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Routes for Reactions of Alkylene Oxides with R-β-Hydroxyalkyl Sulfides: Unusual Exchange of Functional Groups

A. D. Malievskii

N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 117334 Russia
e-mail: chembio@sky.chph.ras.ru

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Abstract—Possible routes of the previously unknown exchange reaction of alkylene oxides with R-β-hydroxyalkyl sulfides have been considered. Each route has intermediates and transition states of its own, but all the directions in the final stage lead to the formation of a single intermediate cyclic bipolar ion with intramolecular hydrogen bonding, which determines the common nature and composition of end products for all routes. The features of the reaction have been analyzed. The quantitative description of each route has been given.

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Earlier it was shown [1] that upon the interaction of alkylene oxides with organic compounds of the elements of 5a- and 6a-subgroups of the periodic table containing β-hydroxyalkyl groups (β-hydroxyalkyl sulfides, -selenides, -amines, -phosphines) at S, Se, N and P heteroatoms in the lower valence state an unusual reaction of the exchange type was discovered. In this reaction, alkylene oxide and an organic compound of a structure different from that of the original (1) with β-hydroxyalkyl group at heteroatom Z are formed as products [1, 2, 3]:

$$\begin{aligned} &R^1CH{-}CH_2 + R^2_{n-1}ZCH_2CH(R^3)OH \\ &\quad\quad O \\ &\rightleftharpoons R^3CH{-}CH_2 + R^2_{n-1}ZCH_2CH(R^1)OH \\ &\quad\quad O \end{aligned} \qquad (1)$$

where Z is S, Se, N, or P; *n* is their lower valence state; and R^1, R^2, and R^3 are radicals that do not contain hydroxyl groups. Reaction (1) is reversible, and after some time the system reaches the state of dynamic equilibrium.

EXPERIMENTAL

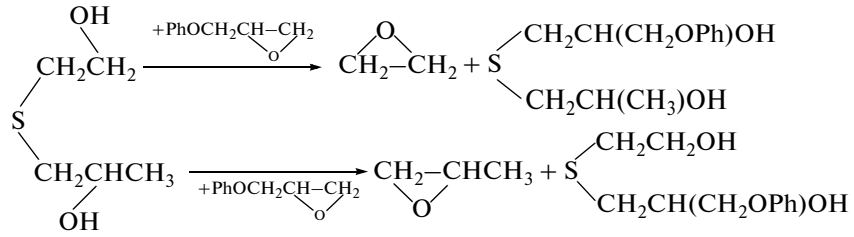
Synthesis of β-hydroxyalkyl sulfides, β-hydroxyalkyl disulfides, -selenides, -amines, and -phosphines, their purification, and elemental analysis were performed by standard methods [4–8]. The experiments were conducted in temperature-controlled glass and metal ampoules in chlorobenzene and other solvents at temperatures ranging from 75 to 180°C [1, 4, 6, 9]. The analysis and identification of the reactants and products were carried out using a variety of instrumental methods (GLC [5–10], infrared spectroscopy [11]); the structure of the compounds was determined by the proton NMR technique [5, 6, 8, 9].

RESULTS AND DISCUSSION

The main feature of the reaction is that alkylene oxide and β-hydroxyalkyl sulfide react as if they exchange radicals R^1 and R^3. As a result of this exchange, alkylene oxide and β-hydroxyalkyl sulfide with radicals R^3 and R^1 are formed, respectively. Such nonspecific exchange by functional groups is unusual. A similar reaction of the exchange type has been shown by numerous examples with R^1 = H, CH_3, C_2H_5, $CH{=}CH_2$, C_6H_5, $CH_2OC_2H_5$, $CH_2OC_4H_9$, $CH_2OC_6H_5$, R^2 = C_6H_5, $C_6H_4CH_3$, C_8H_{17}; R^3 = H, CH_3, C_6H_5, $CH_2OC_6H_5$ [1, 2, 4–9]. In all the cases a relationship between the structure of the product alkylene oxide and the structure of the reactant β-hydroxyalkyl sulfide, -selenide, -amine, and -phosphine has been established as well. This structure is determined by the constitution of β-hydroxyalkyl group of the parent alcohol containing the heteroatom [1, 4, 7]. For example, the reaction of β,β'-dihydroxyethylpropyl sulfide with phenyl glycidyl ether proceeds to yield ethylene oxide from the hydroxyethylene oxide group and propylene oxide from the hydroxypropylene oxide group [4]:

Table 1. Mass balance between the consumed reactant *n*-octyl-β-hydroxyethyl sulfide and the product ethylene oxide ($T = 145$°C; solvent, chlorobenzene)

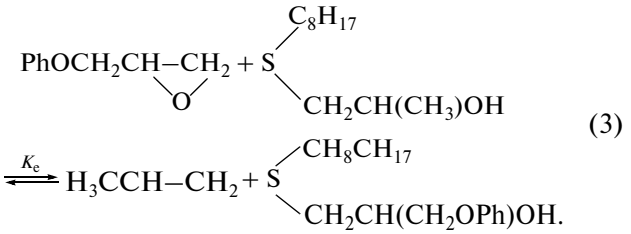
Reactants \ τ, min	0	10	20	30	40	50	60	70
n-Octyl-β-hydroxyethyl sulfide mol/L	1.94	1.86	1.79	1.72	1.67	1.65	1.64	1.64
Ethylene oxide (product) mol/L	0	0.08	0.15	0.22	0.26	0.29	0.29	0.29
Product balance, %	–	100	99	100	100	98.5	98	98



(2)

So, for the reaction of phenyl glycidyl ether (initial oxirane concentration of 4.23 mol/L) with *n*-octyl-β-hydroxyethyl sulfide (initial concentration, 1.94 mol/L) conducted at 145.5°C, the equilibrium state is established in 45–50 min after the start of the experiment with an equilibrium constant of $K_e = 0.013$. In this process, a permanent mass balance between the reactants and the products is observed during the process (Table 1).

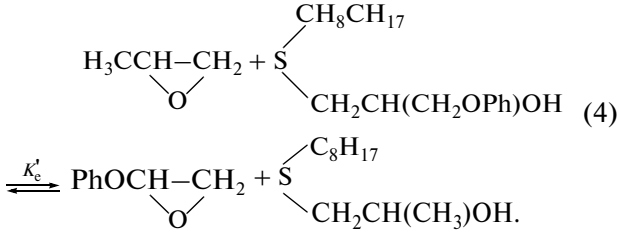
The reaction of phenyl glycidyl ether with *n*-octyl-(β-hydroxypropyl) sulfide in chlorobenzene leads to propylene oxide and β-hydroxy-γ-phenoxypropyl-(*n*-octyl) sulfide [1, 4].



(3)

After a few hours, the system reaches the state of dynamic equilibrium with an equilibrium constant of K_e =3.03 (150°C). In this case, the material balance between the reactants and products holds as well. The equilibrium constant K_e (150°C) for reaction (3) is constant to be 3.0–3.05 when the initial sulfide and oxirane concentrations respectively vary from 2 to 4.2 and from 4.1 to 0.7 mol/L (molar ratio of 1 : 2, 1 : 1, 2 : 1, and 5.5 : 1). With increasing temperature, the equilibration time for reaction (3) decreases from 8–10 h at 140°C to 2 h at 180°C. The equilibrium constant K_e for the reaction in the temperature range of 140–190°C does not change (3.0–3.06), i.e., the heat of the reaction is $Q \cong 0$. In other cases, the heats of reactions for the phenyl glycidyl ether–R-β-hydroxypropyl sulfide system (R = C_6H_5, *p*-$CH_3C_6H_4$, C_8H_{17}) range from –3.7 to 0 kcal/mol.

When reaction (3) is run in the opposite direction (propylene oxide with *n*-octyl-β-hydroxy-γ-phenoxypropyl sulfide), the products are phenyl glycidyl ether and *n*-octyl-β-hydroxypropyl sulfide [1, 4]:



(4)

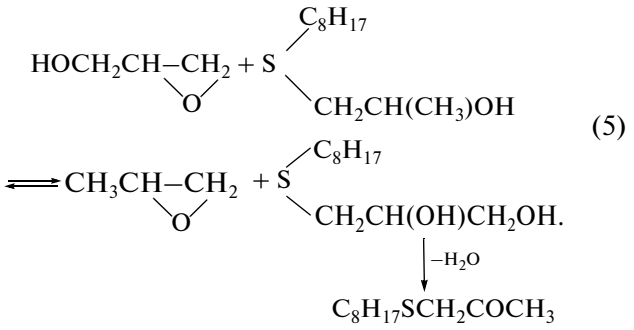
For this reaction, $K'_e = 0.33$ (150°C), while $K_e = 1/K'_e = 3.03$ (150°C), where K_e and K'_e are the equilibrium constants measured in two experiments described above.

It interesting that for the propylene oxide (0.75 mol/L)–*n*-octyl-β-hydroxyethyl sulfide (0.063 mol/L) system at low reactant concentrations and 150°C in chlorobenzene, the equilibrium state is reached in ~100 h [1].

Along with reaction (1) for compounds with Se, N, or P heteroatoms, reactions leading to the formation of carbonyl and unsaturated compounds [1] occur, which impede establishment of the dynamic equilibrium.

In those rare instances when OH groups disappear in the system, the state of dynamic equilibrium is not established. This is typical of systems with two hydroxyl groups at the heteroatom. For example, in reactions involving bis(β-hydroxyalkyl) sulfides, for which the exchange-type reactions were first observed [2], we determined the presence of oxothianes as by-products formed as a result of the dehydration of sulfides [1]. In this case, the system does not reach the state of dynamic equilibrium. The same was observed

in the specific reaction of glycidol with β-hydroxypropyl sulfide [1, 4]. The reason for this is apparently the pinacol rearrangement [12] of dihydroxyalkyl sulfide formed during the exchange reaction; the rearrangement leads to a compound that does not contain β-hydroxyl group (5):



Mechanism of the Exchange Reaction

As shown, the alkylene oxide–R-β-hydroxyalkyl sulfide system is the simplest. In this case, only two products of the exchange reaction are formed, alkylene oxide and β-hydroxyalkyl sulfide, and the system reaches the state of dynamic equilibrium.

Despite the seemingly simple nature of the reaction, a number of facts suggests otherwise. For example, the discrepancy between the overall order determined experimentally for concentrated solutions of β-hydroxyalkyl sulfides and the value that follows from the stoichiometric equation. The reaction order varies from 1 to 2 with increasing sulfide concentration. In addition, acceleration of the exchange by the action of proton-donor compounds was shown among other things. In view of the complex nature of the reaction, to select the right version of the mechanism, the reaction mixture composition for the "propylene oxide–*n*-octyl-β-hydroxyethyl sulfide" system was studied in detail, kinetic and spectral measurements were made, and quantum-chemical calculations of the system were performed.

In *the kinetic study*, the procedure consisted in the determination of the dependence of the reaction rate on the concentration of one component at a low constant concentration of the other. It was shown experimentally [11, 13–15] that at a constant sulfide concentration, the reaction rate increases with an increase in the concentration of alkylene oxide up to a definite value of its concentration. Above this value, the reaction rate slows down and subsequently remains almost constant or close to a limiting value, since the sulfide is almost entirely bound in a complex at an excess of alkylene oxide. Along with the β-hydroxyalkyl sulfide monomer and dimer, alkylene oxide and H-complexes involving the principal reactants starting materials are assumed to present in the mixture. To prove the formation of the complex, the IR spectra of octyl-β-hydroxyethyl sulfide in CCl_4 and its mixture with propylene oxide in the same solvent were taken at 25°C (in the region of stretching vibrations 3000–4000 cm^{-1}) at sulfide concentrations varied from 2.72×10^{-3} to 4.34×10^{-2} mol/L [11]. Bands with maxima at 3655 and 3559 cm^{-1} were detected for hydroxyethyl sulfide, which were attributed to the stretching vibrations of free (in monomer) and bound (in dimer) hydroxyl groups, respectively. The concentrations of the sulfide monomeric and dimeric forms were calculated, and their absorption coefficients and the constants of equilibrium between them were determined as well.

To prove the formation of the H-bonded complex upon the interaction of propylene oxide with octyl-β-hydroxyethyl sulfide, the IR spectra of their solutions in CCl_4 were measured. The sulfide concentration was maintained constant $(3.73–3.96) \times 10^{-2}$ mol/L, when the concentration of propylene oxide varied in the range from 6.6×10^{-3} to 0.7 mol/L.

Propylene oxide is optically transparent in the frequency range of 3000–4000 cm^{-1}. The IR spectra of octyl-β-hydroxyethyl sulfide display two bands, at 3655 and 3559 cm^{-1}. With increasing the propylene oxide concentration, the intensity of the 3655 cm^{-1} band decreases without shifting and the band at 3559 cm^{-1} shifts to lower frequencies to 3540 cm^{-1} with a simultaneous increase in its intensity, which can be explained by the formation of the complex. Thus, the region of 3550–3540 cm^{-1} is characteristic of the OH stretching vibrations of the dimeric form and the H-complex formed by the interaction of the hydroxyl group of the monomeric form of hydroxyethyl sulfide with the oxygen of the oxide ring. The evaluation of the equilibrium constant for the formation of the H-complex leads to a value of $K_p = 3 \pm 2$ l/mol.

The results of processing the spectra of propylene oxide and octyl-β-hydroxy-ethyl sulfide solutions in CCl_4 are shown in Table 2.

The $[C]_c$–[A][B] curve, where C_c is the H-complex and A and B are hydroxyalkyl sulfide and propylene oxide, respectively, clearly indicates the formation of the 1 : 1 complex only. Thus, the reaction mixture contains free alkylene oxide, monomer and dimer of β-hydroxyalkyl sulfide, and the H-complex of alkylene oxide with one molecule of β-hydroxyalkyl sulfide.

In choosing the options for the exchange reaction mechanism, it was taken into account that the order in β-hydroxyalkyl sulfide changes with increasing its concentration in the reaction mixture from 1 (for concentrations ≤0.3–0.5 mol/L) to 2 (for concentrations above 0.8–0.9 mol/L), whereas it is 1 in alkylene oxide and does not change over a wide range of its concentrations. This was shown by the example of propylene oxide–*n*-octyl-β-hydroxyethyl sulfide, phenyl glycidyl ether–phenyl-β-hydroxypropyl sulfide, phenyl glycidyl ether–tolyl-β-hydroxypropyl sulfide, and other systems [1, 4, 11, 16, 17]. The discrepancy between the overall reaction order in β-hydroxyalkyl sulfide determined experimentally for concentrated

Table 2. Results of processing the IR spectra of an *n*-octyl-β-hydroxyethyl sulfide–propylene oxide mixture in CCl_4 at 25°C. D_m, D_{mix}, D_d, and D_c are the optical densities of monomer sulfide, mixture of the sulfide dimer with a complex, dimeric sulfide, and a sulfide monomer–oxirane complex, respectively

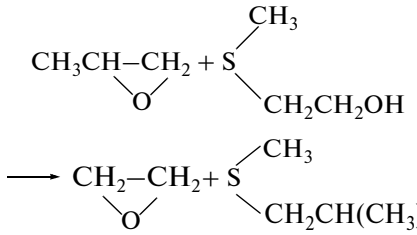
Concentration			Optical densities				Concentrations of monomer, dimer and complex			
$[A]_o$ mol/L sulfide	$[B]_o$ mol/L propylene oxide		D_m ν = 3655 cm^{-1}	D_{mix} ν = 3559–3540 cm^{-1}	D_d ν = 3559 cm^{-1}	D_c ν ≈ 3540 cm^{-1}	$[A]_m$ mol/L	$2[A]_d$ mol/L	$[B]_b \times 10^4$ $(mol/L)^2$	$[C]_c$ mol/L
0.040	0		0.17	0.29	0.30	0	0.0128	0.0265	0	0
0.040	0.040		0.17	0.30	0.30	0.0	0.0128	0.0274	5.12	0.00
0.040	0.057		0.16	0.31	0.27	0.035	0.0120	0.0247	6.61	0.0028
0.039	0.091		0.16	0.31	0.27	0.040	0.0120	0.0247	10.62	0.0028
0.040	0.165		0.15	0.32	0.24	0.080	0.0113	0.0126	18.0	0.0066
0.039		0.314	0.14	0.37	0.21	0.165	0.0105	0.0188	31.9	0.0093
0.590	0.038		0.12	0.40	0.15	0.250	0.0090	0.0138	51.9	0.0150
0.037	0.689		0.10	0.46	0.11	0.355	0.0075	0.0096	50.2	0.0202

solutions and the value that results from the stoichiometric equation shows the complex nature of the exchange reaction.

The following routes of the development of the exchange reaction were suggested: 1) for dilute solutions of R-β-hydroxyalkyl sulfides (concentration ≤0.1–0.15 mol/L): monomolecular intramolecular attack of the sulfide sulfur atom on the carbon atom of the oxide ring in the H-complex; 2) for concentrated solutions of R-β-hydroxyalkyl sulfides (concentration ≥0.4 –0.7 mol/L): (a) the interaction of H-complex with a second molecule of β-hydroxyalkyl sulfide and (b) the interaction of two H-complexes.

Experiments have shown that for all the directions of the reaction the nature and composition of the products are the same.

Dilute solutions of R-β-hydroxyalkyl sulfides (concentration ≤0.1–0.15 mol/L); forward reaction. For the first version of the exchange reaction mechanism, semiempirical calculations (PM3) of changes in the structure and energies of reactants, intermediates, transition states and final products were carried out for the model reaction of propylene oxide with methyl-β-hydroxyethyl sulfide [18]:



(6)

The structures of reagents and possible intermediates were determined, as well as the heat of formation, charge distribution, and bond orders. The reaction order (*n*) was used for analyzing the "spillover" of electron density during the course of the chemical reaction and ascertaining the formation of the hydrogen bond. The calculation showed that the probable reaction mechanism involves three stages with two intermediate products corresponding to the transition states and final products [18].

Let us describe in more detail the formation of the pre-reaction H-complex and bipolar ion II, which predetermine the course of the reaction and the composition and nature of the final products (Figs. 1, 2). The reactants (alkylene oxide and sulfide) are characterized by uneven charge distribution and have notice-

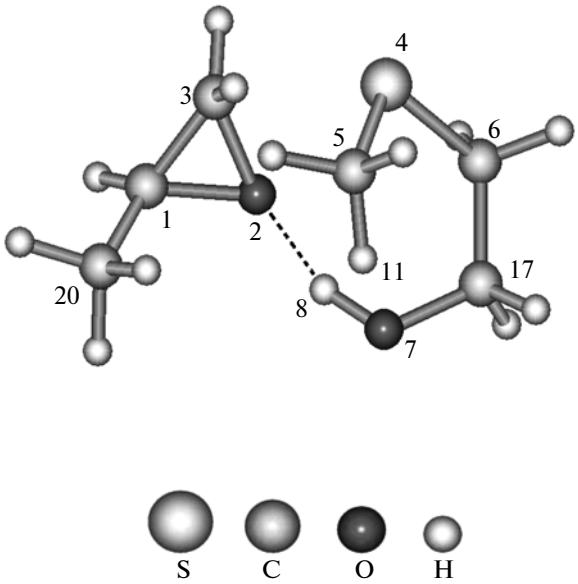


Fig. 1. Pre-reaction complex I. Only the atoms that participate in the exchange reaction are numbered.

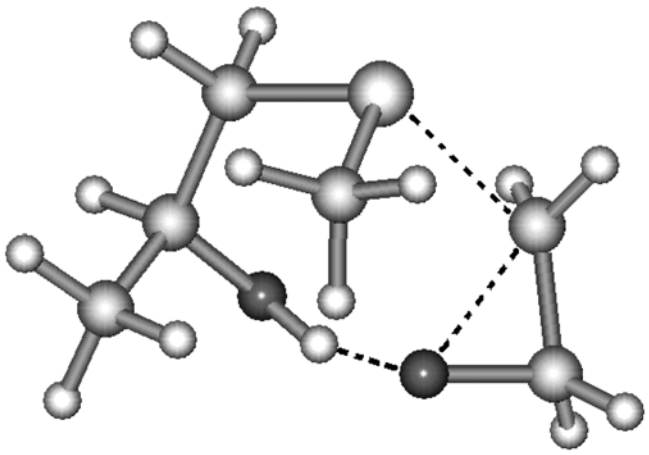
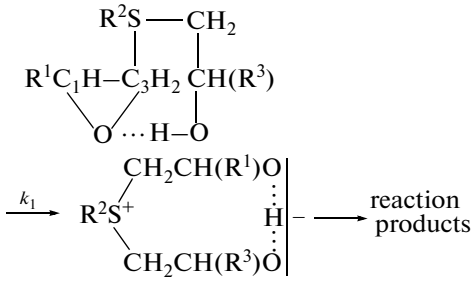


Fig. 2. Intermediate II (a bipolar ion).

able, although not very high dipole moments of 1.83 and 2.11, respectively. In alkylene oxide the largest negative charge (–0.27) concentrates on the oxygen atom; in methylhydroxyethyl sulfide, the highest positive charge (+0.19) is on the hydroxyl hydrogen atom. Obviously, it is by these atoms that the reactants most closely approach one another in the pre-reaction conformation and, hence, facilitate hydrogen bonding (Fig. 1), confirming the results of earlier experiments [11, 14].

The calculations showed that the O2–C3 bond in pre-reaction complex I (Fig. 1) is somewhat weakened (n = 0.94). The bond orders in the O2(–0.30)–H8(+0.24)–O7(–0.37) bridge are 0.04 and 0.87 [18]. Being small (0.04), the bond order n of the hydroxyl hydrogen bond with the oxygen of propylene oxide is still different from zero. The S4 sulfur atom of the sulfide and carbon atom C3 of the oxirane experience interaction, although weak (n = 0.02), but it is probably sufficient for spatial orientation necessary for further structure rearrangement (1). The supposed second stage of the reaction is the nucleophilic attack of the sulfide sulfur atom on the oxide ring inside the H-complex (rate-limiting stage):



(7)

Steric hindrances in the H-complex exert a determining effect on the direction of the attack of the S atom and on epoxide ring opening, which goes mainly on the unsubstituted C3 carbon atom. A similar effect of the steric factor was observed in the reaction of alkylene oxides with the RS^- sulfide ion [19]. As a result, the H-complex transforms in the monomolecular mode with the concerted rupture and formation of corresponding bonds into the products through a number of intermediates and transition states, including intermediate cyclic bipolar ion II with intramolecular hydrogen bonding [1, 2, 18]. In this ion, the formation of the intramolecular hydrogen bond with the proton at the center of the $(O...H...O)^-$ fragment is observed (Fig. 2). The charge on the bridging proton changes little (+0.30, +0.28) in the process. The bridging distances d(02-07) also change slightly: 2.68, 2.70 Å. The formation of complexes with fragments of the $(A...H...B)^{\pm}$ type with a central proton was also observed in the ionization of organic compounds in solutions of acids and bases [20–23].

In the bipolar ion II in accordance with the electronic structure of the sulfur atom three of four sp^3-hybridized orbitals form σ-bonds with C atoms, the fourth is occupied by a lone electron pair. The S(4)–C(3), C(5), C(6) node is a pyramid [18] with the sulfur atom in the apex and C3–S4–C5, C5–S4–C6, and C6–S4–C3 angles of 105°. The positive charge is concentrated mainly on the S(4) sulfur atom (+0.58); the negative one, on the O(7) oxygen atom (–0.75), and the distance between them is 3.06 Å. As a result, the dipole moment is rather high (7.6 D).

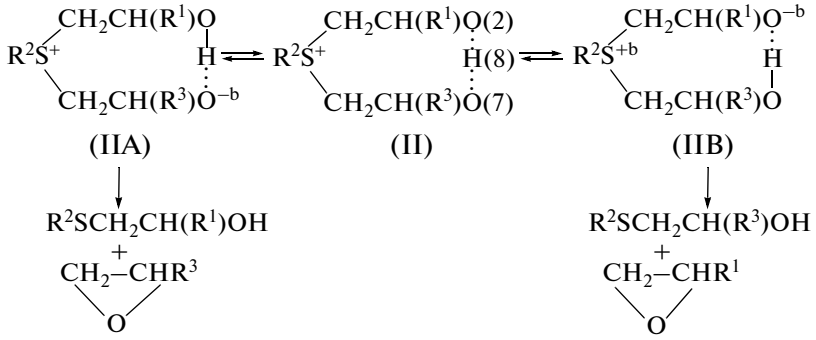
Despite the fact that the O7–H8 distance (1.72 Å) is much greater than the O2–H8 distance (0.98 Å), the O7–H8 bond order is not negligible yet (0.09); the O7–H8–O2 hydrogen bond (due in part to the sequence of charges on the atoms of the chain: –0.75, +0.28, –0.39) stabilizes the eight-membered structure of the ion II. The O2–H8–O7 bridge is retained throughout all the process until the formation of the final products.

The unimolecular transformation of the cyclic bipolar ion II into the final reaction products occurs in the following way. When attacking the CH_2 group bonded to the sulfur atom by nucleophilic fragment O7(q = –0.75), the reaction of the removal of sulfide easily occurs with breaking the S4–C6 bond and the simultaneous closure of the O7–C6 bond with the formation of oxirane. With O7 and C6 getting closer, changes in the charge q(O7) were fixed at intervals of 0.5 Å (2.43, 1.93, 1.44 Å) to be –0.75, –0.59, and –0.28, respectively; the same for q(C6), –0.29, + 0.13, –0.03, and the n(C6O7) bond order varied as follows: –0.07, 0.47, 0.96. The reaction of the conversion of the bipolar ion into the products is exothermic, $\Delta H_r = \Delta H_f^\circ$ (P_r) – ΔH_f° (II) = –18 kcal/mol, and the enthalpy of activation is 32 kcal/mol, which is consistent with experimental data for related compounds (28.4–32.1 kcal/mol) [2, 18].

Thus, the determining influence of the structure of the pre-reaction complex I on the course of the process as a whole was revealed, the role the of O...H...O hydrogen bridge at all stages of the reaction until the

formation of the end products was shown: the reaction occurs with the direct conversion of the bipolar ion II into the reaction products.

The reaction mechanism involving the cyclic bipolar ion II explains not only the occurrence of the process, the nature and composition of the final products, but also the reversible nature of the reaction associated with prototropic tautomeric equilibrium between bipolar ions IIA and IIB with the intramolecular hydrogen bond [7, 18, 25].



(8)

The intermediate IIA transforms with a simultaneous shift of the electron density from O7–H8 bond to O2–H8 bond through II into the intermediate cyclic bipolar ion IIB with the intramolecular hydrogen bond while retaining the O2–H8–O7 hydrogen bridge. Quantum chemical calculations showed that in the above structures the hydrogen bridge is retained throughout all the reaction pathway [18]. This reaction is thermally neutral, and the activation barrier is as low as 4–5 kcal/mol. Intermediates IIA and IIB are in dynamic equilibrium. The reversible nature of the reaction was experimentally shown for many pairs of the oxirane–R^2-β-hydroxyalkyl sulfide system [1–4].

With allowance for the formation of the H-complex I, the reaction scheme for (6) has the following form

$$A + B \overset{K_e}{\rightleftharpoons} [I] \xrightarrow{k_1} \text{reaction products},$$

where A is hydroxyalkyl sulfide and B is oxirane. Assuming that the equilibrium is established quickly and the consumption of the complex for the formation of the products does not violate the equilibrium, the concentration of the complex can be expressed by $[I] = K_e[A]_b[B]_b$. Since the oxirane concentration in our case is much higher than the concentration of hydroxyalkyl sulfide, it can be assumed that $[B]_b \cong [B]_o$, $[A]_b = [A]_o - [I]$; $[A]_o$ and $[B]_o$ are the initial concentrations of hydroxyalkyl sulfide and oxirane, respectively. Then, $[I] = K_e[A]_o[B]_o/(1 + K_e[B]_o)$, and the expression for the initial reaction rate will be as follows:

$$W_o = k_1K_e[A]_o[B]_o/(1+K_e[B]_o).$$

Transforming this expression, we get $[A]_o/W_o = 1/k_1 + 1/k_1K_e[B]_o$.

Using it, the values of k_1 and K_e for the propylene oxide (0.15–1.95 mol/L)–octyl-β-hydroxyethyl sulfide (0.062–0.067 mol/L) system were found for the temperature range 120–160°C in chlorobenzene [11]. For the forward direction of the reaction of the system, it was found that $k_1 = 1.52 \times 10^9$ (exp– 29400/*RT*) (for 150°C $k_1 = 8.4 \times 10^7$ s^{-1}) and $-\Delta S^{\neq} = 12.2$ en. units, the heat of the H-complex I formation $-\Delta H = 2.0 \pm 1.0$ kcal/mol (for 150°C $K_e = 1.85$).

Similarly, the kinetic characteristics have been determined for the forward reaction of the ethylethylene oxide (0.10–1.10 mol/L)– R^2-β-hydroxypropyl sulfide (0.15–0.18 mol/L; chlorobenzene solvent) system with $R^2 = C_6H_5$, $CH_3C_6H_4$, C_8H_{17} [1, 14, 16]. The reaction rate constants $k_1(10^7\ s^{-1})$ change as follows depending on the structure of the substituent in the sulfide: 1.41, 1.58, 8.4 (160°C). The values of the H-complex formation enthalpies, the activation energies of the rate-limiting step of the exchange reaction for several alkylene oxide–R^2-β-hydroxyalkyl sulfide systems are given in Table 3.

For the reaction in the ethylethylene oxide– R^2-β-hydroxypropyl sulfide system in a series of $R^2 = C_6H_5$, $CH_3C_6H_4$, C_8H_{17} an increase in the reaction rate constants and a decrease in the activation energies related to an increase in the electron-donating properties of the substituents in the sulfide are observed (Table 3). The heats of formation for the H-complexes correspond to the heats of formation of the hydrogen bonds of oxiranes with alcohols [26–28]. The accuracy of determination of both *E* and ΔH is ~1 kcal/mol.

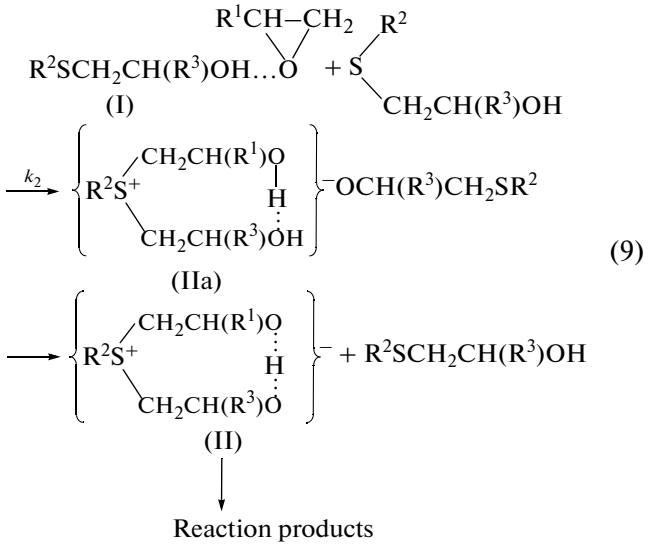
Concentrated solutions of R^2-β-hydroxyalkyl sulfides (≥0.3 mol/L, forward reaction). For concentrated solutions of R-hydroxyalkyl sulfides (concentration ≥0.3 mol/L), taking into account the first order in alkylene oxide and the second order in sulfide after the formation of the H-complex I, the following step of the exchange reaction occurs, namely, the nucleophilic attack of the C–O bond of the oxide ring of the H-complex I by the sulfur atom of a second molecule of R-hydroxyalkyl sulfide. The epoxide ring opens at the unsubstituted carbon atom, as in dilute solutions of hydroxyalkyl sul-

Table 3. Kinetic parameters of the exchange reaction and the values of the enthalpy of the H-complex formation (direct reaction) for systems ethylethylene oxide–R^2-β-hydroxypropyl sulfide and propylene oxide–R^2-β-hydroxyethyl sulfide for diluted solutions (solvent, chlorobenzene)

Oxirane R^1	Sulfide R^2	Sulfide R^3	Preexponential factor $A \times 10^{-9}$, s^{-1}	Activation energy E, kcal/mol	Enthalpy $-\Delta H$, kcal/mol
C_2H_5	C_6H_5	CH_3	2.2	32.1	2.9
C_2H_5	$CH_3C_6H_4$	CH_3	1.6	31.5	2.8
C_2H_5	C_8H_{17}	CH_3	0.17	28.4	3.3
CH_3	C_8H_{17}	H	1.52	29.4	2.0
CH_3	CH_3	H	–	32 – calculation [18]	–

fides. We believe that the reaction results in the formation of sulfonium salt IIA as an intermediate species [1, 4, 17, 29], including the rupture of the C–O bond of the oxide ring of the H-complex; this reaction is the rate-limiting stage of the process as a whole.

In addition, we find that the formation of alkylene oxides and sulfides, the reaction products, at the final stage of the reaction is preceded by the formation of cyclic ion II with intramolecular hydrogen bonding, as in the case of systems with low hydroxyalkyl sulfide concentrations. This explains the same composition and the nature of the set of the end products of the exchange reaction in both cases:



(9)

Sulfonium salt IIa contains two β-hydroxyalkyl groups, apparently linked by an intramolecular hydrogen bond, because of its pyramidal structure [24]. Intramolecular hydrogen bonds with the formation of five-membered or larger cycles were observed for ethylene glycol monomethyl ether and in dilute solutions of polyethylene oxide [30]. The energy of the intramolecular hydrogen bond formation for the eight-membered self-associate of diethylene glycol monoethyl ether is –4.1 kcal/mol [31]. Other examples of formation of sulfonium salts in reactions with oxiranes are known as well [32–37].

In the case of the interaction of H-complex I with the second molecule of hydroxyalkyl sulfide for the forward exchange reaction, it was found by the example of the propylene oxide–*n*-octyl-β-hydroxyethyl sulfide system that $k_2 = 2.37 \times 10^5$ (exp – 19350/*RT*) l/(mol s) [29]. The values of the constants of the forward and reverse routes for several other alkylene oxide–R-β-hydroxyalkyl sulfide systems are given in Table 4.

For the reaction of the phenyl glycidyl ether–R^2–β-hydroxypropyl sulfide system (for all sulfides, $R^3 = CH_3$ in a series of $R^2 = C_6H_5$, $CH_3C_6H_4$, and C_8H_{17}) an increase in the reaction rate constant ($k_2 \times 10^4$ l/(mol s), 150°C) from 0.7 to 1.9 to 8.4 and a decrease in the activation energy from 15.6 to 14.1 to 9.6 cal/mol, respectively, are observed; they are caused by the enhanced electron-donating properties of substituents on the sulfide. On the other hand, the reaction rate constants increase with the increasing electron-withdrawing properties of substituents on alkylene oxides ($k_2 \times 10^4$ l/(mol s), 150°C): 3.7 for $CH_2OC_2H_5$ and 8.4 for $CH_2OC_6H_5$ (and a decrease in the activation energy from 13.7 to 9.53 kcal/mol) at $R^2 = C_8H_{17}$, C_6H_5, and $R^3 = CH_3$ in both cases. The influence of substituents in the reactions for concentrated and dilute solutions of β-hydroxyalkyl sulfides is similar.

The formation of alkylene oxides upon the degradation of sulfonium salts containing β-hydroxyalkyl groups is widely known [38, 39]. In our case the decomposition of the sulfonium salt begins with the proton loss by the OH group. Owing to a positive charge on the sulfur atom of the sulfonium salt, the OH hydrogen atom acquires additional mobility and its separation becomes much easier. As a result of proton abstraction by the anion of salt IIa, the bipolar ion II with intramolecular hydrogen bonding and delocalized negative charge is formed, while the original molecule of R-β-hydroxyalkyl sulfide is regenerated. The decay of bipolar ion II leads to the final reaction products.

Catalytic effect of proton-donating compounds. In H-complex I, the β-hydroxyalkyl sulfide molecule is not only a reactant but also has a catalytic effect on the course of the reaction [17]. Thus, a sharp increase in

Table 4. Rate constants k_2 and k_{-2} for the forward and reverse directions of the exchange reaction for the systems alkylene oxide–R-β-hydroxyalkyl sulfide (concentrated solutions [2, 4])

1-Alkylene oxide		β-hydroxyalkyl sulfide			T, °C	Rate constants k_2, k_{-2} L/(mol s)
sudstituent R^1	mol/L	sudstituent R^2	sudstituent R^3	mol/L		
$C_6H_5OCH_2$	4.44	C_6H_5	CH_3	2.86	118–189	$3.3 \times 10^2(\exp - 5600/RT)$ $15.2(\exp - 12500/RT)$
"–"	4.12	$C_6H_4CH_3$	CH_3	2.64	140–180	$1.2 \times 10^2(\exp - 14100/RT)$ $3.85(\exp - 11000/RT)$
"–"	2.78	C_8H_{17}	CH_3	2.82	140–180	$3.54(\exp - 9530/RT)$ $1.24(\exp - 9600/RT)$
$C_2H_5OCH_2$	2.45–2.83	C_8H_{17}	CH_3	2.81–3.17	141–182	$1.8 \times 10^2(\exp - 13700/RT)$ $2.8 \times 10^2(\exp - 13300/RT)$
$C_6H_5OCH_2$	3.75–3.30	C_8H_{17}	H	1.25–1.45	140–170	$1.1 \times 10^2(\exp - 13000/RT)$ $6.1 \times 10^2(\exp - 10800/RT)$
CH_3	0.747	C_8H_{17}	H	0.0625	150	0.48×10^{-6}; 1.94×10^{-3}
CH_3	–	C_8H_{17}	H	–	–	$2.37 \times 10^5(\exp - 19350/RT)$

the rate was observed in the presence of proton-donating additives (HA) [2, 29, 40, 41].

The effect of proton-donor compounds on the reaction rate for concentrated solutions of β-hydroxyalkyl sulfides follows from the scheme of the exchange process and, in terms of the mechanism proposed above, is due to the formation of the H-complex I in the first stage of the reaction

$$R^1CH{-}CH_2 + HA \underset{}{\overset{K_e}{\rightleftharpoons}} R^1CH{-}CH_2 \quad (10)$$
$$\qquad O \qquad\qquad\qquad\qquad O\ldots HA$$
$$\qquad\qquad\qquad\qquad\qquad (I')$$

At the same time, the replacement of chlorobenzene as a solvent by benzene, a mixture of chlorobenzene with decane, or acetonitrile did not produce any change in the rates of the exchange reaction [1, 29].

In the system with an admixed proton-donating compound, along with reactions without the proton donor, the following new route appears [40, 41]:

$$I' + S\begin{matrix}R^2\\ \diagdown\\ \diagup\\ CH_2CH(R^3)OH\end{matrix} \xrightarrow{k_2'} [R^2S^+\begin{matrix}CH_2CH(R^1)O\\ \diagdown\\ \diagup\\ CH_2CH(R^3)\dot{O}H\end{matrix}\begin{matrix}\\ \\ H\\ \vdots\\ \\ \end{matrix}]A^- \quad (11)$$
$$\xrightarrow{-HA} (II) \longrightarrow \text{reaction products}$$
$$(IIa')$$

Sulfonium salt IIa' and bipolar ion II are formed as intermediates; the decay of bipolar ion II leads to the formation of the same products as in the absence of HA.

The catalytic action of proton-donor compounds (monochloroacetic acid, d_4-acetic acid, phenol, etc.) on the forward reaction of propylene oxide with β-hydroxyethyl sulfide was studied in chlorobenzene at 150°C by measuring the initial rates of ethylene oxide buildup. In this reaction, the proton-donor compounds are arranged in the following order of increasing catalytic activity ($k_2' \times 10^4$ l/(mol s): $C_8H_{17}SCH_2CH_2OH$ (0.2) < C_6H_5OH (2.5) ~ CD_3COOD (2.7) < CH_3COOH (7.5) < $CH_2ClCOOH$ (160) [41]. In addition, isotope effects in the reaction rate constants was observed for acetic and perdeuterated acetic acids: the primary isotope effect upon the replacement of H atom by D in the carboxyl group and the secondary effect upon the introduction of D in the methyl group.

Let us compare the rate constants for the reaction of H-complex I with a sulfide molecule with the corresponding rate constants for the reactions when acetic or monochloroacetic acid is added to the system.

In the presence of acetic acid in the system, $k_2' = 7.5 \times 10^{-4}$ and the k_2'/k_2 ratio is 34, whereas $k_2' = 1.6 \times 10^{-2}$ l/(mol s) and $k_2'/k_2 \approx 730$ in the case of monochloroacetic acid.

Interaction of two H-complexes I. The trend of the initial reaction rate to a limiting value with increasing oxirane concentration and a constant concentration of β-hydroxyoxyalkyl sulfide was shown kinetically [11, 14]. This means that at a large excess of oxirane, it actually starts to play the role of a solvent. A large part of the sulfide is bound in complex I, i.e., it is also necessary to take into account the contribution of the reaction between two H-complexes I to the overall reaction rate in any event. In this case, $[\text{sulfide}]_b = [\text{sulfide}]_o - [I]$, and $[\text{oxirane}]_b \sim [\text{oxirane}]_o$. The final equation obtained in [17] is as follows:

$$Y = \frac{W_o(1 + K_e[\text{oxirane}]_o)^2}{K_e[\text{sulfide}]_o^2[\text{oxirane}]_o}$$
$$- \frac{k_1(1 + K_e[\text{oxirane}]_o)}{[\text{sulfide}]_o} = k_2 + k_3K_e[\text{oxirane}]_o$$

The values of $k_2 = 2.2 \times 10^{-5}$ l/mol s and $k_3K_p = 8.92 \times 10^{-6}$ l^2/(mol s) were determined from the dependence of Y on [oxirane]$_o$, whence it follows that for $K_e = 1.85$ l/mol [17], $k_3 = 4.71 \times 10^{-6}$ l/(mol s) (150°C). The interaction of the two complexes leads to the same products as in the case of the second direction.

For the reaction of two H complexes I in the system octyl-β-hydroxyethyl sulfide–propylene oxide, which leads to the same products as in the previous case through the sulfonium salt IIa and complex II with an inter-ion hydrogen bond, we have $k_3 = 8.2 \times 10^3(\exp - 17820/RT)$ ($k_3 = 4.71 \times 10^{-6}$ l/(mol s) (150°C) against the rate constant for the reaction of the H-complex I with a molecule of hydroxyethyl sulfide $k_2 = 2.37 \times 10^5(\exp -19350/RT)$ [17] (2.2×10^{-5} l/(mol s), 150°C) and $k_3/k_2 = 0.21$. This can be explained by the fact that the steric hindrances in the former case are higher than in the second.

The contribution of the reaction with two H-complexes I to the overall process rate increases with increasing concentration of propylene oxide. At a β-hydroxyethyl sulfide concentration of 2.1 mol/L and that of propylene oxide of 0.4 mol/L, the share of the route with two H-complexes is as low as 7.4%, the remainder being the reaction of the H-complex I with a second hydroxyethyl sulfide molecule (85.5%) and unimolecular conversion of the H-complex I (7.1%). At a sulfide concentration of 0.6–0.9 mol/L and a propylene oxide concentration of ~10 mol/L, the share of the route with two H-complexes increases to ~70%.

When comparing the rate constants for the reaction of two H complexes I with the corresponding rate constants for the reaction of complexes I' + I in the presence of acetic and monochloroacetic acid (HA), we have $k_3' = 3.66 \times 10^{-4}$ mol/(l s) [39] and $k_3'/k_3 = 77$ for the reaction I' + I $\xrightarrow{k_3'}$ products in the case of acetic acid and $k_3' = 8.1 \times 10^{-3}$ l/(mol s) and $k_3'/k_3 = 1720$ l/mol s [40] for the reaction I' + I $\xrightarrow{k_3'}$ products in the case of monochloroacetic acid.

From the ratios of the reaction rate constants k_3'/k_3, the effect of the catalytic action of the addition of proton-donor compounds is especially clear.

In conclusion, it should be noted that this study not only substantially complements the understanding of exchange reactions, but also fundamentally changes the understanding of the reactions of this type, since an unusual and previously unknown mechanism for the nonspecific exchange of functional groups in organic molecules was established for the first time. The determining effect of the structure of the prereaction H-complex on the course of the process as a whole has been shown, and the role of the hydrogen bridge O...H...O at all stages of the reaction until the formation of end products has been elucidated. The intermolecular hydrogen bond O2...H8...O7 remains intact (albeit it is modified) throughout the entire process; it largely determines the character of each elementary event. It is also noteworthy that at the final stage of the reaction. all the routes lead to the formation of a single intermediate cyclic bipolar ion with intramolecular hydrogen bonding, which ion determines the final composition of the products.

The results reported in this paper represent only a small fraction of the possibilities inherent in the exchange reaction. We believe that the study of exchange reactions involving organic compounds containing other elements of 5a and 6a subgroups of the periodic system is of no less interest. The prospects for further study of reactions involving cycles, in which the alkylene oxide oxygen atom is replaced by S or N atom (thiirane and its derivatives, ethyleneimine and its derivatives) are also of interest.

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