function $\varphi$ vs $-\log k_{-1}$ for the three pairs of L parameters. Having conducted an experiment on the chromatographic separation of a mixture of A and B, taken in an equimolar ratio, at two passage rates of the solution, corresponding to any of the proposed L pairs, it becomes possible to calculate $\varphi$. Knowing $\varphi$, the quantity $-\log k_{-1}$ can be determined from the corresponding curve in Fig. 2.

## CONCLUSIONS

1. A system of equations, describing the process of separating a reacting two-component mixture in a chromatographic column, was solved. The exit curves are plotted.

2. Curves, describing the change in the amount of complex in the mixture on exit from the column as a function of the logarithm of the decomposition rate constant of the complex, were constructed on the basis of the calculations for a set of kinetic parameters of the reaction.

3. It was shown that it is theoretically possible to determine the rate constants of complex-formation reactions from the results of two chromatographic experiments.

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# EXCHANGE REACTION BETWEEN EPOXIDES AND CHLOROHYDRINS


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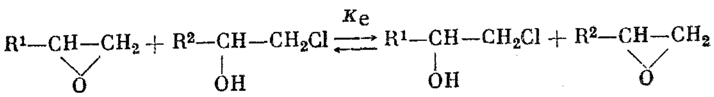
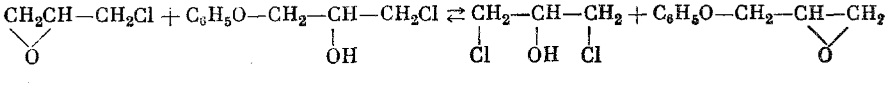
Exchange reaction occurs when epoxides are reacted with chlorohydrins in the presence of a catalyst, which consists in the transfer of HCl from the chlorohydrin to the epoxide and results in the formation of a new epoxide and a new chlorohydrin [1,2]:


(1)

Catalysts for such a reaction are bases (NaOH, KOH, tertiary ammonium salts, tertiary amines), as well as the salts of weak and strong acids ($Na_2CO_3$, $K_2CO_3$, NaCl, $R_4NCl^-$, etc.). The rate with which equilibrium (1) is established depends on the catalyst concentration and increases with increase in the temperature. However, the values of the equilibrium constant have not been determined up to now.

The purpose of the present paper was to determine the values of the constant for the exchange reaction of epichlorohydrin (ECH) with 1-chloro-2-hydroxy-3-phenoxypropane (CHPP), which leads to the formation of phenyl glycidyl ether (PGE) and glycerol 1,3-dichlorohydrin (GDH):


(2)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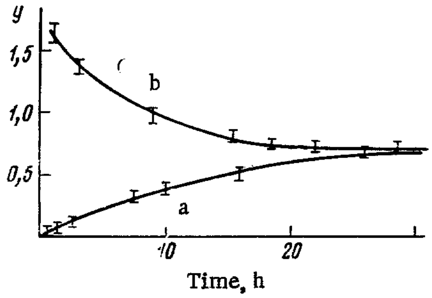


Fig. 1. Relation between y = [PGE][GDH]/[ECH][CHPP] and the time: a) formation of PGE and GDH from ECH and CHPP; b) formation of ECH and CHPP from PGE and GDH at 70°C.

The relation between the ratio y = [PGE][GDH]/[ECH][CHPP] and the time under various initial conditions is plotted in Fig. 1. Curves a and b change in a smooth manner and approach the same limit, which corresponds to the equilibrium, the establishment of which under our selected conditions required 20-30 h. The equilibrium constant of the reaction, determined from two reaction systems, is equal to $K_e = 0.7 \pm 0.1$. As was shown in [3], in neutral and basic media the epoxide ring is opened exclusively as the result of its "normal" attack by Cl ion, and consequently exchange reaction (2) is not accompanied by the formation of CHPP and GDH isomers.

## EXPERIMENTAL

The equilibrium constant of the exchange reaction was determined from two reaction systems: 1) ECH and CHPP; 2) PGE and GDH. The reaction was run in a water–acetone mixture (1:3 by volume) at 70° under the influence of NaCl. Starting concentrations of the reactants: [ECH] = 2.25, [CHPP] = 0.5, [PGE] = 1.5, [GDH] = 0.7, and [NaCl] = $10^{-2}$ mole/liter.

The reaction products were analyzed by GLC on a Chrom-4 chromatograph [katharometer, column length 2.4 m, XE-60 deposited on Chezasorb, 180°, and carrier gas = helium (40 ml/min)]. The current concentrations of the reactants and reaction products were determined using calibration curves.

## CONCLUSIONS

We determined the equilibrium constant of the exchange reaction between epichlorohydrin and 1-chloro-2-hydroxy-3-phenoxypropane, which leads to the formation of phenyl glycidyl ether and glycerol 1,3-dichlorohydrin.

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