature, the molar ratio between ethanol and oxirane, the amount of sodium hydroxide and the alcohol were varied. The experimental conditions are given as follows:

n(ethanol) : n(oxirane) = 3 : 1/2 : 1/1.5 : 1
starting temperature = 40°C/35°C/30°C/25°C
catalyst(NaOH) = 1.3 g/1 g/0.7 g/0.4 g/0.1 g/0 g
alcohol = ethanol/n-propanol/i-propanol/n-butanol

Fig. 1 shows the calorimetric curves of the ethanolysis on varying the molar ratio of oxirane and ethanol at a starting temperature of about 35°C. On comparing the maximum temperature jumps in case of 3 : 1 with that of 2 : 1 it is to be noticed, that the difference is only 1 K . In case of the ratio 1.5 : 1, the maximum temperature jump was about 9 K. This demonstrates the decreasing reaction rate with the excess of ethanol.

Varying the starting temperature it is expected that the reaction rate would increase with the temperature, which is demonstrated in Fig. 2. In case of 25°C, the reaction rate is relatively low, the temperature decrease beyond the maximum is only 1 K in 14 000 s. At a starting temperature of 30°C, the reac-

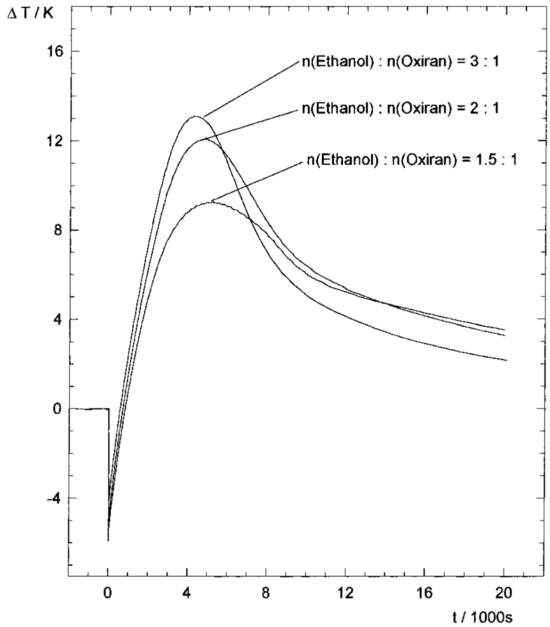


Fig. 1. Influence of the molar ratio n(EtOH) : n(Oxiran) $T_0 = 35°C$; [NaOH] = 0.548 mol/l.

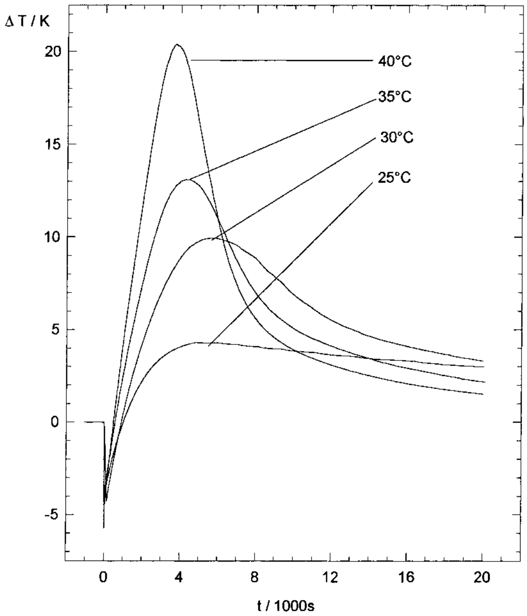


Fig. 2. Influence of the starting temperature; n(EtOH) : n(Oxiran)=3 : 1; [NaOH] = 0.548 mol/l.

tion rate increases and, thus, the conversion of the oxirane grows. A further increase in the starting temperature has only a proportionate influence on the reaction behavior, but not exponential.

As shown above [2], a reaction without a catalyst is possible only under extreme conditions. Therefore it is important to know at which minimum concentration the catalyst sodium hydroxide is necessary for a reaction. This is shown in Fig. 3. It is relevant, that the time to reach the temperature maximum is nearly the same for all calorimetric curves. On comparing the non-catalytic reaction with that of 0.042 mol/l sodium hydroxide as catalyst, it is observed that the step from 0.000 to 0.042 mol/l sodium hydroxide is sufficient to start the reaction, even if the reaction rate is very low. On increasing the amount of sodium hydroxide further, up to 0.169 mol/l, the temperature increase in the reaction is nearly equal to the temperature decrease of mixing, but a visible increase of the reaction rate occurs for the first time when 0.295 mol/l of sodium hydroxide is added.

To determine the influence of the kind of alcohol, several experiments have been made at a molar ratio alcohol : oxirane=1.5 : 1 and mass of sodium hydroxide of 0.295 mol/l. In Fig. 4 it is shown that the

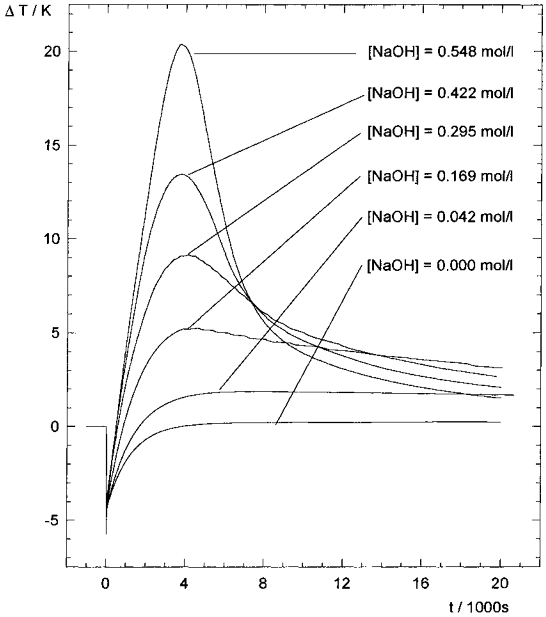


Fig. 3. Influence of the concentration of the catalyst (sodium hydroxide); T_0 = 40°C; n(EtOH) : n(Oxiran)=3 : 1.

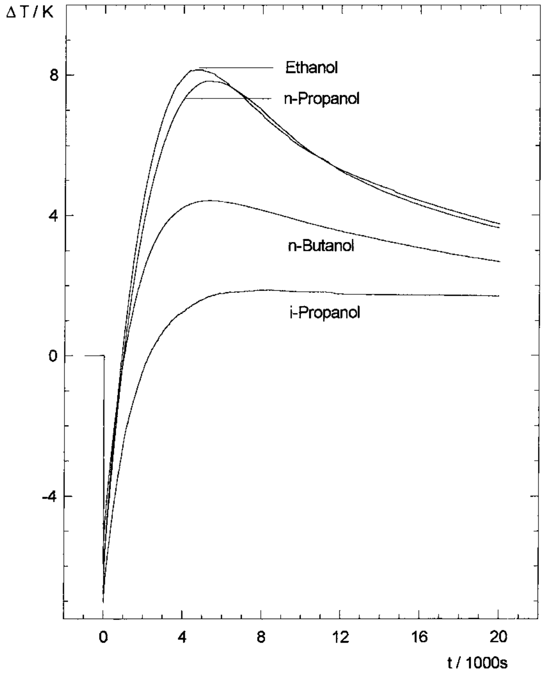


Fig. 4. Influence of the kind of alcohol; n(alcohol) : n(oxirane)=1.5 : 1; T_0 = 40°C; [NaOH] = 0.295 mol/l.

reaction rate decreases with increasing chain length or link. On comparing ethanol and *n*-propanol it is clear that the reaction rate is nearly the same, but the temperature maximum in the case of ethanol was attained 500 s earlier than the *n*-propanol. On the contrary, comparing *n*-butanol with the other *n*-alcohol's, the reaction is seen to be distinctively slower, but there is no shift in the time interval till the temperature maximum is attained. The reaction rate of *i*-propanol is remarkably lower than that of *n*-butanol.

3. Results

In Ref. [2] it has been shown that the ethanolysis of propylene oxide with base catalysts leads only to one product. Analysis of the reaction mixtures by GC/MS has demonstrated the same result for the alcoholysis of 1,2-epoxybutane. Fig. 5 gives an example of such an analysis. The main product is monoether. Under this condition, the nonlinear evaluation becomes simplified.

The described experiments have been evaluated by the nonlinear program TA-kin v3.3 [5]. This program was developed in our group and could be applied to solve various kinetic problems.

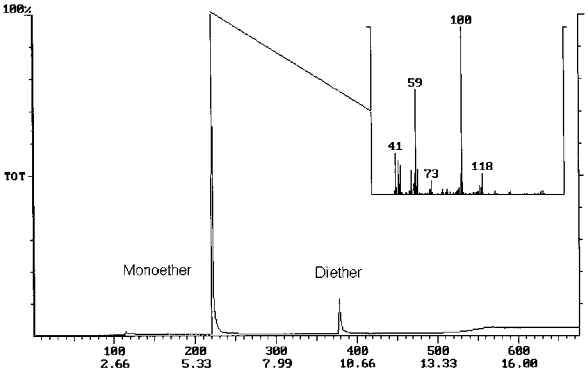
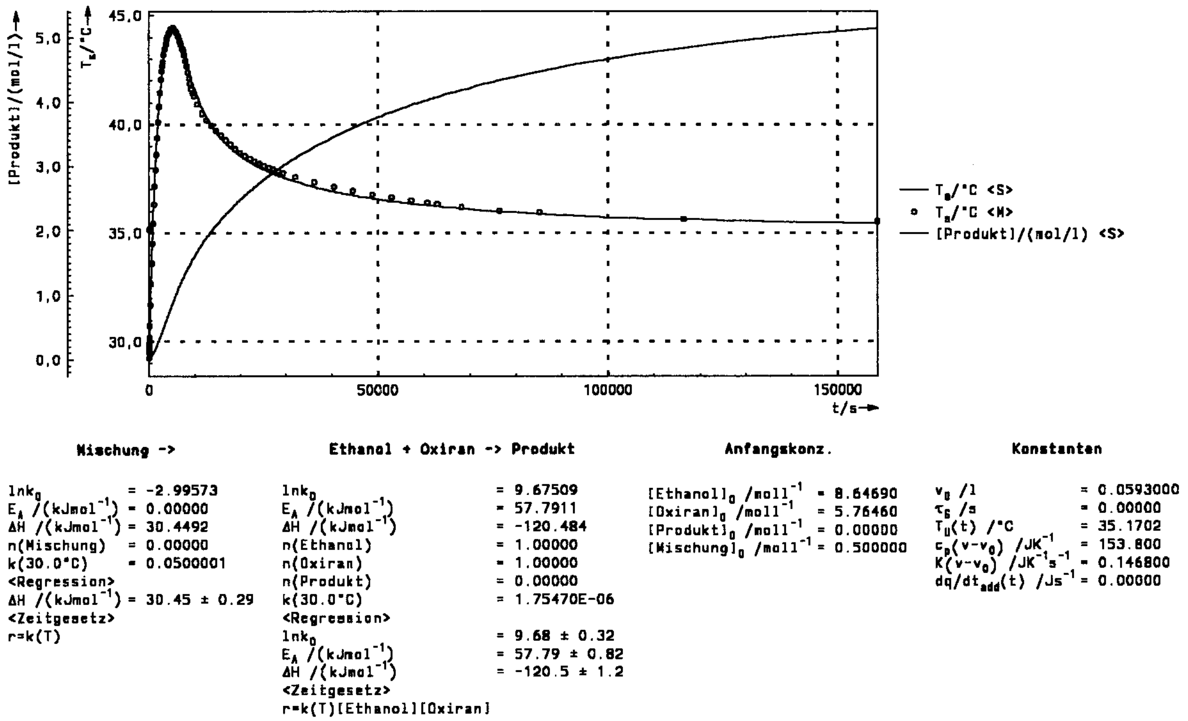


Fig. 5. Result of the analysis of a reaction mixture by GC/MS.



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Mischung ->

lnk0               = -2.99573
EA /(kJmol-1)      = 0.00000
ΔH /(kJmol-1)      = 30.4492
n(Mischung)        = 0.00000
k(30.0°C)          = 0.0500001
<Regression>
ΔH /(kJmol-1)      = 30.45 ± 0.29
<Zeitgesetz>
r=k(T)

Ethanol + Oxiran -> Produkt

lnk0                         = 9.67509
EA /(kJmol-1)                = 57.7911
ΔH /(kJmol-1)                = -120.484
n(Ethanol)                   = 1.00000
n(Oxiran)                    = 1.00000
n(Produkt)                   = 0.00000
k(30.0°C)                    = 1.75470E-06
<Regression>
lnk0                         = 9.68 ± 0.32
EA /(kJmol-1)                = 57.79 ± 0.82
ΔH /(kJmol-1)                = -120.5 ± 1.2
<Zeitgesetz>
r=k(T)[Ethanol][Oxiran]

Anfangskonz.

[Ethanol]0 /moll-1   = 8.64690
[Oxiran]0 /moll-1    = 5.76460
[Produkt]0 /moll-1   = 0.00000
[Mischung]0 /moll-1  = 0.500000

Konstanten

v0 /l                  = 0.0593000
τG /s                  = 0.00000
TU(t) /°C              = 35.1702
cp(v-v0) /JK-1         = 153.800
K(v-v0) /JK-1s-1       = 0.146800
dq/dtadd(t) /Js-1      = 0.00000
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Fig. 6. Result of a nonlinear evaluation by the program TA-kin v3.3.

Table 1
Results of the nonlinear evaluation by the program TA-kin v3.3

ROH	n(ROH) : n(Oxiran)	[NaOH] (mol l^{-1})	T (°C)	$\ln k_0$	E_A	$\Delta_R H$
EtOH	3 : 1	0.548 0.422 0.295	40	9.0	52.4	−81.4
EtOH	1.5 : 1	0.295	40	4.7	45.6	−144.4
n-PrOH						
EtOH	1.5 : 1	0.548	40 35	8.1	52.9	−52.9
EtOH	2 : 1	0.548	40 35	14.8	68.6	−62.0
EtOH	3 : 1	0.548	40 35	5.2	44.1	−91.2

For the nonlinear evaluation of the alcoholysis of 1,2-epoxybutane, a rate law of second order was assumed. The calorimetric curves have been evaluated in an overall manner, that means by a common computation in one procedure. The kinetic investigations have shown that the concentration of sodium hydroxide has a significant influence on the kinetic parameters, which is evident even from the series of calorimetric curves. Therefore, the concentration of the catalyst has been involved in the evaluation.

An example of nonlinear evaluation with TA-kin v3.3 is given in Fig. 6. The measured data are displayed as circles and the fitted ones as a straight line. The curves demonstrate that beyond 1.5×10^5 s the reaction may remain incomplete, up to 5%. This establishes the relatively slow reaction of 1,2-epoxybutane under the selected conditions.

Table 1 summarizes the parameters, found by overall evaluation.

In addition to the presented experiments, the acid-catalyzed alcoholysis and the base-catalyzed hydrolyses of 1,2-epoxybutane will also be investigated.

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