

# Reactions of 1-chloro-2,3-epoxy-2-methylpropane with lower aliphatic alcohols. II. Kinetics

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The reaction of 1-chloro-2,3-epoxy-2-methylpropane with aliphatic alcohols in the presence of  $F_3B \cdot O(C_2H_5)_2$  catalyst is of the first order with respect to the epoxide. The reaction rate is proportional to the effective catalyst concentration and increases with an initial molar ratio of methanol to epoxide until the value of about 10 is achieved, then it is almost constant. From the temperature dependence of the rate constants the parameters of Arrhenius equation were calculated. The ratio of the products, 1-alkoxy-3-chloro-2-methyl-2-propanols and 2-alkoxy-3-chloro-2-methyl-1-propanols, decreases with the increasing temperature and increases with the length and the degree of branching of the hydrocarbon chain of the alcohol. The values of activation entropies confirm the  $S_N2$  mechanism of the reaction.

Реакция 1-хлор-2,3-эпокси-2-метилпропана с алифатическими спиртами при каталитическом действии  $F_3B \cdot O(C_2H_5)_2$  является реакцией первого порядка на эпоксид. Скорость реакции пропорциональна эффективной концентрации катализатора и растет с начальным молярным отношением метанола к эпоксиду до его величины приблизительно 10, затем остается почти постоянной. Из термической зависимости констант скорости были вычислены параметры уравнения Аррениуса. Отношение продуктов, 1-алкокси-3-хлор-2-метил-2-пропанолов и 2-алкокси-3-хлор-2-метил-1-пропанолов, понижается с возрастающей температурой и нарастает с длиной и разветвлением цепи спирта. Величины активационных энтропий подтверждают, что реакция происходит в сущности механизмом  $S_N2$ .

1-Chloro-2,3-epoxy-2-methylpropane ( $\beta$ -methylepichlorohydrine) (MECH) reacts with lower aliphatic alcohols in the presence of boron trifluoride etherate catalyst to yield, in the first stage by the simultaneous reactions, in addition to 1-alkoxy-3-chloro-2-methyl-2-propanols (A) also the corresponding 2-alkoxy-3-chloro-2-methyl-1-propanols (B) [1]. Since the reaction products are monohydric alcohols, the total content of hydroxy groups in the reaction mixture is constant.

However, the reaction system is complicated by the possibility of consecutive reactions of products with the epoxide. The course of these reactions depends on the initial molar ratio of the alcohol to the epoxide and on the reactivity of hydroxy groups of the starting alcohol and individual reaction products.

Therefore in this work we have studied the kinetics of the reaction of MECH with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol in the presence of a catalytic amount of  $F_3B \cdot O(C_2H_5)_2$  in the concentration range  $0.897 \times 10^{-2}$  to  $14.531 \times 10^{-2}$  mol dm<sup>-3</sup> at 15 to 35°C and initial molar ratios  $Q$  (alcohol:epoxide) = 3 to 30. We have studied mainly the effect of the catalyst concentration, initial molar ratio of the alcohol to the epoxide ( $Q$ ), temperature, and alcohol—alkyl structure on the reaction rate as well as the influence of both temperature and alcohol used upon the composition of products.

## Experimental

The specification of chemicals used was given in the preceding paper [1].

### *Working procedure*

The reaction-kinetic experiments were carried out by means of a closed jacketed beaker of 100 cm<sup>3</sup> volume equipped with a magnetic stirrer, thermometer, and an opening for sampling. The temperature of the reaction mixture was maintained constant ( $\pm 0.1^\circ\text{C}$ ) by a thermostat with water. The tempered reaction mixture (50 cm<sup>3</sup>) was added to the beaker and the reaction was initiated by adding the chosen quantity of  $F_3B \cdot O(C_2H_5)_2$ . In cases, when the amount of the catalyst was small,  $F_3B \cdot O(C_2H_5)_2$  was added as a solution in the corresponding alcohol. In these cases the volume of reaction mixture was 50 cm<sup>3</sup>.

During the reaction period six to nine 0.5 cm<sup>3</sup> samples were withdrawn. The reaction in the samples was quenched by means of efficient shaking (1 min) with powdered NaHCO<sub>3</sub>. The composition of the sample processed in this way has not changed for several hours. The samples were analyzed by g.l.c. after tempering to the reaction temperature, a few minutes after sampling. The experiments were terminated after a period of 90—180 min after which time the MECH conversion was 20—90%, usually 50—80%. During the reactions the density of the reaction mixture increased in most cases by 1 to 3%, and occasionally by a maximum of 7%.

### *Analytical methods*

The chromatographic determination (g.l.c.) of the conversion of MECH to the products A, B was described in [1].

### *Kinetic data evaluation*

The rate constants  $k_1$  were calculated from a linearized form ([2] p. 96) of the integrated kinetic equation of the first order. For the calculation of rate constants  $k_2$ ,  $k_{2A}$ ,  $k_{2B}$  the

relations (2—4) given below were used. For the  $c_A/c_B$  ratio its average value from the measurement during the reaction was used. The activation energy ( $E$ ) and frequency factor ( $A$ ) were evaluated from a logarithmic form of Arrhenius equation ([2] p. 14<sup>1</sup>). The activation entropy ( $\Delta S_{298}^*$ ) was calculated according to ([2] p. 336), and while the dimension of the frequency factor was  $\text{dm mol}^{-1} \text{s}^{-1}$ .

The least square method was used when calculating the linear function parameters. The average standard errors (%) of the individual parameters were as follows:  $k_1$ ,  $c_A/c_B$  1.3;  $k_2$  2.7;  $q$  87 (for  $\text{CH}_3\text{OH}$  113, for the other alcohols 41);  $E$  2.7;  $\log A$  3.0.

## Results and discussion

In most cases the time dependence of the concentration of MECH in its reaction with alcohols, is in accord with the first-order kinetic equation

$$-\frac{dc_E}{d\tau} = k_1 c_E \quad (1)$$

where  $c_E$  is a molar concentration of the epoxide in time  $\tau$ . Exceptions are the reactions of MECH with branched-chain alcohols. At lower initial molar ratios of the alcohol to the epoxide ( $Q = 3$  and  $Q = 3, 10$  in the case of isopropyl alcohol and *tert*-butyl alcohol, respectively) the reaction rate systematically deviated with time to higher values than those corresponding to eqn (1). In these cases the rate constants  $k_1$  were evaluated from initial parts of kinetic curves which still obeyed the kinetic equation of the first order.

As follows from the results (Figs. 1 and 2) the dependence of the rate constant  $k_1$  on the catalyst concentration  $c_K$  in the studied range can be expressed by the equation

$$k_1 = k_2(c_K - q) \quad (2)$$

where  $q$  is the intercept on the  $c_K$  axis. For very low catalyst concentrations the accurate form of the dependence of  $k_1$  on  $c_K$  is difficult to determine. The values  $k_2$  and  $q$  for different experimental conditions are given in Tables 1 and 2.

It is shown (Table 1) that in the case of the reaction of MECH with methanol  $q$  is negative and has a very low absolute value. The dependence of  $q$  on the initial molar ratio of the alcohol to the epoxide was not determined since  $q$  fluctuated only within experimental errors. Substitution of hydrogen atoms of methanol by methyl groups and lengthening of the hydrocarbon chain causes an increase of  $q$ , but the differences for ethanol and propanols are not substantial. The fact that the reaction rate of the reaction of ethanol and higher alcohols with MECH is not affected by the proportion of the catalyst, is obviously not due to the moisture in the chemicals used, as follows e.g. from the measurement with ethanol in the presence of water (Table 1). The effect of possible impurities which could act as

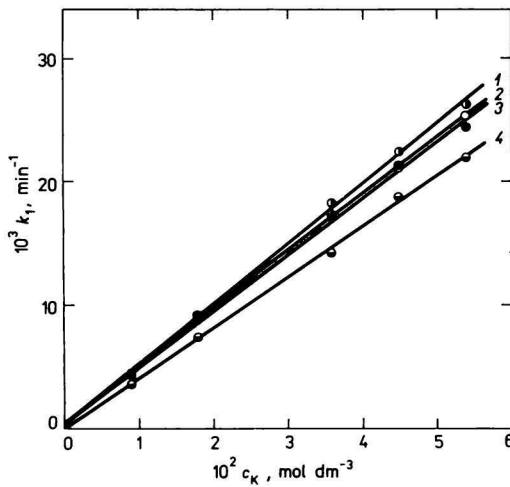


Fig. 1. Dependence of the reaction rate constant  $k_1$  on the concentration of  $F_3B \cdot O(C_2H_5)_2$  for the reaction of methanol with 1-chloro-2,3-epoxy-2-methylpropane at 25°C.

1.  $Q = 30$ ; 2.  $Q = 15$ ; 3.  $Q = 10$ ; 4.  $Q = 5$ .

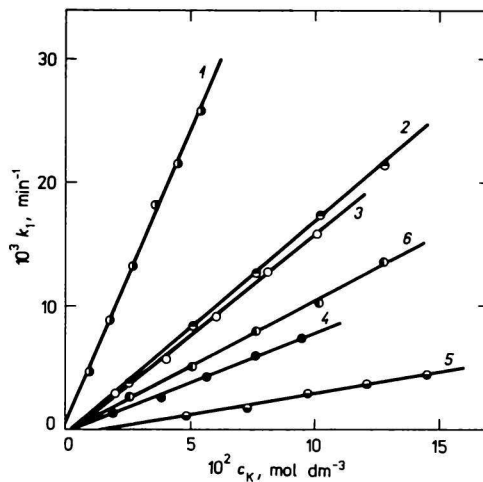


Fig. 2. Dependence of the reaction rate constant  $k_1$  on the concentration of  $F_3B \cdot O(C_2H_5)_2$  for the reaction of 1-chloro-2,3-epoxy-2-methylpropane with aliphatic alcohols at 25°C;  $Q = 25$ .

1.  $CH_3OH$ ; 2.  $C_2H_5OH$ ; 3.  $n-C_3H_7OH$ ; 4.  $i-C_3H_7OH$ ; 5.  $tert-C_4H_9OH$ ; 6.  $C_2H_5OH$ .

( $c_{H_2O} = 0.231 \text{ mol dm}^{-3}$ ).

Table 1

Parameters of the dependence of the reaction rate constant  $k_1$  on the concentration of  $F_3B \cdot O(C_2H_5)_2$  catalyst in the reaction of MECH with alcohols at 25°C

Alcohol	$Q$	$k_2$ $dm^3 mol^{-1} min^{-1}$	$10^2 q$ $mol dm^{-3}$
CH <sub>3</sub> OH	3 <sup>a</sup>	0.320	-0.11
	5	0.409	-0.02
	7	0.441	-0.05
	10	0.452	-0.16
	15	0.469	-0.07
	25	0.473	-0.11
	30	0.491	-0.06
C <sub>2</sub> H <sub>5</sub> OH	25	0.174	0.26
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	25	0.164	0.37
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	25	0.081	0.37
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> OH	25	0.035	0.76
C <sub>2</sub> H <sub>5</sub> OH <sup>b</sup>	25	0.106	0.17

a) At  $Q = 3$  for the calculation of  $k_2$  the same  $q$  value as for  $Q = 25$  was taken.

b) In the presence of water ( $c_{H_2O} = 0.231 mol dm^{-3}$ ).

catalyst poisons can be excluded. In an analogical reaction [3] with 1-chloro-2,3-epoxypropane,  $q$  was explained in terms of the reaction of epoxide with boron trifluoride etherate.

It follows from Fig. 3 that the rate constant  $k_2$  increases considerably and depends on the initial molar ratio of methanol to MECH up to about  $Q = 10$ ;  $k_2$  then increases only moderately.

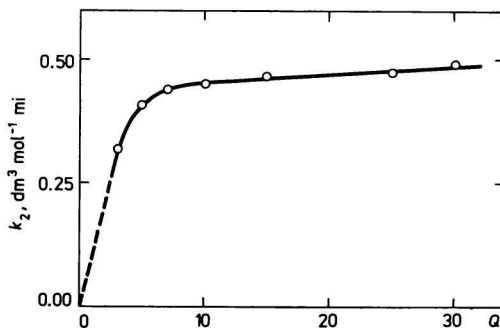


Fig. 3. Dependence of the reaction rate constant  $k_2$  on the initial molar ratio ( $Q$ ) of methanol to 1-chloro-2,3-epoxy-2-methylpropane; catalyzed by  $F_3B \cdot O(C_2H_5)_2$  at 25°C.

$k_2$  for  $Q = 3$  calculated with  $q$  equal as for  $Q = 25$ .

Table 2

Temperature dependence of the reaction rate constants  $k_2$  of the  $F_3B_2O(C_2H_5)_2$ -catalyzed alcoholysis of MECH and the parameters of Arrhenius equation

O	ROH	$10^2 c_K$ mol dm	$k_2$ [dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> ] at $t$ [°C]							E kJ mol <sup>-1</sup>	A dm <sup>3</sup> mol <sup>-1</sup> min
			15	20	25	30	35	40			
25	CH <sub>3</sub> OH	1.794	0.181	0.310	0.465	0.712	1.078		65.1	$1.17 \times 10^{11}$	
	C <sub>2</sub> H <sub>5</sub> OH	5.107	0.075	0.114	0.176	0.265	0.409		62.4	$1.56 \times 10^{10}$	
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	4.040	0.064	0.100	0.158	0.239	0.354		63.4	$1.99 \times 10^{10}$	
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	5.695	0.030	0.049	0.080	0.122	0.179		66.6	$3.60 \times 10^{10}$	
	<i>tert</i> -C <sub>4</sub> H <sub>9</sub> OH	7.265		0.031	0.064	0.118	0.256		107.7	$2.36 \times 10^{17}$	
10	CH <sub>3</sub> OH	4.901	0.179	0.288	0.451	0.656		62.8	$4.34 \times 10^{10}$		
	C <sub>2</sub> H <sub>5</sub> OH	9.744	0.052	0.086	0.126	0.203		65.3	$3.59 \times 10^{10}$		
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	9.744	0.060	0.086	0.160	0.228	0.343	63.9	$2.37 \times 10^{10}$		
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	9.744	0.025	0.042	0.065	0.103		68.4	$6.35 \times 10^{10}$		
	<i>tert</i> -C <sub>4</sub> H <sub>9</sub> OH	9.744		0.032	0.049	0.079	0.124	68.3	$4.64 \times 10^{10}$		
3	CH <sub>3</sub> OH	2.108	0.121		0.320		0.748	67.4	$2.05 \times 10^{11}$		
	C <sub>2</sub> H <sub>5</sub> OH	4.205	0.051		0.109		0.256	59.3	$2.84 \times 10^9$		
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	4.205	0.044		0.109		0.265	66.3	$4.63 \times 10^{10}$		
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	9.744	0.020		0.062		0.152	75.3	$9.32 \times 10^{11}$		
	<i>tert</i> -C <sub>4</sub> H <sub>9</sub> OH	9.744		0.031	0.050		0.135	74.6	$5.98 \times 10^{11}$		

Assuming an equal character of the dependence upon the catalyst concentration, of the rate of the formation of both isomers  $A$ ,  $B$ , it holds

$$k_2 = k_{2A} + k_{2B} \quad (3)$$

where  $k_{2A}$ ,  $k_{2B}$  stand for the rate constants of the conversion to products  $A$  and  $B$ , respectively. Considering that at the beginning of the reaction the products are not present in the reaction mixture, for the parallel reactions the ratio of molar concentrations  $c_A/c_B$  of products  $A$  and  $B$  is time-independent ([2] p. 181)

$$\frac{k_{2A}}{k_{2B}} = \frac{c_A}{c_B} \quad (4)$$

From the relations (1—3) it follows for the total reaction rate

$$-\frac{dc_E}{d\tau} = (k_{2A} + k_{2B})(c_K - q)c_E \quad (5)$$

For  $Q = 10$ , the studied alcohols and the applied temperature range, we verified that the ratio  $c_A/c_B$  varies only within experimental errors. The measured rate constants  $k_{2A}$ ,  $k_{2B}$  are given in Table 3. In the reaction of *tert*-butyl alcohol the

Table 3

Temperature dependence of the reaction rate constants  $k_{2A}$ ,  $k_{2B}$  [ $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ ] of the  $\text{F}_3\text{B} \cdot \text{O}(\text{C}_2\text{H}_5)_2$ -catalyzed reaction of MECH with alcohols ( $Q = 10$ ) and the parameters of Arrhenius equation

ROH	$t, ^\circ\text{C}$					$E$ kJ mol <sup>-1</sup>	$A$ dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>
	15	20	25	30	35		
CH <sub>3</sub> OH	0.144	0.228	0.325	0.498		59.6	9.30 × 10 <sup>9</sup>
	0.034	0.060	0.096	0.158		74.3	1.05 × 10 <sup>12</sup>
C <sub>2</sub> H <sub>5</sub> OH	0.044	0.072	0.104	0.165		62.9	1.13 × 10 <sup>10</sup>
	0.008	0.014	0.022	0.038		77.3	7.96 × 10 <sup>11</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	0.053		0.135	0.190	0.281	61.6	8.13 × 10 <sup>9</sup>
	0.008		0.024	0.038	0.062	76.2	5.35 × 10 <sup>11</sup>
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	0.022	0.037	0.057	0.088		66.6	2.64 × 10 <sup>10</sup>
	0.003	0.005	0.008	0.014		81.6	1.71 × 10 <sup>12</sup>

$c_K = 9.744 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $c_K = 4.901 \times 10^{-2} \text{ mol dm}^{-3}$  for CH<sub>3</sub>OH.

content of *B* product in the reaction mixture was very low (Table 4). Since in these analyses there is a greater experimental error than in the case of other alcohols, the rate constants were not calculated.

It follows from the measurements that the course of the reaction of MECH with lower aliphatic alcohols in the presence of a catalytic amount of  $F_3B \cdot O(C_2H_5)_2$  depends largely on the alcohol used. The total reaction rate is highest in the case of methanol. The reaction rate markedly decreased by going from methanol to ethanol, isopropyl alcohol, and *tert*-butyl alcohol. With linear alcohols the reaction rates are very similar. At 15 to 30°C the reactivity of ethanol at  $Q = 25$  is a little higher and at  $Q = 10$ , on the contrary, somewhat lower than with 1-propanol. An additional, moderate increase of the reactivity at  $Q = 10$  can be recorded when passing from 1-propanol to 1-butanol for which at 25°C  $k_1 = 15.28 \times 10^{-3} \text{ min}^{-1}$  ( $c_K = 9.744 \times 10^{-2} \text{ mol dm}^{-3}$ ),  $k_2 = 0.163 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ ; when the same  $q$  is used for the calculation as for 1-propanol ( $Q = 25$ ,  $t = 25^\circ\text{C}$ ).

The longer and more branched is the alkyl of the alcohol the lower is the proportion of *B* in the products at  $Q = 10$ . The values  $k_{2A}$ ,  $k_{2B}$  decrease in the order: methanol, ethanol, 2-propanol; with nonbranched alcohols (ethanol, 1-propanol, 1-butanol)  $k_{2B}$  is almost constant and  $k_{2A}$  moderately increases.

The proportion of compounds *B* in the primary reaction products can be favoured, roughly to the same extent with all  $C_1$ — $C_3$  alcohols studied by increasing the reaction temperature. This follows from the fact that the apparent activation energies for the conversion to the  $C_\alpha$  ether (*A*) are lower than to the  $C_\beta$  ether, whereas the differences between the individual alcohols are rather unimportant (Table 3).

In the case of a high excess of alcohols ( $Q = 25$ ), both activation energy and frequency factor, calculated from the temperature dependence of  $k_2$  (Table 2), decreased when going from methanol to ethanol and increased slightly with lengthening and branching of the alcohol. Relatively high  $E$  and  $A$  in the reaction of *tert*-butyl alcohol can be attributed to steric hindrances.

The results of our study are consistent with the results of analogical works on  $F_3B \cdot O(C_2H_5)_2$ -catalyzed reaction of alcohols with 1-chloro-2,3-epoxypropane [3—10], 2-methyl-1,2-epoxypropane [11], and 1,2-epoxypropane [12]. An impor-

Table 4

Temperature dependence of the concentration ratio of isomers *A* and *B* in the product of reaction of *tert*-butyl alcohol with MECH at  $Q = 10$  and catalyst concentration  $c_K = 9.744 \times 10^{-2} \text{ mol dm}^{-3}$

$t, ^\circ\text{C}$	20	25	30	35
$c_A/c_B$	116	110	77	74



tant difference, however, is in the finding that the reaction rate of 1-chloro-2,3-epoxypropane with alcohols [4, 5], 1-alkoxy-3-chloro-2-propanols [6], glycolethers [7], and  $\alpha,\omega$ -diols [8, 9] in the presence of  $F_3B \cdot O(C_2H_5)_2$  catalyst is independent of the initial molar ratio of the hydroxy compound to the epoxide or, that reaction rate may even moderately increase in the case of 2-chloroethanol with decreasing  $Q$  [10]. In a dilute dioxan solution the reaction is of the first order with respect to the alcohol [13]. When the reaction of 1-butanol with 1-chloro-2,3-epoxypropane is catalyzed by perchloric acid,  $k_2$  depends on the alcohol concentration [14] similarly as in our case for the reaction of MECH with methanol in the presence of  $F_3B \cdot O(C_2H_5)_2$  catalyst.

In contrast to our results as well as to those of a recent study on the reaction of 1-chloro-2,3-epoxypropane with alcohols and diols [3, 8—10], older papers [4—7, 11—13] claim that for the reaction of epoxides with hydroxy compounds the linear dependence of the reaction rate upon the catalyst concentration commences in the origin of coordinates ( $q = 0$ ). In the reaction of  $\alpha,\omega$ -diols with 1-chloro-2,3-epoxypropane,  $q$  is proportional to the initial molar ratio of the alcohol to the epoxide [9]. A further difference is in the fact that temperature favours the formation of  $C_\beta$  ethers from MECH more extensively than from 1,2-epoxypropane.

When compared to analogous reactions of 1,2-epoxypropane [12] and 1,2-epoxy-2-methylpropane [11], the reaction of MECH is much slower, under the same conditions but somewhat faster than that of 1-chloro-2,3-epoxypropane [3—5]. While the substituents exerting +I effect on the oxiran ring cause an increase of the reaction rate, -I substituents decrease it.

It can be assumed on the basis of previous studies [14, 15, 20—22], that the first stage of the reaction of epoxides with alcohols, catalyzed by "proteoacids" is a fast equilibrium protonation of the epoxide. The following reaction of protonized epoxide with alcohol is the rate-determining step.

Similarly, in the case of  $F_3B \cdot O(C_2H_5)_2$  catalysis *Sekiguchi et al.* [6, 7, 11—13] assume the reaction to proceed *via* boron trifluoride etherate-complex with the epoxide.

Considering the basicity of alcohols and epoxides towards  $BF_3$  [16, 17] and the concentration conditions a balanced exchange reaction of alcohols with  $BF_3 \cdot O(C_2H_5)_2$  must also be taken into account. Compounds formed from  $BF_3$  and alcohols are known [18] to be strong proteoacids. We assume therefore, that at high values of  $Q$  the studied reaction proceeds largely *via* boron trifluoride alcoholates and protonized epoxides. A similar assumption was expressed on the basis of the cationic polymerization of cyclic ethers in the presence of alcohols [19] or water [17]. However, at low  $Q$  values, the mechanism *via*  $BF_3$ -epoxide complex may be more important.

Additional complications, which are discussed in detail in our next work [23], are polyaddition reactions of epoxides taking place especially at low  $Q$  and with

alcohols bearing less reactive OH group on tertiary or secondary carbon atom. From this reason, greater part of our measurements was done at high  $Q$ , in which case the occurrence of consequent reactions was considerably restricted.

This complicated analytically difficult situation manifests itself in the character of the dependences of  $k_2$  on  $Q$  and  $k_1$  on  $c_K$ , and, possibly of  $q$  on the type of alcohol; moreover the order of the reaction, and  $E$  and  $A$  at low values of  $Q$  may also vary.

The authors of preceding works [3—15, 20—22] discuss the character of the transition complex in the acid-catalyzed reaction of epoxides with alcohols; they compare the values of apparent activation entropy, calculated from the experimental rate constants. The activation entropies for the reaction of MECH with alcohols (Table 5) show that  $C_\alpha$  and  $C_\beta$  ethers are formed *via*  $S_N2$  and "borderline  $S_N2$ " mechanisms, respectively.

Table 5

Activation entropies  $\Delta S_{298}^\ddagger$  [ $J K^{-1} mol^{-1}$ ] for the  $F_3B \cdot O(C_2H_5)_2$ -catalyzed reaction of MECH with alcohols

ROH	$Q = 25$	$Q = 10$	$Q = 10 (A)$	$Q = 10 (B)$
$CH_3OH$	-75.3	-83.7	-96.4	-57.2
$C_2H_5OH$	-92.0	-85.4	-94.8	-59.5
$n-C_3H_7OH$	-90.0	-88.7	-97.6	-62.8
$i-C_3H_7OH$	-85.4	-80.3	-87.8	-53.1
$tert-C_4H_9OH$	+45.2	-83.3		

An analogous conclusion has been drawn from the study of the reaction of methanol with 1,2-epoxypropane in the presence of perchloric acid as a catalyst [22]. The reaction of *tert*-butyl alcohol with MECH is an exception. Here, the  $\Delta S_{298}^\ddagger$  value is evidently (already at  $Q = 10$ ) influenced by consecutive reactions; at  $Q = 25$ , when the polyaddition of MECH is restricted owing to steric hindrances the value of  $\Delta S_{298}^\ddagger$  is typical for  $S_N1$  reactions.

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