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INVESTIGATION OF THE REACTION OF EPICHLOROHYDRIN WITH 1-BUTANOL BY GEL CHROMATOGRAPHY

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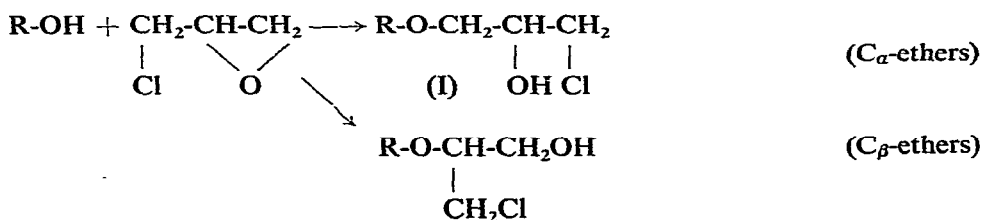
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SUMMARY

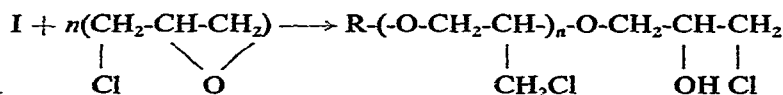
The products of the acid-catalysed reaction of epichlorohydrin with butanols were examined by gel chromatography. For starting molar ratios of 0.2-3, the experimental results were compared with values calculated using a mathematical model comprising varying combinations of the reaction rates ($K = k_p/k_t$) of the first six propagation stages. The best approximation was obtained for the combination $K = 0.15, 0.20, 0.24, 0.24, 0.24, 0.24$, which gave 85.7% agreement between the comparative compositions of the first three derivatives of *n*-butanol. The rate of the initiation reaction is unity.

INTRODUCTION

The reaction of 1-chloro-2,3-epoxypropane (epichlorohydrin) with butanol is known to proceed very readily in the presence of acid catalysts, with opening of the epoxide ring of the epichlorohydrin. The products formed are predominantly 3-chloro-2-hydroxypropyl butyl ethers (C_α -ethers)^{1,2}. The presence of C_β -ethers is assumed, although in only small amounts; so far they have not been isolated and their properties have not been described.



As I contains a hydroxyl group that is able to react (similar to the starting butanol), the 3-chloro-2-hydroxypropyl ethers formed compete with the starting alcohol in the reaction with epichlorohydrin:



$n = 1$, compound II; $n = 2$, compound III; $n = 3$, compound IV. Polyaddition of epichlorohydrin takes place in this reaction. Owing to the possibility of opening of the epoxide ring, 2^n isomers may be formed in the n th polyaddition stage, which is an inconveniently high number of compounds from the viewpoint of separation and identification.

I-III derived from 1-butanols and 2-methyl-1-propanol have been identified by gas chromatography^{3,4} and the use of paper chromatography has also been described⁵. An investigation of the reaction of epichlorohydrin with methanol showed⁶ that both C_α and C_β ethers are formed; the number of isomers found for compounds of types I-III was 2^n .

The reaction investigated in this work was a system of irreversible competitive reactions. The polyaddition of epichlorohydrin results in a certain amount of unreacted starting alcohol remaining in the reaction mixture⁷, even with epichlorohydrin present in molar excess. Not only a single predominant compound is obtained, but also a number of similar molecules with different molecular weights are formed. The form of the distribution curve depends on the starting molar ratio of epichlorohydrin to the hydroxyl compound and on the ratio of the reactivities of hydroxyl groups in the starting alcohol (initiation) and in the 3-chloro-2-hydroxypropyl ethers formed (propagation). For some butanols and compounds of type I the constants of the reaction with epichlorohydrin are known^{6,7}. Their ratios, $K = k_p/k_i$ (propagation: initiation), are 9.38 (*n*-butanol) and 9.37 (isobutanol). Kinetic experiments were carried out with an excess of alcohol; therefore, they do not correspond exactly to the actual reaction conditions for the synthesis of poly-adducts. This is probably also the main reason why the results for the composition of adducts at various starting molar ratios of epichlorohydrin to *n*-butanol (Q) obtained by using $K = 9.38$ in the calculation by means of the mathematical model⁸ are at variance with the experimental values². It was found that a much better approximation was achieved with a mathematical model using $K = 1.0$. Hence, in contrast to what one might expect, the propagation reaction is much more rapid than the initiation reaction.

Although gas chromatography yields good qualitative results, quantitative results must be corrected⁴ and the scope of investigation must be restricted to compounds of types I-III, which is why we attempted to utilize the possibilities offered by gel chromatography in the study of the composition of adducts of epichlorohydrin with butanols, and by doing so to determine a more exact relationship between the rates of the initiation and propagation reaction.

Gel chromatography, first applied in the investigation of polymers, has recently also been used in the evaluation of the kinetics and mechanisms of reactions of low-molecular-weight compounds, as well as in the study of the formation of oligomeric mixtures. If suitably modified, gel chromatography makes possible both a qualitative

and a quantitative evaluation of the molecular-weight distribution of products arising by the polyaddition reaction. For the polyaddition reaction under investigation, the use of the above analytical system leads to the possibility of a quantitative evaluation of the formation of first addition stages, while at the same time providing a survey of the overall distribution of the products. We based our study on the results of an investigation of the reaction of epichlorohydrin with methanol by using gel chromatography⁹.

EXPERIMENTAL

For the preparation of standards, compounds of type I–III and the adducts under investigation were prepared with various starting ratios using epichlorohydrin (b.p. 115.6°/10.0 kPa); the content of epoxide groups was 99.98% (theoretical)¹⁰ and the purity was 99.94% (gas chromatography). The butanols were of analytical grade (Lachema, Brno, Czechoslovakia, and Reanal, Budapest, Hungary).

To the alcohol plus boron trifluoride diethyl etherate, epichlorohydrin was added dropwise at regular intervals in an amount corresponding to the chosen value of Q . The temperature was kept within the range 50–60° even after the dosage had been completed until all of the epichlorohydrin had reacted. The reaction mixture was then neutralized by stirring with fine sodium carbonate powder. Solid particles were removed by filtration and the filtrate was subjected to repeated fractional distillation *in vacuo* in order to obtain standards, or used directly in the analysis by gel chromatography. The ethers thus obtained are colourless liquids at room temperature. Their physicochemical characteristics are summarized in Table I. The chlorine content was determined by hydrolysis¹¹ and the content of hydroxyl groups was determined by acetylation with acetic anhydride¹².

The calculations were performed with a National Elliott 803 B computer, using a program described earlier⁸.

TABLE I
CHARACTERIZATION OF STANDARDS

Compound*	Content (equiv. per 100 g)		B.p. t °C (kPa)	n _D ²⁵	d ₄ ²⁵
	Cl**	OH**			
In	0.6001	0.6001	93.5–94 (1.333)	1.4437	1.041
	0.596	0.604			
IIIn	0.7717	0.3858	100–102 (0.013)	1.4627	1.138
	0.764	0.381			
IIIIn	0.8530	0.2843	158–160 (0.053)		
	0.881	0.292			
Ii	0.6001	0.6001	97–98 (3.199)	1.4399	1.033
	0.604	0.594			
Is	0.6001	0.6001	95–96 (2.799)	1.4397	1.031
	0.595	0.632			
It	0.6001	0.6001	97–98 (3.332)	1.4416	1.034
	0.590	0.608			

* n = 1-Butanol; i = 2-methyl-1-propanol; s = 2-butanol; t = 2-methyl-2-propanol.

** Calculated values first, found values underneath.

Analyses of the polyaddition products were performed with a gel chromatograph built at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences. The system contained five columns packed with S 232 gel. A Waters R 403 differential refractometer was used as detector. This system permits the analysis of oligomers up to a molecular weight of *ca.* 2500. Tetrahydrofuran was used as solvent, and *ca.* 5% solutions of poly-adducts were used in the analysis.

Model compounds for the first polyaddition stages (compounds of types I–III) were checked for purity and subsequently used in a quantitative calibration of the apparatus. The concentration dependence of the refractive index difference for the calibrating compounds I, II and III was extrapolated for the first six adducts. This provided the possibility of a quantitative characterization of the purities of the model compounds and of the composition of the polyaddition reaction products over a wide range.

Composite distributions of the polyaddition mixtures were analyzed by using a DuPont Curve Resolver 310 curve analyser.

RESULTS AND DISCUSSION

Model compounds and quantitative calibration of the apparatus

The standard compounds used were characterized by determining the contents of other components. It was found that they contained small amounts of side adducts, which were determined by the dependence of the refractive index difference on the polymerization degree by means of a curve analyser using an integral procedure. The adducts are characterized by counts common for all isomers of the same degree of addition (they are not separated in gel chromatography). The compositions of these compounds are given in Table II. The values obtained were used in the quantitative calibration of the apparatus in analyses of the reaction products. It was confirmed, that even with molar ratios Q chosen so as to support the formation of the main compound only, small amounts of side isomers with the polymerization degree under consideration are also formed, together with a certain amount of compounds with adjacent degrees of addition.

Resolution of isomers

To verify the possibility of separating 3-chloro-2-hydroxypropyl ethers of the

TABLE II
PURITY OF STANDARDS

Compound*	Content of individual adducts (wt.-%)				Elution volume (counts)
	I	II	III	IV	
In	96.6	3.4	—	—	108.0
IIn	4.9	94.9	0.2	—	101.7
IIIn	—	5.0	82.8	12.1	96.0
Ii	99.5	—	—	—	109.0
Is	96.1	3.9	—	—	108.8
It	86.2	8.5	—	—	107.6

* n, i, s and t as in Table I.

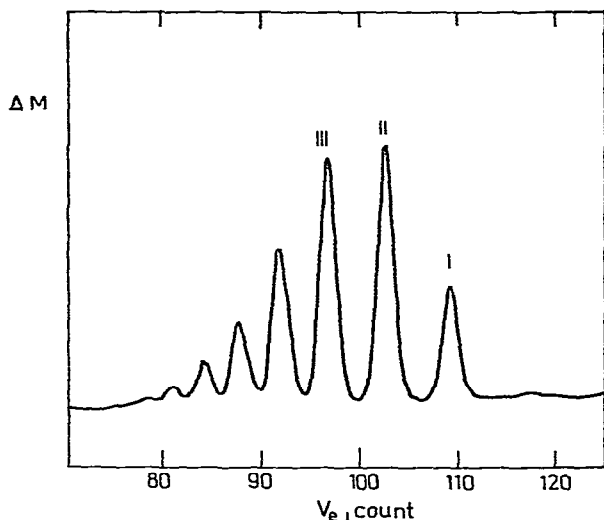


Fig. 1. Chromatogram of an adduct of the reaction between epichlorohydrin and 1-butanol prepared at the starting molar ratio $Q = 2.5$. V_e = elution volume; Δn = refractive index difference. I, II, III = adducts of 1, 2 and 3 molecules, respectively, of epichlorohydrin with 1-butanol (Table II).

individual butanols by using gel chromatography, we prepared four compounds of type I. As demonstrated in Table II, which presents elution volumes of the individual compounds for the conditions employed, various adducts of the same alcohol can be readily resolved while adducts of the same degree of isomeric alcohols exhibit similar elution volumes.

Analyses of products

Gel chromatograms of products of the individual reactions each contained several peaks characteristic of the adducts. An example of the distribution formed in the polyaddition reaction can be seen in the record of the analysis of the reaction products with a starting molar ratio $Q = 2.5$ shown in Fig. 1.

The results of a quantitative evaluation of the content of the first addition

TABLE III
COMPOSITION OF REACTION PRODUCTS (ADDUCTS) OF 1-BUTANOL

Q	Content of individual compounds in adducts in molar ratios		
	I	II	III
1/5	100	1-2	
1/4	100	2-3	
35/100	100	3-4	
1/2	100	5-6	
1	100	17-19	1-2
1.5	100	43-48	10-13
2	100	83-93	36-40
2.5	100	101-112	59-65
3	100	122-136	99-109

stages in the reaction products of epichlorohydrin with 1-butanol are summarized in Table III. Mutual ratios of the compounds are characteristic of the kinetic conditions used in the polyaddition. As one of the main factors (the starting molar ratio, Q) is always known in advance, the results help to estimate the other factor, *viz.*, the propagation rate: initiation rate ratio (K).

Comparison with a mathematical model

Various combinations of the first six comparative reaction rates of the degree of propagation were inserted in the mathematical model used in calculating the composition of products of the reaction between epichlorohydrin and alcohols. The rate of the initiation reaction was regarded as unity. By comparing the calculated molar volumes of compounds I–III for various starting molar ratios Q (0.2–3) with the experimentally determined values, we gradually approached a combination which best describes the actual situation. It was found that the polyaddition of epichlorohydrin with 1-butanol proceeded more slowly than it would according to the kinetic studies^{13,14} and according to the content of the epoxide groups and the residual organically bound chlorine in raw butyl glycidyl ether formed in the dehydrochlorination of the adducts. Table IV gives molar ratios for three combinations which best agree with each other. For combination No. 1 of the reaction rate constants (0.15, 0.20, 0.24, 0.24, 0.24, 0.24), agreement was reached for 12 values of 14 investigated. Unlike the reaction of epichlorohydrin with methanol⁹, in which the best results were obtained with the descending combination 0.2, 0.15, 0.1, 0.08, 0.07, 0.06, an ascending series is operative in this instance. This means that higher degrees of polyaddition have a higher reaction rate than that of the first propagation step, and that these propagation reactions are four to five times slower than the initiation reaction with 1-butanol.

TABLE IV

MOST SUITABLE COMBINATION OF RELATIVE REACTION CONSTANTS (K_1 – K_6) AND THE CORRESPONDING COMPOSITION OF THE REACTION PRODUCTS (FOR $Q = 1/5$ –3)

Parameter	Combination								
	1			2			3		
K_1	0.15			0.15			0.15		
K_2	0.20			0.20			0.20		
K_3	0.24			0.24			0.25		
K_4	0.24			0.27			0.30		
K_5	0.24			0.30			0.35		
K_6	0.24			0.32			0.40		
	I	II	III	I	II	III	I	II	III
$Q = 0.2$	100	2		100	2		100	2	
0.25	100	2		100	2		100	2	
0.35	100	3		100	3		100	3	
0.5	100	5		100	5		100	5	
1	100	17	2	100	17	2	100	17	2
1.5	100	43	13	100	43	13	100	43	13
2	100	74	38	100	73	38	100	73	36
2.5	100	101	70	100	99	68	100	99	65
3	100	123	105	100	121	101	100	118	94
Percentage agreement	85.7			78.6			78.6		

REFERENCES

- 1 H. Flores-Gallardo and C. B. Polland, *J. Org. Chem.*, 12 (1947) 831.
- 2 J. Novák, *Angew. Makromol. Chem.*, 35 (1974) 169.
- 3 J. Novák and J. Řezníček, *J. Chromatogr.*, 43 (1969) 437.
- 4 J. Novák and J. Horáková, *Symposium MAKROTEST, Pardubice, 1973*, DůmTechniki, 1973, p. 135.
- 5 J. Novák, *J. Chromatogr.*, 31 (1967) 137.
- 6 J. Novák and J. Řezníček, *J. Chromatogr.*, 91 (1974) 757.
- 7 J. Novák, *Kunstst.-Rundsch.*, 16 (1969) 703.
- 8 J. Novák and V. Šváb, *Makromol. Chem.*, 168 (1973) 131.
- 9 J. Novák, M. Bleha and J. Čoupek, *Angew. Makromol. Chem.*, in press.
- 10 D. W. Knoll, *Chicago Meeting, Amer. Chem. Soc.*, 18 (1958) 2.
- 11 M. Lidařík, *Kunstst.-Plast.*, 6 (1959) 16.
- 12 A. Bring and F. Kadleček, *Plaste Kautsch.*, 5 (1958) 43.
- 13 S. Sekiguchi, I. Takase and K. Matsui, *Kogyo Kagaku Zasshi*, 66 (1963) 1827; 68 (1965) 287, 945 and 2413.
- 14 J. Novák, *Int. J. Chem. Kin.*, 5 (1973) 919.