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Evolution of Bond Orders in the Reversible Reactions of Alkylene Oxides with R-β-Hydroxyalkyl Sulfides and the Role of the Intermolecular Hydrogen Bond in Initiation and at Intermediate Reaction Stages

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Abstract—Semiempirical (PM3) calculations of the changes in the structures and energies of the reactants, intermediates, transition states, and final products have been carried out for the reversible reaction of β-hydroxyethyl methyl sulfide with propylene oxide. The evolution of the electron density distribution during the reaction is analyzed. It is demonstrated that the transformation proceeds via two intermediate products and the O…H…O bridge persists throughout the reaction pathway.

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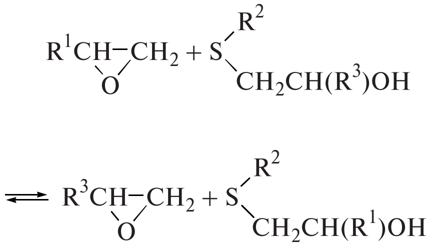
As was shown earlier [1–3] by numerous examples, the reactions of alkylene oxides with R-(β-hydroxyalkyl) sulfides are reversible (Table 1):

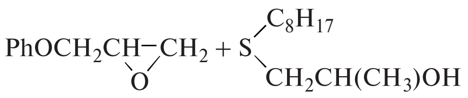


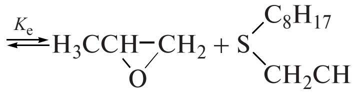
(I)

$R^1 \neq R^3$, R^1=H, Me, Et, CH=CH_2, Ph;
R^2 = Ph, C_6H_5Me, C_8H_{17};
R^3 = H, Me, Ph, CH_2OPh

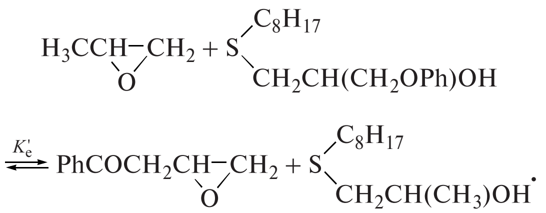
This reaction yields only two products, namely, alkylene oxide and β-hydroxyalkyl sulfide with structures other than that of the initial reactants. In all cases, the structure of the resulting alkylene oxide is determined by the structure of the β-hydroxyalkyl group of the sulfide.

For instance, the reaction of phenyl glycidyl ether with β-hydroxypropyl β-octyl sulfide in chlorobenzene affords propylene oxide and β-hydroxy-γ-phenoxypropyl *n*-octyl sulfide:





When the initial reactants are propylene oxide and β-hydroxy-γ-phenoxypropyl *n*-octyl sulfide, the reaction yields phenyl glycidyl ether and β-hydroxypropyl *n*-octyl sulfide in equilibrium with the starting reactants:



Here, $K_e = 1/K'_e = 3.03$ (150°C), where K_e and K'_e are the experimental equilibrium constants of these two reactions.

Clearly, a specific feature of the reactions is that the reactants seemingly exchange their R^1 and R^3 groups.

The purpose of the present work is to determine the structures of the reactants and probable intermediates and their important parameters, such as the heat of formation, charge distribution, and bond orders. Based on the calculated and experimental data, we suggest a reaction mechanism; i.e., we attempt to understand the changes in the electronic structure and to calculate the energies and structures of the transition states.

Table 1. Kinetic parameters of reaction (I) and the enthalpies of formation of the hydrogen-bonded complex in the oxirane–β-hydroxyalkyl sulfide system for dilute solutions

R^1	R^2	R^3	$A \times 10^{-9}$, s^{-1}	E_a, kcal/mol	$-\Delta H$, kcal/mol
			Experiment		
Et	Ph	Me	2.2	32.1	2.9
Et	MeC_6H_4	Me	1.6	31.5	2.8
Et	C_8H_{17}	Me	0.17	28.4	3.3
Me	C_8H_{17}	H	1.52	29.4	2.0
			Calculation (PM3, this work)		
Me	Me	H	–	32	–

In recent years, ab initio computational procedures have been constantly improved (complicated). Naturally, the final step is a comparison between the calculated and experimental data. As a rule, the calculated values gradually (but not monotonically) come closer to the experimental data as the computational procedure is complicated by passing from the minimal basis set (6-31G) to larger ones. In recent DFT/B3LYP calculations of the ArO–H bond dissociation energies for substituted phenols (which, as well as oxiranes and sulfides, have atoms with lone electron pairs) [4], the authors obtained the following values for phenol, 2-hydroxyphenol, and 2-methoxyphenol: 88.5, 81.7, and 84.7 kcal/mol, respectively. Good agreement with experimental data (87.0–88.7, 81.6, and 84.5 kcal/mol, respectively) was achieved only after the procedure was substantially complicated by including an unconventional basis set (6-31G(, p) or 6-31+G(, 3pd)).

This tendency to the improvement of quantum-chemical methods will probably persist. However, one should take into account that quantum-chemical calculations suffer from a number of intrinsic limitations arising from the fact that any quantum mechanical model of the structure and behavior of polyatomic systems is somewhat uncertain, approximate, and probabilistic (see, e.g., [5]). In particular, the heat of formation and the equilibrium geometry of a molecule are defined by a minimum on the potential energy surface (PES). This minimum is found by optimization of the molecular structure. However, the important concept of PES is rather rigorous only in the Born–Oppenheimer (fixed-nuclei) approximation. In addition, systematic and random errors (for example, getting into local false PES minima) are inevitable in these calculations. For this reason, we believe that simpler and more convenient semiempical methods are still indispensable for medium-size molecules. Such methods were developed by M. Dewar and his students and followers and are included in various versions of the MOPAC program package. They were parametrized on the basis of extensive experimental thermodynamic and structural data for many organic and inorganic compounds. Undoubtedly, these methods will give reliable results for the ground state—this is precisely what we are interested in.

In this work, we carried out calculations for the model reaction of propylene oxide with β-hydroxyethyl methyl sulfide. The semiempirical method PM3 was employed, which is considered to be the best among the methods used for molecules having adjacent atoms with lone electron pairs [6, 7], including the ab initio methods [8, 9]. The protocol of iterations was always analyzed during the calculation of energies. In the case of a nonmonotonic energy decrease (spikes indicating falling into false minima), the result was rejected and the computational experiment was repeated [9].

The accuracy of calculation of the heat of formation (1.0–1.5 kcal/mol) is approximately equal to the experimental accuracy and can be considered acceptable. Similar heats of formation, dipole moments, ionization potentials, and geometric parameters (but less consistent with experiment) are obtained by the semiempirical method AM1, whereas the MNDO method can give absurd results (a similar conclusion was made in [7, 8]).

The activation energy was calculated as the difference between the heats of formation of the transition state and the reactant, for example, $\Delta H_f^\circ(\mathrm{TS}(\mathbf{I}\text{–}\mathbf{II})) - \Delta H_f^\circ(\mathbf{I})$. The values of $\Delta H_f^\circ(\mathrm{TS})$ were determined using the key word SADDLE. The calculated heats of formation and dipole moments (Figs. 1, 2) are almost insensitive to the accepted range of configuration interaction (CI) in the interval between CI = 1HOMO + 1LUMO and CI = 3HOMO + 3LUMO. It was accepted in the computational experiments that CI = 1HOMO + 1LUMO.

Bond orders were calculated by the PM3 method (Table 2). This is a very important parameter [10], especially useful in the analysis of electron density transfer during the chemical reaction and in the establishment of the fact of hydrogen bond formation. The bond order (n) is 5–7 times more sensitive to changes in the molecular structure than the bond length. For instance, in 5-methylbutadiene, the bond length ratio is d(C–C)/d(C=C) = 1.46/1.33 = 1.10, whereas the bond order ratio is n(C=C)/n(C–C) = 1.97/1.00 = 1.97 (PM3 calculation). So, the bond length changes by only ~10%, whereas the change in the bond order is

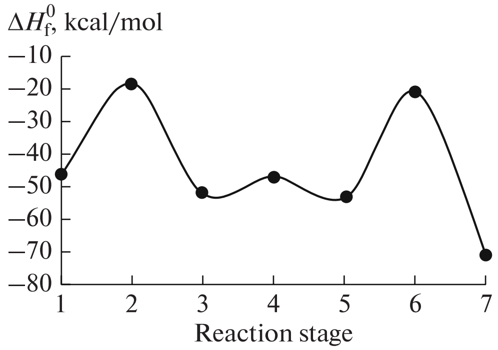


Fig. 1. Heats of formation of the combination of the reactants at different reaction stages (see Scheme 1).

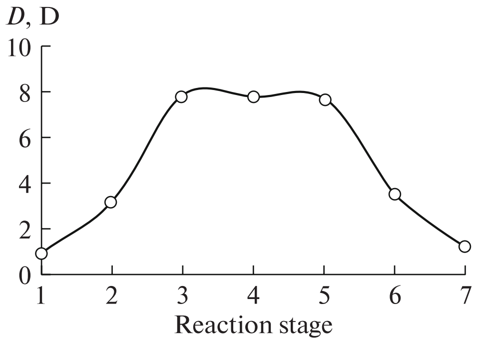


Fig. 2. Dipole moments of the combination of the reactants at different reaction stages (see Scheme 1).

almost twofold. Unfortunately, bond orders are analyzed unfairly rarely in the present-day literature.

RESULTS AND DISCUSSION

In this work, we studied the reaction between propylene oxide and β-hydroxyethyl sulfide (Scheme 1). The starting compounds are characterized by nonuniform charge distribution and by appreciable, but not very high, dipole moments of 1.83 and 2.11 for the oxirane and sulfide, respectively. In the oxirane, the maximum negative charge (–0.27) is concentrated on the oxygen atom; in hydroxyethyl methyl sulfide, the highest positive charge (+0.19) is on the hydrogen atom (Table 2). Evidently, precisely these atoms of the reactants will be closest together in the prereaction conformation and this will favor hydrogen bond formation. Indeed, optimization of the structure of the prereaction conformation of the initial reactant pair oxirane–sulfide (**OS**) (see column **OS** in Table 2) shows that the order of the bond between the hydroxylic hydrogen and the oxygen of the oxirane is low (~0.04) yet nonzero, while the n(O–H) value (0.87) is well below the n(O–H) value for isolated hydroxyethyl methyl sulfide (0.94). This means the formation of a hydrogen-bonded complex (Scheme 2).

In addition, the calculation shows (Table 2, column **OS**) that the sulfur atom of the sulfide and the carbon atom of the alkylene oxide interact. Although this interaction is weak (n = 0.02), it is probably sufficient for spatial orientation necessary for the further rearrangement of the **OS** structure (Scheme 1).

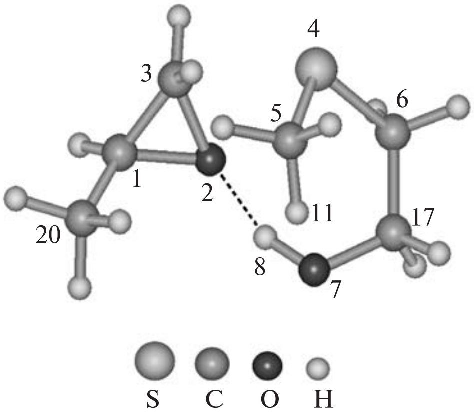
The formation of an H-complex was established experimentally by kinetic and spectroscopic methods [11] for both dilute and concentrated solutions of the reactants.

The semiempirical calculation of the probable reaction mechanism shows that the process consists of three steps with the intermediate products **I** and **II**, the final product **Pr**, and the corresponding transition states **TS(OS-I)**, **TS(I-II)**, and **TS(II-Pr)** (Scheme 1). The parameters of these structures, listed in Table 2, make it possible to interpret the course of the chemical transformation informatively.

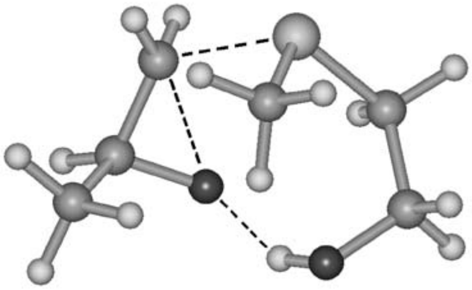
In the prereaction complex **OS**, the O2–C3 bond is somewhat weakened (n = 0.94), and, in the transition state **TS(OS-I)**, it is weakened to a greater extent (n = 0.44): the C3–S4 bond has not formed yet, but its order already differs noticeably from zero (n = 0.34). The bond orders in the O2(–0.75)–H8(+0.3)–O7(–0.4) bridge for structure **I** (the charges of the atoms are given in parentheses) are 0.10 and 0.79, respectively (Table 2). This indicates that there is indeed a weak H bond between the oxygen atoms. A nucleophilic attack of the sulfur atom on the oxide ring inside the H-complex of **OS** occurs in the next step (Scheme 1).

In intermediate product **I** (Scheme 1, *3*) the O2–C3 bond is completely cleaved (d = 2.42 Å, n = 0.08), but the C3–S4 bond already exists (d = 1.84, n = 0.91). The O2–H8 bond has not formed yet, the O7–H8 bond is only weakened (n = 0.79), and the O2–H8–O7 bridge is intact and strongly polarized: the charges are –0.75, +0.30, and –0.41, respectively (Table 2). At the same time, the charge on the sulfur atom increased from +0.13 to +0.56, the charge on the O2 oxygen atom is changed from –0.57 to –0.75, and that the charge on C3 is changed from +0.11 to –0.30. On going from **TS(OS-I)** (Scheme 1, *2*) to **I**, the dipole moment increases from 3.15 to 7.74 D and a zwitterion forms.

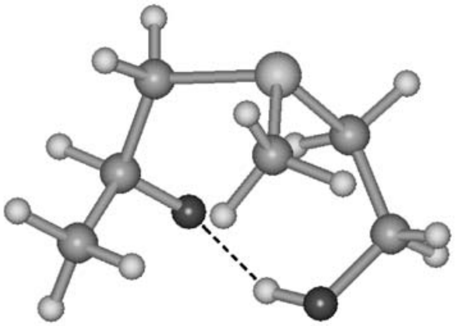
Next, with synchronous electron density transfer from the O7–H8 bond to the O2–H8 bond through the **TS(I-II)** transition state (Scheme 1, *4*), intermediate **I** transforms into an intermediate cyclic bipolar ion with an intramolecular hydrogen bond (**II**) [3] (Scheme 1, *5*). Nevertheless, the O2–H8–O7 bridge is retained. This reaction is thermally neutral, with a low activation barrier of 4–5 kcal/mol. Therefore, intermediates **I** and **II** are in dynamic equilibrium. The reversible character of the reaction is due to the prototropic tautomeric equilibrium existing between bipolar ions **I** and **II** with an intramolecular hydrogen bond.



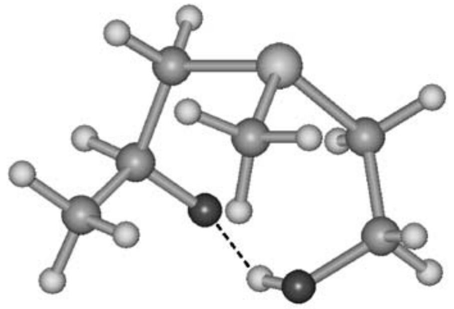
1 Prereaction complex **OS**



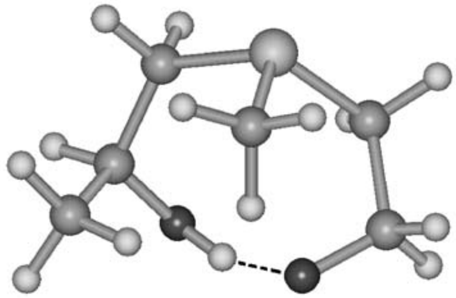
2 Transition state **TS(OS-I)**



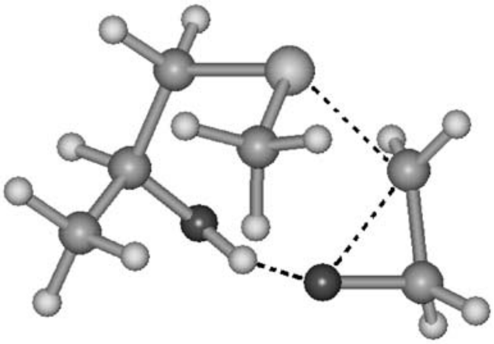
3 Intermediate product **I**



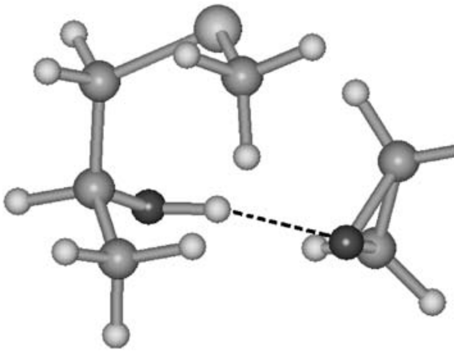
4 ransition state **TS(I-II)**



5 Intermediate product **II**



6 Transition state **TS(II-Pr)**



7 Postreaction complex **Pr**

Scheme 1.

Table 2. Bond lengths (*d*, Å), bond orders (*n*), and charges of atoms (*q*) calculated by the PM3 method for the initial reactants of the oxirane + sulfide pair linked by the hydrogen bond (**OS**), intermediate products **I** and **II**, transition states **TS**, and final products linked by the hydrogen bond (**Pr**)

Parameter*	Initial reactants	**OS**	**TS(OS-I)****	**I**	**TS(I-II)**	**II**	**TS(II-Pr)**	**Pr**
d(C1O2)	1.44	1.42	1.38	1.32	1.32	1.39	1.40	1.40
n(C1O2)	0.96	0.95	1.00	1.22	1.21	1.03	1.02	1.01
d(O2C3)	1.43	1.48	1.97	2.42	2.42	2.45	2.46	2.45
n(O2C3)	0.97	0.94	0.44	0.08	0.08	0.03	0.03	0.03
d(C1C3)	1.49	1.47	1.49	1.59	1.60	1.55	1.55	1.54
n(C1C3)	0.99	0.99	0.99	0.83	0.81	0.93	0.95	0.96
d(C1C20)	1.50	1.50	1.52	1.54	1.55	1.53	1.53	1.53
n(C1C20)	0.99	0.99	0.96	0.96	0.93	0.98	0.98	0.98
q(C1)	+0.004	−0.003	+0.11	+0.27	+0.26	+0.13	+0.12	+0.10
q(O2)	−0.27	−0.30	−0.57	−0.75	−0.75	−0.39	−0.37	−0.34
q(C3)	−0.09	−0.03	+0.11	−0.30	−0.29	−0.25	−0.23	−0.21
q(C20)	−0.11	−0.12	−0.16	−0.19	−0.20	−0.18	−0.18	−0.17
d(C3S4)	*	2.58	2.28	1.84	1.84	1.84	1.83	1.82
n(C3S4)	*	0.02	0.34	0.91	0.91	0.94	0.95	0.98
d(O2H8)	*	1.84	1.76	1.70	1.70	0.98	0.97	0.96
n(O2H8)	*	0.04	0.06	0.10	0.10	0.81	0.86	0.89
d(S4C5)	1.80	1.81	1.81	1.81	1.81	1.84	1.81	1.80
n(S4C5)	0.99	0.99	0.98	0.97	0.97	0.96	0.98	0.99
d(C5H11)	1.10	1.11	1.11	1.13	1.13	1.55	1.12	1.10
n(C5H11)	0.98	0.95	0.94	0.92	0.93	0.83	0.93	0.97
d(S4C6)	1.82	1.84	1.83	1.85	1.85	1.84	2.26	3.77
n(S4C6)	0.98	0.96	0.96	0.94	0.94	0.92	0.35	0.008
d(C6O7)	2.47	2.44	2.47	2.46	2.45	2.43	1.93	1.44
n(C6O7)	0.02	0.02	0.03	0.03	0.03	0.07	0.47	0.96
d(C6C17)	1.53	1.50	1.53	1.54	1.53	1.58	1.48	1.48
n(C6C17)	0.97	0.98	0.97	0.95	0.96	0.84	1.02	1.006
d(O7C17)	1.40	1.40	1.40	1.39	1.39	1.33	1.38	1.44
n(O7C17)	1.01	1.00	1.02	1.03	1.03	1.16	0.98	0.96
d(O7H8)	0.95	1.03	0.97	0.98	0.99	1.72	1.77	1.84
n(O7H8)	0.94	0.87	0.85	0.79	0.79	0.09	0.06	0.03
q(S4)	−0.10	−0.06	+0.13	+0.56	+0.56	+0.58	+0.12	−0.03
q(H8)	+0.19	+0.24	+0.27	+0.30	+0.29	+0.28	+0.25	+0.23
q(C5)	−0.20	−0.25	−0.27	−0.32	−0.32	−0.38	−0.28	−0.22
q(H11)	+0.09	+0.13	+0.09	+0.18	+0.18	+0.24	+0.16	+0.07
q(C6)	−0.23	−0.20	−0.24	−0.25	−0.27	−0.29	+0.13	−0.03
q(O7)	−0.30	−0.37	−0.38	−0.41	−0.42	−0.75	−0.59	−0.28
q(C17)	+0.07	+0.08	+0.10	+0.11	+0.11	+0.24	+0.08	−0.002

* For the numbering of atoms, see Scheme 1.

** These bonds do not exist for the separated reactants.

The formation of complexes containing $(A...H...B)^{\pm}$ fragments with the central proton was observed during the ionization of organic compounds in solutions of acids and bases [12].

Stable proton solvates and hydroxide ions $(A...H...B)^{\pm}$ in aqueous solutions form strong symmetric hydrogen bonds between the central proton and molecules or ions A and B having atoms with lone electron pairs [13]. Their stability is due to the fact that the proton of the $(O...H...O)^{\pm}$ fragment is located at the center of the ligands linked by quasi-symmetric hydrogen bonds.

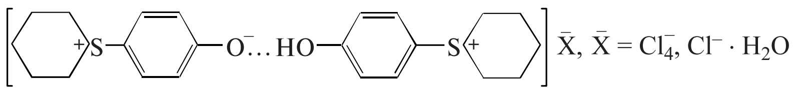
For instance, the mainly ionic complexes $[(H_3C)_2SO...H...OS(CH_3)_2]^+$ and $[CH_3SO_2O...H...OSO_2CH_3]^-$ with a strong quasi-symmetric hydrogen bond exist in the methanesulfonic acid–dimethyl sulfoxide system in concentrated solutions of CH_3SO_3H [14].

The negative ions $(HO...H...OH)^-$ and $(H_3CO...H...OCH_3)^-$ with a strong symmetric hydrogen bond were identified by IR spectroscopy in methanolic solutions of KOH and $KOCH_3$ [15].

The simplest stable solvates are the proton hydrate $H_5O_2^+$ and the hydroxide ion hydrate $H_3O_2^-$. Their structures $(H_2O...H...OH_2)^+$ and $(HO...H...OH)^-$ are formed by strong symmetric hydrogen bonds involving the central proton [16]. The hydroxide ion monohydrate $(HO...H...OH)^-$ can be considered with good reason as a proton solvated by two hydroxide ions.

The calculated energies of O...H bond formation in the $H_5O_2^+$ and $H_3O_2^-$ ions (32.8 and 34.9 kcal/mol) are close to the experimental values (31 ± 2 kcal/mol) obtained for several tens of $(A...H...A)^+$ ions in which A is a water, alcohol, ether, aldehyde, ketone, or acid molecule. The charges on the bridging protons of the positive and negative ions are similar, –0.502 and +0.436, respectively, and the O–O bridge lengths are 2.36 and 2.36 Å [16].

For bissulfonium salts,



the hydrogen bond energy is 15.8 kcal/mol, the distance between the O^- ion and the O atom involved in the hydrogen bond is 2.47 Å, and the distances between the proton and the O^- ion and the proton and the O atom are 1.45 and 1.06 Å, respectively [17].

In our case, the charge on the bridging proton changes slightly during the process (+0.30, +0.28, +0.23). The bridge length d(O2–O7) also changes insignificantly (2.68, 2.70, and 2.80 Å).

In bipolar ion **II**, the positive charge is mainly concentrated on the S(4) atom (+0.58) and the negative charge is concentrated on the O(7) atom (–0.75), the distance between the sulfur atom and the oxygen atom being 3.06 Å. As a result, the dipole moment is rather high (7.6 D).

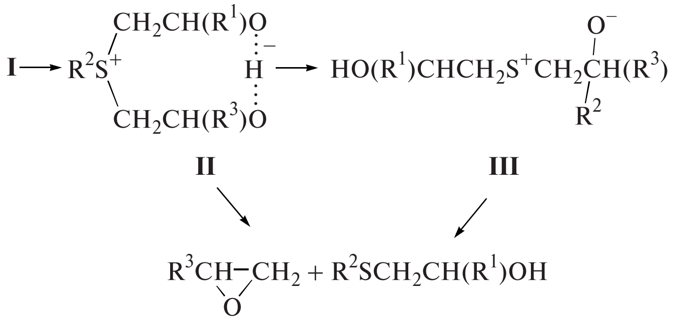
According to the electronic structure of the sulfur atom, three of the four sp^3-hybridized orbitals form σ bonds with C atoms and the fourth orbital is occupied by a lone electron pair. Therefore, this fragment is a pyramid [3, 18] whose vertices are occupied by sulfur atoms with C3–S4–C5, C5–S4–C6, and C6–S4–C3 angles of 105°.

Although the O7–H8 distance is considerably longer than the O2–H8 distance, the order of the O7–H8 bond is not vanishingly small (0.09, see Table 2), and the O7–H8–O2 hydrogen bond stabilizes the eight-membered structure partly due to the specific sequence of charges on the atoms of this chain: –0.75, +0.28, and –0.39.

The monomolecular transformation of cyclic bipolar ion **II** into the final products occurs as follows. When the nucleophilic fragment O7 (q = –0.75) attacks the H9–C–H10 (CH_2) group bonded to the sulfur atom, the sulfide is readily eliminated with S4–C6 bond dissociation and the simultaneous closure of the O7–C6 bond, yielding an oxirane (Scheme 1, *6*,*7*). It can be seen from Fig. 1 that the reaction **II** ⟶ **Pr** is exothermic: $\Delta H_f^\circ(\mathrm{Pr}) - \Delta H_f^\circ(\mathbf{II}) = -18$ kcal/mol, and the activation enthalpy is 32 kcal/mol, which is in agreement with experimental data for related compounds (Table 1) [3].

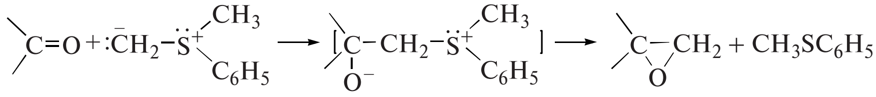
Thus, the O2...H8...O7 hydrogen bond exists (though changes) throughout the process. This determines, to a considerable extent, the character of each step. The extravalent interaction of the sulfur atom with the C3 atom ($n \approx 0.02$) in the **OS** structure generates an additional unit in the eight-membered cycle through which the electron density is transferred along the bonds during the chemical transformation. It is likely that the cycle is rather rigid, which exerts a certain steric effect on the CH_3 group getting inside the eight-membered "cavity." The C5–H11 bond in intermediate **II** is anomalously long (1.55 Å), and, accordingly, its order is decreased to 0.83.

Two variants of the conversion of **II** into the reaction products are possible. The first variant is direct conversion into the reaction products, and the second is conversion via bipolar ion **III** [3], which results from O...H bond dissociation in **II** with the fixation of the negative charge on the O atom and then turns into the reaction products (Scheme 2). In both cases, C–O bond closure takes place to yield an epoxide cycle and, simultaneously, the S–CH_2 bond in the initial sulfide breaks to yield the product sulfide.



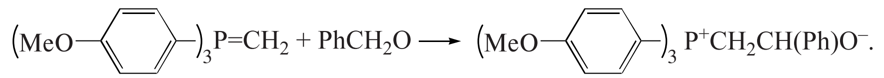
Scheme 2.

The epoxide and sulfide result from the reaction of stable dimethylsulfonium fluorenilide with the aromatic aldehyde through an intermediate compound like **III'**. In the reaction of a phosphorane having strong electron-donating substituents with benzaldehyde, a similar betaine was isolated and turned out to be stable [18]:



III'

The formation of structures similar to structure **III** as intermediate compounds was suggested in a number of studies [18, 19]. Their transformations result in epoxides. The interaction of phenylmethylsulfonium methylilide with a carbonyl compound occurs via intermediate compound **III'**:



Semiempirical calculations make it possible to decide between the two possible routes of the reaction examined. The calculations demonstrated that, in our case, the reaction proceeds via the first route.

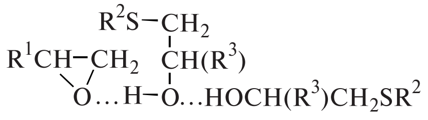
The O2–H8–O7 bridge persists until the very rearrangement of the transition state **TS(I-II)** into the zwitterion. This is evident from the data in Table 2, which show, for structure **II** (last three columns), how the lengths and orders of the O7–H8, O2–H8, C6–S4, and O7–C17 bonds and the charges on the C6, O7, and S4 atoms change as O7 and C6 are brought closer together in 0.5-Å steps (2.43, 1.93, and 1.44 Å).

As for the reaction in concentrated solutions of hydroxyalkyl sulfide, which is second-order with respect to the sulfide and first-order with respect to alkylene oxide, its mechanism can be as follows. The oxirane and the sulfide dimer are involved in the reaction. The dimerization of β-hydroxyalkyl sulfide increases its proton-donating power and nucleophilicity. This is confirmed by the example of the linear forms of alcohol and phenol dimers:

$$H^{\alpha}-\underset{A}{\underset{|}{O}}\ldots H-\underset{A}{\underset{|}{O^{\beta}}},$$

where A = R or Ph. Quantum-chemical calculations show a decrease in the electron density on the H^{α} atom and an increase in the electron density on the O^{β} atom relative to the corresponding monomeric forms of alcohols and phenols [20]. This enhances the reactivity of the hydroxyl group of alcohols and phenols in nucleophilic addition reactions [21].

The first step is the formation of an H-complex between the oxirane and the hydroxyalkyl sulfide dimer:



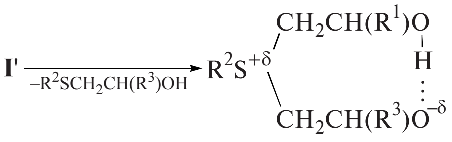
I'

The formation of association species of this type was established in [22–24]. Charge redistribution occurs in association species **I'**, as was observed in proton donor–Et_3N systems [25]. The second hydrogen bond weakens the H8–O7 bond and increases the probability of the migration of the proton of the OH group to the oxygen atom of the oxide ring (transfer of H8 to O2), facilitating the abstraction of the second hydroxyalkyl sulfide molecule (**I'** ⟶ products + hydroxyalkyl sulfide); i.e., hydroxyalkyl sulfide is both a reactant and a catalyst.

To confirm this assertion, it was shown experimentally that the exchange reaction rate is higher in the presence of proton donors [3]. The catalytic activity of proton-donating compounds increases in the following order (the rate constant of the direct reaction ($k_2' \times 10^{-4}$, l mol^{-1} s^{-1}) is given in parentheses): $C_8H_{17}SCH_2CH_2OH$ (hydroxyalkyl sulfide) (0.23) < C_6H_5OH (2.5) ~

CD_3COOD (2.7) < CH_3COOH (7.46) < $CH_2ClCOOH$ (160) (chlorobenzene as a solvent, 150°C).

It is assumed that the reactivity of complex **I'** in nucleophilic reactions is higher than the reactivity of the prereaction complex **OS** in the case of dilute sulfide solutions. As in the latter case, zwitterion **II** is formed due to the intramolecular nucleophilic attack of the sulfide sulfur atom on the C–O bond:



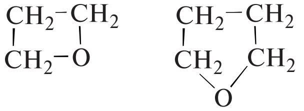
II'

Another possible variant of exchange reaction (I) for concentrated sulfide solutions was considered earlier [3]. For both dilute and concentrated solutions of the sulfide, the decomposition of zwitterion **II** formed in the final step of the reaction determines the nature and composition of the final products. These variants of the mechanism for concentrated solutions of hydroxyalkyl sulfides explain the change in the reaction order with respect to hydroxyalkyl sulfide with an increase in its concentration and account for the composition of the products.

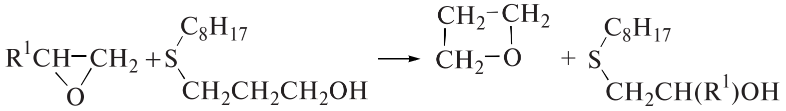
The reaction mechanism suggested by us for dilute and concentrated hydroxyalkyl sulfide solutions makes it possible to understand details of the mechanism of the reactions involving organic compounds containing other elements with similar chemical properties (Groups VA and VIA elements of the periodical table, for example, Se, N, and P) in place of the sulfur atom. In this case, the reaction type is the same [3]. However, for some organic compounds, the formation of the main products of the exchange reaction (alkylene oxides and β-hydroxyalkyl selenides for Se, alkylene oxides and β-hydroxyalkylamines for N, and alkylene oxides and β-hydroxyalkylphosphines for P is accompanied by the formation of by-products (unsaturated, carbonyl, and other compounds), whose yield sometimes exceeds the yield of the main products [3].

For instance, the products of the reaction of styrene oxide with 1-diethylaminopropan-2-ol contain propylene, styrene, acetone, and acetophenone along with propylene oxide and the corresponding amine. The N-oxide forming under the experimental conditions is likely unstable. It is possible that part of the oxirane molecules (initial reactant and/or reaction product) undergoes polymerization.

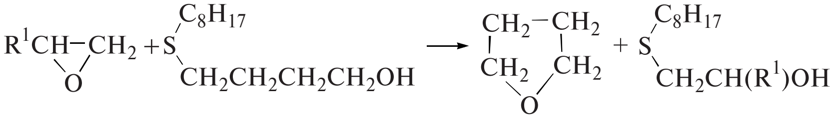
It is assumed that the scheme of the formation of the by-products involves the same intermediates as the scheme of the main route of the reaction. Of course, the appearance of side processes disturbs the dynamic equilibrium of the reaction. The formation of four- and five-membered oxygen-containing heterocycles can be explained in terms of a common mechanism for the hydroxyalkyl sulfide containing the OH group in the β-position to the sulfur atom ($RSCH_2CH_2OH$) and for the hydroxyalkyl sulfides in which the OH group is in the γ- or δ-position to the sulfur atom ($RSCH_2CH_2CH_2OH$ or $RSCH_2CH_2CH_2CH_2OH$). If the structure of the expected heterocycle is determined by the structure of the hydroxyalkyl group, the following products will form [13]:



The corresponding reactions are



and



where R^1 = Me, CH_2OPh, Ph, or CH_2OBu. In both cases, the product ($C_8H_{17}SCH_2CH(R^1)OH$) has the same structure.

The reactions involving cycles in which the oxirane oxygen atom is replaced with an S or N atom (thiirane and its derivatives, ethyleneimine and its derivatives) are of equal interest.

Thus, using semiempirical calculations, we have determined the changes in the structures, energies, and other parameters, including such an informative (but, unfortunately, unfairly rarely analyzed) parameter as the bond order, for the reaction of β-hydroxyalkyl sulfides with alkylene oxides. The reaction proceeds via the formation of two intermediate products and, accordingly, three transition states. The intermolecular hydrogen bond O2...H8...O7 persists (though changes) throughout the process. This bond determines, to a considerable extent, the character of each elementary event. In addition, the interaction of the sulfur atom with the nearest carbon atoms (C3 and C6) creates one more unit in the eight-membered cycle, through which the electron density is transferred along the bonds during the chemical transformation.

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