Multiple bond migration with participation of a protophilic agent
4.* Double bond migration in 3-methylthioprop-1-ene and 3-methoxyprop-1-ene: a comparative study

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Ab initio study of the pathways of migration of the double bond in the 3-methylthioprop-1-ene (**1**) and 3-methoxyprop-1-ene (**2**) molecules with participation of hydroxide ion was carried out by the RHF/6-31+G* and MP2/6-31+G//RHF/6-31+G* methods. Conformational isomerism of the initial molecules and reaction products was considered. The distinctions are discussed in the spatial and electronic structure of intermediate carbanions stabilized (for **1**) due to the negative hyperconjugation. Stationary points corresponding to complexes between the molecules under study and the hydroxide ion and between the corresponding carbanion and water molecule were localized on the potential energy surfaces of the proton transfer reactions. For **2**, the single-stage mechanism of prototropic rearrangement involving the H atom of the hydroxide ion was found to be more energetically preferable than the two-stage mechanism, whereas both mechanisms are expected to be equiprobable for **1**.

Key words: 3-methylthioprop-1-ene, 3-methoxyprop-1-ene, acidity, 1,3-hydrogen shift, hydroxide ion, reaction mechanism, potential energy surface, *ab initio* quantum-chemical calculations.

Previously,[1,2] we showed that migration of the double bond in the propene molecule with participation of hydroxide ion can occur *via* the formation of an intermediate complex with the water molecule formed from the attacking hydroxide ion and one of the H atoms of the methyl group of the propene molecule, *i.e.*, formally without exchange of the migrating proton with the medium ("intramolecularly"). This mechanism can also be realized in the case of 3-methoxyprop-1-ene.[3] In both cases, the transition states determining the activation barriers to the prototropic rearrangement lie on the energy scale below the reagents and reaction products and much lower than the system that formed comprising anion and the water molecule. This suggests that, at least in the gas phase, this mechanism of rearrangement of the molecules of the above-mentioned compounds is more energetically preferable than the known two-stage mechanism[4] involving separate stages of (i) proton abstraction by a base with the formation of a carbanion and (ii) reprotonation of the carbanion by proton-containing species of the medium.

Compared to ethers, organic sulfides are characterized by a much higher acidity of protons bonded to the α-C atom at the substituent.[5] In particular, isomerization of 3-methylthioprop-1-ene into 1-methylthioprop-1-ene under the action of bases occurs more readily than that of its oxygen-containing analog.[6,7] In this connection it is of interest (i) to study the possibility for a single-stage 1,3-hydrogen shift involving a proton of the base to occur in the molecule of methylthiopropene **1** and (ii) to compare it with analogous isomerization reaction of methoxypropene **2**.

Calculation procedure

Calculations were carried out following the known procedure.[2] Optimization of geometric parameters of the structures under study was performed by the restricted Hartree—Fock (RHF) method in the 6-31+G* basis set and followed by checking for the absence of negative eigenvalues of the Hesse matrix. The energies were calculated at the second-order Moller—Plesset (MP2) level of perturbation theory with inclusion of correlation effects using the GAMESS program package[8] on a PC with a PENTIUM® II CPU and the LINUX operating system. Molecular orbitals were localized using the Ruedenberg procedure.[9] Charge density difference maps were plotted using the MOLDEN program.[10]

* For Parts 1—3, see Refs. 1—3.

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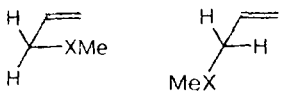
Results and Discussion

Initial compounds

Characteristic of the unsubstituted propene molecule is a cisoid conformation of the allyl group with respect to rotation about the C(2)—C(3) bond, which corresponds to the minimum repulsion between the electrons of the C—H σ-bonds and the C(1)=C(2) π-bond. In the molecules of the compounds under study, the substituent can be either in *cis*- (**a**) or in *gauche*-position (**b**) with respect to the vinyl group.

As should be expected, rotation about the C(2)—C(3) bond is nearly free. The barrier to internal rotation for conversion **1a** → **1b** is ~0.6 kcal mol^{-1}, the latter conformer being ~1.9 kcal mol^{-1} more stable than the former. The barrier separating the two *gauche*-conformers of **1b** is estimated at 1.0 kcal mol^{-1}. The energy difference between the *cis*- and *gauche*-forms of molecule **2** (**2a** and **2b**, respectively) is smaller than for **1** (0.1 kcal mol^{-1}), whereas the barriers to internal rotation are somewhat higher, namely, 3.0 kcal mol^{-1} for conversion **2a** → **2b** and 1.3 kcal mol^{-1} for transition between the *gauche*-conformers **2b**.



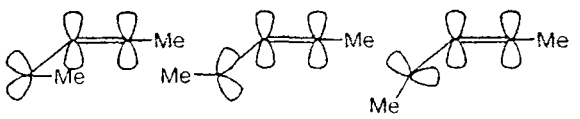
1a, 2a **1b, 2b**

X = S (**1**), O (**2**)

The 1,3-hydrogen shift mechanism studied in this work implies that the reaction begins with the attack of the base on a H atom at the C(3) atom in *gauche*-position with respect to the vinyl group. In the case of **2**, the hydroxide ion attacks conformer **2a** (**2b**) to give (*Z*)- or (*E*)-1-methoxyprop-1-ene, respectively.[3] The energy difference between *cis*- and *gauche*-conformers of the above-mentioned initial structures suggests that migration of the double bond toward the substituent results in preferable formation of *E*-isomers for **1** and in equiprobable formation of *E*- and *Z*-isomers for **2**.

Reaction products

Migration of the double bond in molecules **1** and **2** results in 1-methylthio-1-propene (**3**) and 1-methoxy-1-propene (**4**), respectively, with the general formula MeX—CH=CH—Me (X = S, O). Each of these compounds can exist in both *E*- and *Z*-forms. The following conformations of the molecules of compounds with O or S atoms neighboring the double bond can exist due to rotation about the C(1)—X bond:



s-cis *s-trans* *s-gauche*

s-trans-Structures are characterized by maximum repulsion between the electrons of the π-MO of the vinyl fragment and the equivalent lone electron pairs (LEP) of the heteroatom. This type of structures corresponds to the transition states of conversion between two *s-gauche*-conformers of systems **3** and **4** studied in this work rather than to minima on their potential energy surfaces (PES).

The potential curves of internal rotation (Fig. 1) indicate that *E*-isomers of compounds **3** and **4** can exist as two rotamers among which the *s-cis*-conformer of 1-methoxy-1-propene and the *s-gauche*-rotamer of 1-methylthio-1-propene are the most stable (Table 1). According to microwave spectroscopy data, the *s-gauche*-form of vinylthiol[11] is more stable (the energy difference between the *s-cis*- and *s-gauche*-conformers was estimated at 0.14 kcal mol^{-1}), whereas this value for vinyl alcohol equals 1.06 kcal mol^{-1}.[12] The *s-gauche*-conformation becomes more preferable on going from vinylthiol to *E*-prop-2-ene-1-thiol.[11]

The potential curves of internal rotation (see Fig. 1) reveal marked distinctions for the *s-gauche*-forms of **3** and **4**. The dihedral angles C(2)C(1)XCH$_3$ decrease (Table 2), whereas the barriers to conversion between the two *gauche*-structures become higher on going from compound **4** to its sulfur-containing analog **3** (see Table 1). These results are in good agreement with the data of experimental studies of methyl vinyl ether (MVE) and

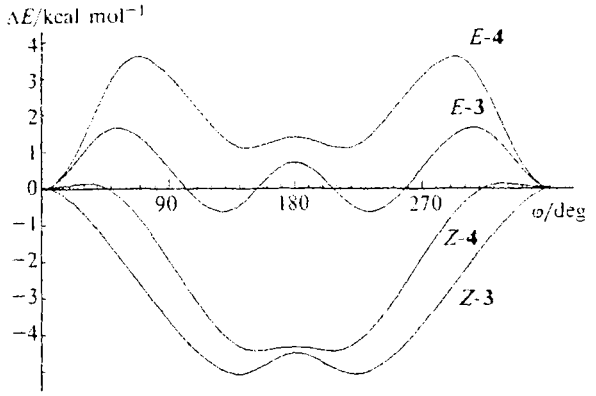


Fig. 1. Potential curves of internal rotation in the molecules of *E*- and *Z*-isomers of compounds **3** and **4**.

Table 1. Relative energies of *s-cis*- and *s-gauche*-conformers (ΔE) and barriers to internal rotation for transitions from *s-cis*- to *s-gauche*-conformation (ΔE_{cg}) and between two *s-gauche*-conformers (ΔE_{gg})

Structure	ΔE	ΔE_{cg}	ΔE_{gg}
	kcal mol^{-1}		
E-**3**	−0.5	1.8	1.4
Z-**3**	−5.1	0.0	0.5
E-**4**	1.1	3.6	0.3
Z-**4**	−4.4	0.1	0.1

Table 2. Bond angles C(2)C(1)X, dihedral angles C(2)C(1)XCH$_3$ (θ) and C(2)C(1)X—LEP (φ), the C(1)X—LEP angles (α), and the s-characters of the LEP orbitals (s) (X = S (**3**), O (**4**))

Rotamer	Angle		LEP1			LEP2		
	C(2)C(1)X/deg	θ/deg	α/deg	φ/deg	s (%)	α/deg	φ/deg	s (%)
s-cis-E-**3**	103.4	0	107.7	114.3	39.4	107.7	−114.3	39.4
s-gauche-E-**3**	100.4	126.8	108.6	13.1	39.7	107.8	−120.9	38.8
s-gauche-Z-**3**	100.0	138.4	109.6	24.5	39.5	107.5	−109.4	38.4
s-cis-E-**4**	118.5	0	106.3	120.4	29.5	106.3	−120.4	29.5
s-gauche-E-**4**	115.5	143.9	106.0	24.8	31.2	108.5	−97.2	29.5
s-gauche-Z-**4**	115.8	151.1	108.6	30.2	30.9	106.0	−91.6	29.4

methyl vinyl sulfide. Based on the analysis of gas-phase vibrational spectra of MVE,[13] it was concluded that an *s-gauche*-rotamer with a rotation angle of 144° should exist (this value coincides with that found for the *E*-isomer of compound **4** in this work). Microwave spectroscopy data[14] also made it possible to draw an analogous conclusion about the existence of a less stable *s-gauche*-rotamer. At the same time, this conformer is also considered as an *s-trans*-structure.[15] In particular, this opinion is based on the results of electron diffraction study.[16] Thus, two conformers are observed for the MVE molecule. The *s-cis*-rotamer is more stable, whereas the other conformer, which in some instances is identified as an *s-trans*-structure, is characterized by a large-amplitude motion between two *s-gauche* positions. The same should also be valid for the *E*-isomer of **4**.

Because of obvious steric hindrances, *Z*-isomers of compounds **3** and **4** can exist only as *s-gauche*-conformers. A shallow minimum corresponding to the *s-cis*-rotamer of **4** is separated from a deeper minimum corresponding to the *s-gauche*-conformer by a potential barrier of ~0.1 kcal mol^{-1} only, while the energy difference between this pair of conformers is ~4.4 kcal mol^{-1} (see Table 1). The *s-cis*-conformer of **3** corresponds to a transition state rather than to a PES minimum (the Hesse matrix has one negative eigenvalue at this point).

The IR spectrum of the *Z*-isomer of compound **4** was studied in detail using the results of *ab initio* (RHF and MP2) quantum-chemical calculations in the 6-31G* basis set.[17] The calculated energy characteristics, which are very close to those obtained in this work, are in more than satisfactory agreement with the experimental vibrational frequencies. According to these results,[17] the major contribution to the potential of internal rotation comes from the mutual repulsion between methyl groups, and the methyl group of the OMe fragment should be in *s-trans*-position in the absence of other interactions. The deviation from the *s-trans*-position by ~30° is due to the interaction of the LEP of the O atom with π-electrons of the double bond. The contribution of conjugation between the LEP and the double bond is negligible in the RHF approximation; however, it becomes significant when performing calculations at the MP2 level.

Unlike MVE, the two *s-gauche*-conformers of methyl vinyl sulfide with a dihedral angle of 132±3° are separated by a potential barrier estimated at 0.6—0.7 kcal mol^{-1}, which affects the structure of vibrational levels.[18] The dihedral angle found for the *Z*-isomer of compound **3** is somewhat larger, whereas for the *E*-isomer it is somewhat smaller. At the same time, both of them are also close to 130° and are much smaller than the corresponding angles obtained for isomers of compound **4**. Finally, our calculations predict the existence of a rather high barrier separating the two *s-gauche*-rotamers of the *E*-isomer.

The LEP of heteroatoms are often discussed when considering preferable conformations. Analysis of the parameters of molecular orbitals localized using the energy criterion (see Table 2) suggests that the s-character of the LEP of the S atom in molecule **3** is ~39% and that of the LEP of the O atom in molecule **4** is ~30%. This is in agreement with the magnitudes of the C(2)C(1)X bond angles.

Different directionality of the LEP axes of the O and S atoms is due to different s-characters of the LEP. The dihedral angle between the planes formed by the C(1)—X bond and the axis of each LEP is close to 120° for the O atom and to 130° for the S atom. It is of interest to analyze the LEP orientation in the *s-gauche*-conformers of the *Z*-isomers of compounds **3** and **4** (see Table 2). In molecule **3**, one of the LEP axes makes an angle of 19° with respect to the axis of the p-AO of the π-system, whereas the other LEP axis deviates by 25° from the plane passing through the C(2), C(1), and S atoms. It should be noted that the axis of the same LEP in *E*-isomer makes an angle of 13° with the plane of the three-carbon skeleton. The increase in the dihedral angle can be connected with greater steric hindrances in *Z*-structure. For instance, the C(2)C(1)SCH$_3$ angle increases from 127° in the *E*-isomer to 138° in the *Z*-isomer.

In the *Z*-isomer of compound **4**, one of the LEP axes also deviates by ~30° from the plane of the three-carbon skeleton. The direction of the axis of the other LEP and that of the p-AO of the π-system nearly coincide. Therefore, the O atom interacts with the C(1)=C(2) π-bond more effectively than the S atom. This is also indicated by the energy difference between the *s-cis*- and *s-gauche*-conformers of the *E*-isomers of compounds **3** and **4**.

Such a LEP orientation is responsible for the distinctions in positions of the PES minima corresponding

to the *s-gauche*-conformers of the *Z*-isomers of compounds **3** and **4**. The *s-gauche*-conformer of **3** is characterized by a deviation of 41.6° from the *s-trans*-position, whereas this deviation is only 28.9° for molecule **4**. This fact, as well as different heights of the potential barriers, are the reasons why the *Z*-isomers of 1-alkoxyalk-1-enes are often identified as *s-trans*-conformers.

Mutual repulsion between methyl groups can be explained by different heights of the barriers separating two *gauche*-conformers of the *E*- and the *Z*-isomers (see Table 1). For the *E*-isomers, the barrier corresponding to passing through the *s-trans*-conformation is only due to maximum repulsion between the LEP of the heteroatom and π-electrons of the double bond. In the *Z*-isomers, this electron repulsion also increases the energy of the intermediate *s-trans*-structure; however, it is accompanied by simultaneous weakening of steric interaction. As a result, the net barrier for the *Z*-isomers of compounds **3** and **4** becomes lower than for the corresponding *E*-isomers.

Migration of the double bond toward the MeX substituent decreases the total energy of molecule **1**. Rearrangements **1b** → *E*-**3** and **1a** → *Z*-**3** are accompanied by energy changes of −4.0 and −4.1 kcal mol^{-1}, respectively. A decrease in the energy due to the formation of the *Z*-isomer of compound **3** from the most stable initial conformer **1b** is estimated at 3.8 kcal mol^{-1}. For compound **2**, the largest energy decrease (by 5.9 kcal mol^{-1}) is observed for the rearrangement of conformer **2b** into the *s-cis*-form of the the *E*-isomer of compound **4**, in which the position of the double bond near the substituent is to the greatest extent stabilized by conjugation. The energy changes observed for rearrangements **2a** → *Z*-**4** and **2b** → *Z*-**4** (5.0 and 4.8 kcal mol^{-1}, respectively) are greater than those observed for analogous transformations of compound **1**.

The *E*-isomers of compounds **3** and **4** are more stable than the corresponding *Z*-isomers. The energy difference between the corresponding isomers of **3** and **4** is 0.2 and 1.1 kcal mol^{-1}, respectively. Thus, it is expected that the equilibrium mixtures will contain nearly equal amounts of both isomers of compound **3** and a larger amount of *E*-isomer in the case of its oxygen-containing analog.

Carbanions

Intermediate $[MeXCHCHCH_2]^-$ (X = S (**5**), O (**6**)) carbanions that form in the course of migration of the multiple bond can also exist in both *E*- and *Z*-forms. Relative stability of the *E*- and *Z*-isomers of the carbanions can affect the composition of the final products under conditions of kinetically controlled reactions. Much higher mobility of protons bonded to the α-C atom of the methylthiopropene molecule is a significant distinction between this compound and its oxygen-containing analog.

Abstraction of a proton from molecule **2** by the hydroxide ion to give carbanion **6** and a water molecule is energetically unfavorable. The formation of the most stable *Z*-anion from **2a** is associated with an increase in the energy of 4.4 kcal mol^{-1}. The energy of anion **6** with *E*-structure is 2.9 kcal mol^{-1} higher. The formation of this anion from **2b** increases the energy by 7.5 kcal mol^{-1}. The energy difference between the isomeric anions **6** can provide the preferable kinetically controlled formation of the *Z*-isomers of compound **4** observed experimentally.[19]

Unlike **2**, the total energy of water molecule and anion **5** is lower than the sum of the energies of the initial reagents (**1** and the hydroxide ion). The formation of isomers of anion **5** from **1a** (*Z*-isomer) and **1b** (*E*-isomer) by abstraction of a proton at the C(3) atom is accompanied by a decrease in the energy of the system of 9.6 and 9.1 kcal mol^{-1}, respectively. The energies of the isomeric anions are close: the *Z*-isomer is only 0.2 kcal mol^{-1} more stable than the *E*-isomer.

The formations of the corresponding anions formed from molecules **1** and **2** result in essentially different changes in the spatial and electronic structure. The formation of the *Z*-isomer of anion **5** is accompanied by appreciable shortening of the C(3)—S bond, lengthening of the S—CH_3 bond, and by corresponding changes in the bond orders (Table 3). On the contrary, abstraction of a proton from conformer **2a** results in lengthening of the C(3)—O bond, decrease in its order, and in shortening of the O—CH_3 distance. The structure of the propene fragment in these anions is also different. In anion **5**, the C(1)—C(2) bond is shorter than the C(2)—C(3) bond and can to a good approximation be considered as a double bond, whereas these bonds in **6** have close lengths and orders, the latter having a somewhat greater degree of double bonding.

The Mulliken atomic charges (Table 4) show that the abstraction of a proton results in different types of distribution of the excess negative charge in anions **5** and **6**. Almost no additional negative charge is trans-

Table 3. Bond lengths (*d*) and bond orders (*b*)

Structure	Bond							
	C(1)—C(2)		C(2)—C(3)		C(3)—X		X—CH_3	
	d/Å	*b*	*d*/Å	*b*	*d*/Å	*b*	*d*/Å	*b*
1a	1.321	1.968	1.510	0.960	1.813	0.956	1.810	0.958
Z-**5**	1.371	1.654	1.403	1.337	1.746	1.060	1.828	0.891
2a	1.320	1.956	1.501	1.040	1.391	0.844	1.393	0.866
Z-**6**	1.393	1.486	1.372	1.525	1.400	0.802	1.388	0.922

ferred to the methoxy group "saturated" with electron density, whereas that of the SMe group becomes appreciably larger, which corresponds to the qualitatively well-known high π-acceptor ability of the sulfur atom.[20] At the same time, the Mulliken charge distribution is likely inadequate to correctly describe changes in the atomic charges of the propenyl fragment. The results of analysis of the Löwdin populations (see Table 4) seem to be more realistic and are in good agreement with the estimates obtained in the comparative study of the dimethyl sulfide and dimethyl ether acidity[21] using a more complex procedure. This approach predicts small changes in the charges on the C(2) atom and the H atom bonded to the former. The greatest increase in the electron density in the isomers of anion **5** is observed for the C atom nearest to the substituent, whereas the largest excess negative charge in the corresponding oxygen-containing analogs is localized on the terminal C(1) atom. Such a charge distribution is consistent with the above-mentioned differences in the spatial structure of anions **5** and **6**.

Quantitative changes in the charges on the substituents due to the formation of anions **5** and **6** obtained in the framework of the Löwdin approach are not so large as those found using the Mulliken approach. However, as in the preceding case, the SMe group carries an appreciably larger negative charge than the methoxy group. The methyl group bonded to the S atom has a larger negative charge than the heteroatom. Taken together with shortening of the S—C(3) bond length and lengthening of the S—CH_3 bond, this charge distribution is consistent with the description of stabilization of the carbanions in terms of the model of negative

Table 4. Changes in the Mulliken (Δq_M) and Löwdin (Δq_L) populations due to the formation of anions

Molecule	Anion	Group	Δq_M	Δq_L
			au	
1a	*Z*-**5**	$C(1)H_2$	−0.583	−0.394
		C(2)H	+0.139	+0.041
		C(3)H	−0.326	−0.492
		S	−0.214	−0.051
		Me	−0.015	−0.104
2a	*Z*-**6**	$C(1)H_2$	−0.696	−0.494
		C(2)H	+0.369	−0.021
		C(3)H	−0.662	−0.430
		O	+0.017	+0.003
		Me	−0.025	−0.059
1b	*E*-**5**	$C(1)H_2$	−0.431	−0.392
		C(2)H	−0.063	+0.046
		C(3)H	−0.241	−0.470
		S	−0.231	−0.069
		Me	−0.034	−0.114
2b	*E*-**6**	$C(1)H_2$	−0.795	−0.512
		C(2)H	+0.429	+0.040
		C(3)H	−0.618	−0.412
		O	−0.010	−0.018
		Me	−0.006	−0.098

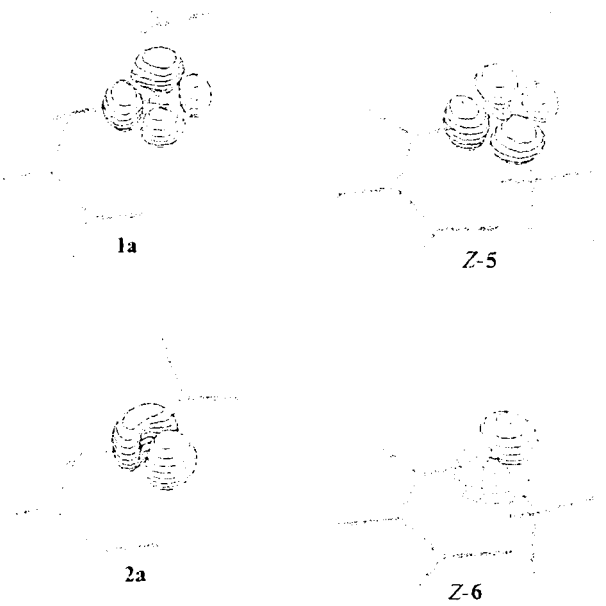


Fig. 2. Charge density difference maps obtained using basis sets augmented with d-functions for S and O atoms (the contour level is 0.007 au $Å^{-3}$).

hyperconjugation.[22] This effect is pronounced for 3-methylthioprop-1-ene and is not observed for its oxygen-containing analog.

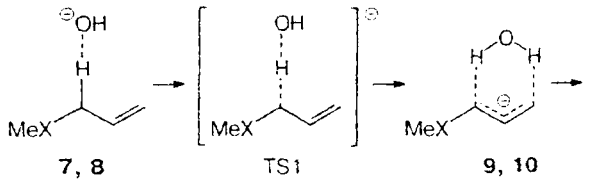
Increased acidity of the C—H fragments in α-position with respect to the S atom is often associated with additional stabilization of the carbanions formed due to unoccupied d-AO.[19] However, it should be kept in mind that atomic d-orbitals differ from d-functions included in the basis sets used in the MO LCAO approach. In essence, the role of the latter is reduced to increasing the basis set "flexibility" for a more correct description of the electron density distribution in the entire molecule.[21,23] Changes in the electron density observed upon exclusion of d-functions of the O and S atoms from the 6-31+G* basis set are equally significant both for neutral compounds **1a** and **2a** and for anions **5** and **6**. In particular, mention may be made that augmentation of the basis set with *d*-functions leads for both anions to a decrease in the total electron density in the region of the LEP of the heteroatoms and to its increase in the region of the S—C and O—C bonds (Fig. 2). Thus, the role of these functions is likely limited to providing the possibility of more correct description of the bonding area.

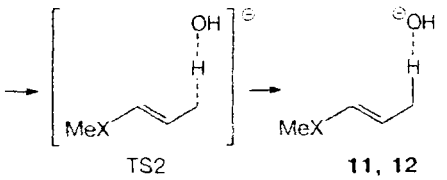
Mechanism of prototropic isomerization of 3-methylthioprop-1-ene and 3-methoxyprop-1-ene

Strongly different proton affinities of anions **5** and **6** require a more detailed study of the energy profile of the rearrangement of molecule **1** in the presence of hydroxide ion. The profile of rearrangement **1a** → *Z*-**3** obtained

in this work was compared with the PES cross section of rearrangement **2a** → *Z*-**4**.[3]

As in the case of system **2**, the hydroxide ion attacks structure **1a** to give complex **7**, which is transformed into complex **9** of anion **5** with a water molecule *via* the transition state TS1.





7, **9**, **11**: X = S; **8**, **10**, **12**: X = O

Addition of a proton to the C(1) terminal atom occurs with overcoming of the energy barrier (transition state TS2) to give complex **11** between the *Z*-**3** conformer and the hydroxide ion. Dissociation of this complex completes the migration of the double bond. The energy profile obtained (Fig. 3) indicates that the single-stage proton transfer mechanism with participation of the H atom of the hydroxide ion can also be realized for 3-methoxyprop-1-ene.

Increased stability of isomeric anions **5** compared to that of their analogs **6** is responsible for lower relative energies of all stationary points on the PES of compound **1** (see Fig. 3) compared to those of molecule **2**

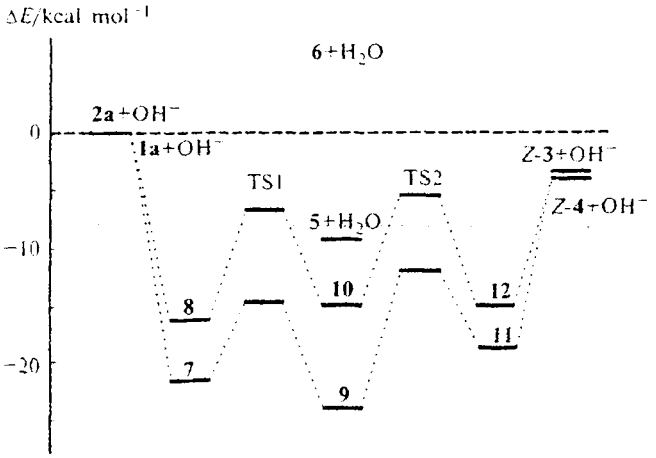


Fig. 3. Relative energies (ΔE) of the structures characterizing the profiles of isomerization reactions of 3-methoxyprop-1-ene and 3-methylthioprop-1-ene.

Table 5. Relative energies (ΔE) of stationary points on the PES for prototropic isomerization of 3-methylthioprop-1-ene and 3-methoxyprop-1-ene

1a → *Z*-**3**	ΔE /kcal mol^{-1}	**2a** → *Z*-**4**	ΔE /kcal mol^{-1}
1a + OH^-	0.0	**2a** + OH^-	0.0
7	−21.0	**8**	−15.8
TS1	−14.9	TS1	−6.4
9	−24.4	**10**	−14.8
TS2	−12.2	TS2	−6.2
11	−18.4	**12**	−16.0
3 + OH^-	−3.8	**4** + OH^-	−4.2
5 + H_2O	−9.0	**6** + H_2O	4.8

(Table 5). The largest energy difference (9.7 kcal mol^{-1}) is observed for complexes of carbanions with the water molecule. As should be expected, the smallest are the energy differences between the complexes of the final products with the hydroxide ion. This is due to the weakening of the substituent effect with distance so that it becomes rather small for the C(1) terminal atom. For both compounds **1** and **2**, the energies of both transition states are lower than those of the initial reagents and final products.

The reaction profiles significantly differ in relative positions of the energy levels of the transition states and systems comprising isolated anions **5** and **6** and a water molecule. Abstraction of a proton from molecule **2** by a hydroxide ion followed by its transfer into the reaction medium is energetically unfavorable. At the same time, for molecule **1** the energies of transition states TS1 and TS2 are respectively 5.9 and only 3.2 kcal mol^{-1} lower than the total energy of anion **5** and a water molecule. Thus, the rearrangement of the complex between anion **5** and the water molecule into the final product *via* transition state TS2 following both a single-stage and a conventional two-stage mechanism for **1** seems to be equiprobable.

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