

Reactions of 1-chloro-2,3-epoxy-2-methylpropane with lower aliphatic alcohols. III. Mathematical model of polyaddition

J. SVOBODA and V. MACHO

*Research Institute for Petrochemistry,
972 71 Nováky*

Received 6 September 1977

Accepted for publication 10 January 1978

A mathematical model is proposed for acid-catalyzed polyaddition of 1-chloro-2,3-epoxy-2-methylpropane to lower aliphatic alcohols. Based on simplifying assumptions the distribution of the products, depending upon the initial molar ratio of the alcohol to the epoxide, is calculated for four addition steps and complete conversion of the epoxide. The validity of the model has been verified on the reaction of 1-chloro-2,3-epoxy-2-methylpropane with 1-propanol at 35°C in the presence of a catalytic amount of boron trifluoride etherate. The distribution constants for this particular case have been found by comparing the calculated and experimentally found amounts of alcohol and of the products after the first polyaddition step.

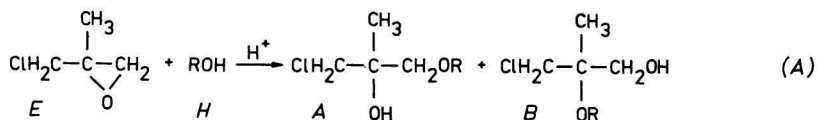
Предлагается математическая модель кислотами катализируемой полиаддиции 1-хлор-2,3-эпокси-2-метилпропана к низшим алифатическим спиртам. При упрощенных предпосылках вычисляется распределение компонентов продуктов в зависимости от начального молярного отношения спирта к эпоксиду для четырех степеней присоединения и полной конверсии эпоксида. Модель была проверена на реакции 1-хлор-2,3-эпокси-2-метилпропана с 1-пропанолом при каталитическом действии $F_3B \cdot O(C_2H_5)_2$ при температуре 35°C. Сопоставлением вычисленного и экспериментальным путем полученного содержания спирта и продуктов первой степени полиаддиции в реакционной смеси были найдены величины констант распределения для этого случая.

The composition of the reaction mixture of a nonsymmetrically substituted oxiran with an alcohol (and the catalyst, as the case may be) depends on the extent of parallel, consecutive and, with respect to the epoxide, competitive reactions. The extent of consecutive reactions is governed by the initial alcohol/epoxide ratio and by the reactivity of the hydroxy groups in both the starting material and products. The distribution of the products of the polyaddition of epoxides has been calculated [1—6] only for stereospecific opening of the epoxide ring. The present work deals

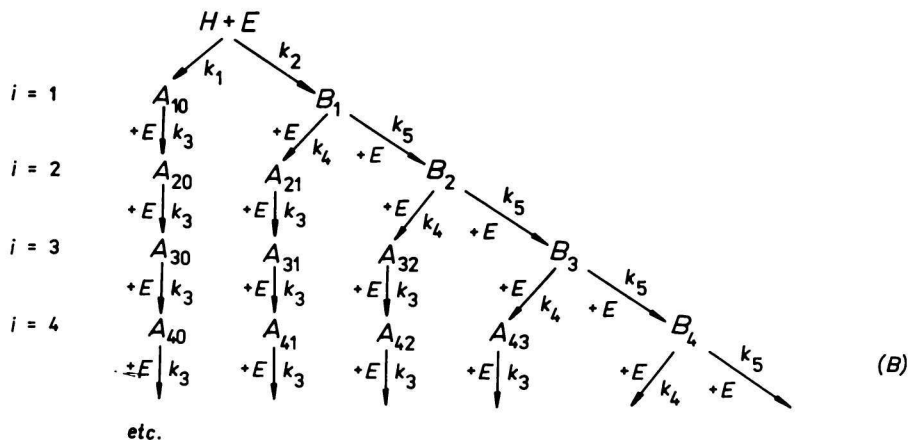
with the calculation of the distribution of products of boron trifluoride etherate-catalyzed reaction of 1-chloro-2,3-epoxy-2-methylpropane (β -methyl-epichlorohydrine) (MECH) with alcohols.

Theoretical

In addition to 1-alkoxy-3-chloro-2-methyl-2-propanols [(A), or "normal" products (C_α ethers)], the first step of the reaction (A) gives also 2-alkoxy-3-chloro-2-methyl-1-propanols [(B), or "abnormal" products (C_β ethers)] [7, 8]



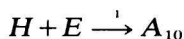
Based on a kinetic study [8] at 15—35°C it can be assumed that starting with the second reaction step the rate constants will be equal for products with an equal type of the hydroxy group, and that the formation of C_β ethers from tertiary alcohols and MECH can be neglected. Thus, the polyaddition of MECH to primary aliphatic alcohols can be written as



where i stands for the step number of the polyaddition. In B_i type products all epoxide units are linked as C_β ethers. In A_{ik} type products having the last epoxide unit linked as C_α ether k stands for the number of epoxide units linked to the alcohol consecutively as C_β ether.

By solving the system of differential kinetic equations describing the scheme (B) integrated concentration—concentration type relations can be obtained. We have

done calculations related to the scheme (B) using the method of *Weibull* and *Nycander* [3], and that of *Novák* and *Šváb* [5, 6]. All partial reactions involved in the scheme (B) were related to the reaction



The respective distribution constants are then given by a ratio of the particular rate constant and the rate constant of the fundamental reaction

$$K_2 = \frac{k_2}{k_1}, \quad K_3 = \frac{k_3}{k_1}, \quad K_4 = \frac{k_4}{k_1},$$

$$K_5 = \frac{k_5}{k_1} \left(K_1 = \frac{k_1}{k_1} = 1 \right) \quad (1)$$

For the calculation by a digital computer the gradual change of the concentration during the reaction of the components in the reaction mixture is replaced by a system of small discrete changes. The basis of the calculation is the interval during which a certain portion (L) of the alcohol reacts to give substance A_{10} . The index j denotes the state of the reaction mixture before j calculation step. It holds for the j calculation step: The decrease of the hydroxy compound

$${}_j\Delta H = {}_jH - {}_{j+1}H = {}_jH L(1 + K_2) \quad (2)$$

and the formed products

$${}_j\Delta A_{ik} = {}_{j+1}A_{ik} - {}_jA_{ik} \quad (3)$$

$$i = 1 \quad {}_j\Delta B_i = {}_{j+1}B_i - {}_jB_i \quad (4)$$

$${}_j\Delta A_{10} = L({}_jH - K_3 {}_jA_{10}) \quad (5)$$

$${}_j\Delta B_1 = L[{}_jH K_2 - (K_4 + K_5) {}_jB_1] \quad (6)$$

$$i = 2 \quad {}_j\Delta A_{20} = L K_3({}_jA_{10} - {}_jA_{20}) \quad (7)$$

$${}_j\Delta A_{21} = L(K_4 {}_jB_1 - K_3 {}_jA_{21}) \quad (8)$$

$${}_j\Delta B_2 = L[K_5 {}_jB_1 - (K_4 + K_5) {}_jB_2] \quad (9)$$

The equations for further polyaddition steps are set up in a similar way. It holds for the decrease of the epoxide

$${}_j\Delta E = {}_jE - {}_{j+1}E = L[{}_jH(1 + K_2) + K_3({}_jA_{10} + {}_jA_{20} + \dots$$

$$+ {}_jA_{21} + \dots) + (K_4 + K_5) ({}_jB_1 + {}_jB_2 + \dots)] =$$

$$= L \left[{}_jH(1 + K_2) + K_3 \sum_{i=1}^n \sum_{k=0}^{i-1} {}_jA_{ik} + (K_4 + K_5) \sum_{i=1}^n {}_jB_i \right] \quad (10)$$

The calculations of the distribution of the first 14 assumed products of the reaction of MECH with primary aliphatic alcohols, depending upon the initial molar ratio of the alcohol to the epoxide, $Q = H_0/E_0$, were based on the afore-mentioned relations. The values of the distribution constants for the given reaction system can be determined by comparing the calculated dependences with the experimentally found data.

The applicability of the above-mentioned calculation of the distribution of the polyaddition products was verified on boron trifluoride etherate-catalyzed reaction of MECH with 1-propanol at 35°C.

Experimental

The chemicals used were specified previously [7]. The apparatus used was the same as that used in the kinetic studies [8].

Working procedure

To a solution (50 cm³) of MECH in 1-propanol (initial molar ratio $\dot{Q} = 0.3$ —3.0) was added boron trifluoride etherate (1—3 mole %, based on MECH). Since the reaction is strongly exothermic larger amounts of the catalyst ($Q = 0.5$ and 0.3) were added portion-wise. The reaction temperature was maintained at 35°C for 5.5—10 h, while the conversion of MECH was 94.7—98.5%. The catalyst was then neutralized with powdered sodium hydrogen carbonate.

Analytical methods

The composition of the reaction mixture was determined by gas—liquid chromatography using a Perkin—Elmer 900 gas chromatograph equipped with a flame ionization detector and s.s. column, $l = 200$ cm, inner diameter 3 mm, packed with 3 wt. % of polyethylene glycol adipate on Chromaton NAW DMCS (0.16—0.20 mm). The temperature was programmed (10°C min⁻¹) from 60 to 170°C. The inject port temperature was 160°C. Gas flows: hydrogen, 40 cm³ min⁻¹; air, 270 cm³ min⁻¹, nitrogen (carrier gas), 35 cm³ min⁻¹. Diethylene glycol was used as the solvent and 1-hexanol as the internal standard. Elution times (min): (C₂H₅)₂O 0.51; *n*-C₃H₇OH 2.23; MECH 4.23; *n*-C₆H₁₃OH 6.17; ClCH₂C(CH₃)(OH)CH₂On-C₃H₇ 8.59; ClCH₂C(CH₃)(On-C₃H₇)CH₂OH 11.69; diethylene glycol 15.04.

Calculations

The calculations for the four addition steps ($n = 4$), taking into account also the reactions of compounds A_{4k} and B_4 with the epoxide, were carried out using a Hewlett—Packard calculator, Model 9830 A. The starting points were $E_0 = 100$ moles of the epoxide and the respective number of moles of the alcohol (H_0), according to the given Q . The calculations were terminated when the conversion of the epoxide first exceeded 100%. As a rule, the

number of moles of unreacted alcohol and that of the individual products at a conversion closest to (below and over) 100% was recorded.

Results and discussion

The accuracy of the calculation increases with the decrease of the calculation step L . From the practical point of view, considering the experimental errors, $L = 0.01$ is satisfactory. For $L = 0.1$ the calculation is too inaccurate, and for $L = 0.001$ the calculation is too time consuming. Only the concentrations of the alcohol, epoxide and those of the products of the first addition step could be analytically determined. Examples of the dependence of the content of the alcohol and of the products A_{10} and B_1 in the reaction mixture (for epoxide conversion 100%) upon the distribution constants K_2 and K_3 are given in Figs. 1—4. The influence of the remaining distribution constants can be pictured in a similar manner.

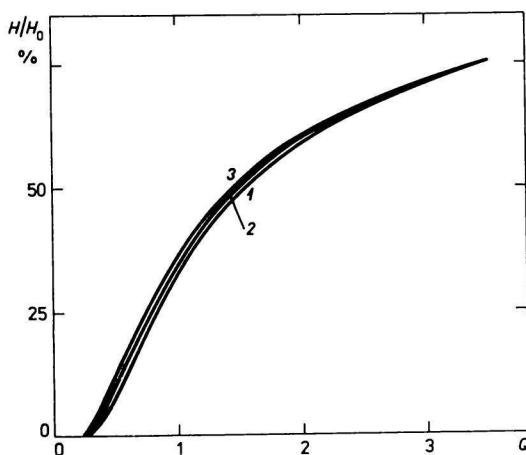


Fig. 1. Dependence of the calculated composition of the reaction mixture vs. the initial alcohol/epoxide molar ratio ($E_0 = 100$ moles; epoxide conversion = 100%) upon the distribution constants.

$$K_3 = K_4 = K_5 = 1.$$

$$K_2: 1. 1; 2. 0.5; 3. 0.1.$$

Of the constants K_2 — K_5 needed to predict the composition of the reaction mixture only K_2 (0.22) could be relatively accurately estimated from the kinetic measurements [8]. From the comparison of the rate constants of the reaction of MECH with *tert*-butyl alcohol and 1-propanol to give the product A an approximate estimate was made that K_3 will probably be less than 0.5. It is further probable that the ratio K_5/K_4 will not differ much from K_2 . The next calculations were based on these values.

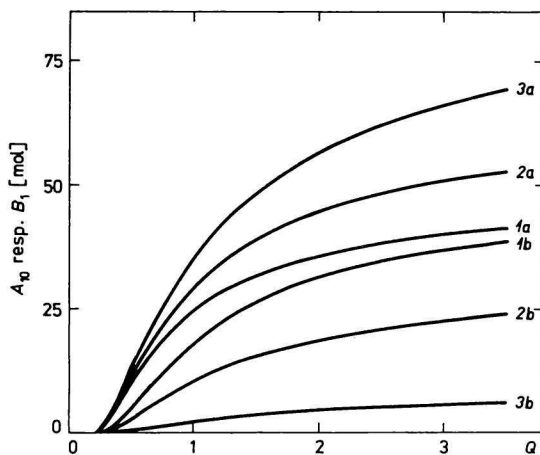


Fig. 2. Dependence of the calculated composition of the reaction mixture vs. the initial alcohol/epoxide molar ratio ($E_0 = 100$ moles; epoxide conversion = 100%) upon the distribution constants.

$K_3 = K_4 = K_5 = 1$.
 K_2 : 1. 1; 2. 0.5; 3. 0.1.
 a) For A_{10} ; b) for B_1 .

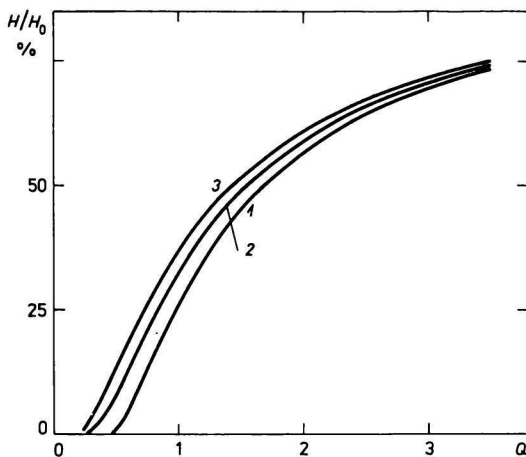


Fig. 3. Dependence of the calculated composition of the reaction mixture vs. the initial alcohol/epoxide molar ratio ($E_0 = 100$ moles; epoxide conversion = 100%) upon the distribution constants.

$K_2 = K_4 = K_5 = 1$.
 K_3 : 1. 0.1; 2. 1; 3. 2.

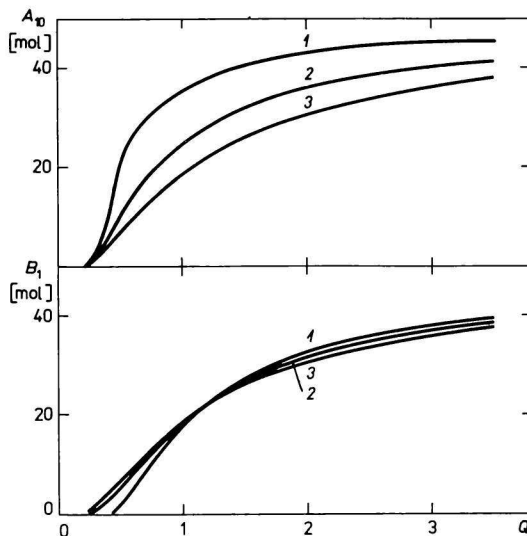


Fig. 4. Dependence of the calculated composition of the reaction mixture vs. the initial alcohol/epoxide molar ratio ($E_0 = 100$ moles; epoxide conversion = 100%) upon the distribution constants.

$$K_2 = K_4 = K_5 = 1.$$

$$K_3: 1. 0.1; 2. 1; 3. 2.$$

The experimentally found composition of the reaction mixture best coincided with the calculated values when for K_2 , K_3 , K_4 , and K_5 (Fig. 5) values 0.27, 0.1, 0.45, and 0.15, respectively, were taken.

The amounts of alcohol as well as of all considered products in the reaction mixture calculated for this case are summarized in Table 1. The calculated amount of unreacted 1-propanol is somewhat smaller in the whole range of Q than that found by analysis. The reason for this is mainly the fact that the 100% conversion of the epoxide, assumed by the calculations, was not reached. The other deviations occur only with the lowest Q values which, firstly, is the result of the simplifying assumptions and, secondly, the result of the fact that only four addition steps were considered. The "best" value $K_2 = 0.27$, used in the calculation, does not differ significantly from 0.22 which is the value based on kinetic measurements. Besides being affected by experimental errors the determination of the "best" combination of K_2 — K_5 is, to some extent, subjective.

It can be concluded, when the polyaddition of 1-chloro-2,3-epoxypropane to primary aliphatic alcohols [5] is compared with the same reactions of MECH that the reactions of the latter are accompanied by side reactions to give C_β ethers. On the other hand, the relative polyaddition reaction rates of MECH are considerably smaller than those of 1-chloro-2,3-epoxypropane.

Table 1

Composition of the products (moles) calculated for the reaction of MECH with 1-propanol at 35°C vs. initial alcohol/epoxide molar ratio (epoxide conversion = 100% ; $E_0 = 100$ moles)

Q	H_0	H/H_0 %	$(E_0 - E)/E_0$ %	A_{10}	A_{20}	A_{30}	A_{40}	A_{21}	A_{31}	A_{41}	A_{32}	A_{42}	A_{43}	B_1	B_2	B_3	B_4
3.0	300	68.15	98.72	74.08	1.21	0.01	0	1.40	0.02	0	0.02	0	0	18.53	0.44	0.01	0
		67.29	101.51	76.05	1.29	0.01	0	1.49	0.02	0	0.02	0	0	18.97	0.47	0.01	0
2.0	200	52.78	99.73	72.38	2.02	0.04	0	2.26	0.04	0	0.06	0	0	17.12	0.69	0.02	0
		52.11	101.26	73.36	2.09	0.04	0	2.33	0.04	0	0.06	0	0	17.30	0.71	0.02	0
1.0	100	15.28	99.67	60.72	5.72	0.32	0.01	5.36	0.32	0.01	0.40	0.02	0.02	10.48	1.35	0.11	0.01
		15.08	100.01	60.82	5.78	0.33	0.01	5.41	0.33	0.01	0.40	0.02	0.02	10.46	1.36	0.11	0.01
0.5	50	0	100.01	18.20	13.99	5.45	1.43	4.31	2.54	0.82	1.18	0.53	0.29	0.12	0.13	0.07	0.03
0.3	30	0	99.99	2.45	5.55	6.28	4.75	0.60	1.23	1.28	0.18	0.33	0.05	0	0	0	0

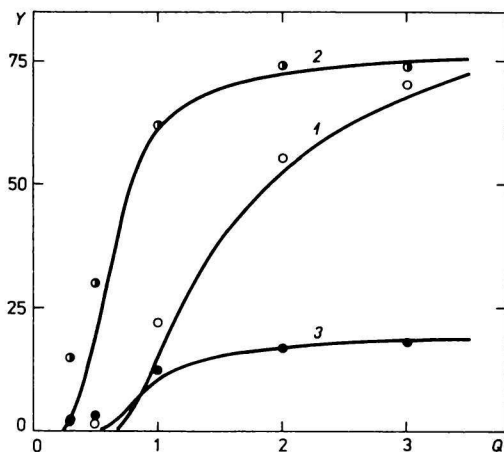


Fig. 5. Comparison of the found composition of the reaction mixture in the reaction of MECH with 1-propanol at 35°C (epoxide conversion, 94.7—98.5%) with that calculated for the epoxide conversion of 100% ($E_0 = 100$ moles).

Y: 1. H/H_0 (%); 2. A_{10} (mol); 3. B_1 (mol).

In spite of the above-mentioned shortcomings the presented model makes it possible to get an idea about the composition of the reaction mixture resulting from the polyaddition of MECH to primary aliphatic alcohols, the products of which are not easily obtainable at present. Thus, the model is a contribution to the isolation and structure elucidation of products of the reaction of MECH with 1-propanol among which, in addition to products A_{10} and B_1 , also the presence of substances A_{20} , A_{21} and perhaps A_{30} and A_{40} should be expected.

Acknowledgements. The authors thank Ing. M. Baláková and Ing. F. Hrázský of this Institute for the help with the analysis of the samples and for data processing, respectively.

References

1. Flory, P. J., *J. Amer. Chem. Soc.* **62**, 1561 (1940).
2. Natta, G. and Mantica, E., *J. Amer. Chem. Soc.* **74**, 3152 (1952).
3. Weibull, B. and Nycander, B., *Acta Chem. Scand.* **8**, 847 (1954).
4. Maget, H. J. R., *J. Polym. Sci., Part A-2*, 1281 (1964).
5. Novák, J. and Šváb, V., *Makromol. Chem.* **168**, 131 (1973).
6. Novák, J. and Šváb, V., *Makromol. Chem.* **176**, 999 (1975).
7. Svoboda, J. and Macho, V., *Chem. Zvesti* **33**, 252 (1979).
8. Svoboda, J. and Macho, V., *Chem. Zvesti* **33**, 259 (1979).

Translated by P. Kováč