Multiple bond migration with participation of a protophilic agent
3.* Double bond migration in 1-methoxy-2-propene molecule with participation of hydroxide ion

N. M. Vitkovskaya,[a] V. B. Kobychev,[a] E. Yu. Larionova,[a] and B. A. Trofimov[b]*

[a]*Irkutsk State University,*
1 ul. K. Marksa, 664003 Irkutsk, Russian Federation.
Fax: +7 (395 2) 33 2238. E-mail: vita@cc.isu.ru
[b]*Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,*
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 35 6046. E-mail: bat@acet.irkutsk.su

The pathways of migration of the double bond in the 1-methoxy-2-propene molecule with participation of a hydroxide ion were investigated by the *ab initio* RHF/6-31+G* and MP2/6-31+G* methods. Stationary points corresponding to complexes between the molecule under study and the hydroxide ion and between the corresponding carbanion and a water molecule were found on the potential energy surfaces of the proton transfer reactions. As in the propene molecule, migration of the double bond in the 1-methoxy-2-propene molecule can occur in the gas phase by the mechanism of intramolecular proton transfer involving the proton of the hydroxide ion. Conformational isomerism of the initial molecule and reaction products was considered. The proposed mechanism of 1,3-hydrogen shift involving the proton-containing base suggests the formation of both *E*- and *Z*-products with predominance of the latter irrespective of the nature of the substituent. In this case the direction of multiple bond migration will be completely determined by the energy difference between the initial reagents and final products.

Key words: propene, methoxypropenes, 1,3-hydrogen shift, hydroxide ion, reaction mechanism, potential energy surface, *ab initio* quantum-chemical calculations.

Previously,[1,2] we studied the mechanism of multiple bond migration in the propene molecule with participation of a hydroxide ion and showed that it can occur *via* the formation of an intermediate complex of the three-carbon system with the water molecule formed from the attacking hydroxide ion and one of the methyl protons of propene, *i.e.*, formally without exchange of the migrating proton with the medium ("intramolecularly").

In an unsaturated system containing a heteroatomic substituent the multiple bond usually migrates toward the heteroatom.[3,4] In contrast to the degenerate process in propene, a multiple bond migration in a molecule containing the substituent at the sp^3-hybridized C atom can lead to both *Z*- and *E*-isomers. In the case of alkyl substituents, *Z*-alkenes are mostly formed as a result of prototropic shift.[5] For 1-alkoxy-2-propenes, the preferable kinetically controlled formation of *Z*-isomers is initially observed, which is followed by their partial isomerization into the *E*-isomers.[6] This regularity holds also in the case where the allyl group is bonded to the nitrogen atom.[7–12]

This work is dedicated to studying the effect of a heteroatomic substituent (methoxy group) on the double bond migration in the propene fragment of the 1-methoxy-2-propene molecule (**1**) in the presence of a hydroxide ion.

*For part 2, see Ref. 1.

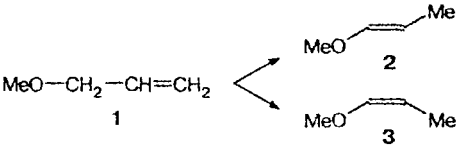
Calculation procedure

The procedure for calculations was described previously.[1] The sections of the potential energy surfaces (PES) of the reactions under discussion were obtained in the framework of the restricted Hartree—Fock (RHF) method and with inclusion of correlation effects at the second-order Møller—Plesset (MP2) level of perturbation theory using the 6-31+G* basis set. Calculations were performed using the GAMESS program[13] with a PENTIUM® II chip with the LINUX operating system and on a SunSparc-1000 computers.

Results and Discussion

Spatial and electronic structure of methoxypropenes

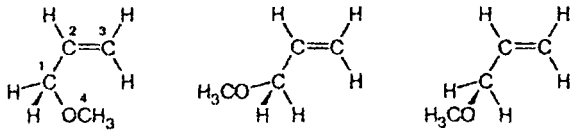
Double bond migration in the 1-methoxy-2-propene molecule can result in the formation of *E*- and *Z*-isomers of 1-methoxy-1-propene-1 (**2** and **3**, respectively).



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 658—663, April, 1999.

The spatial structure of initial reagents and final products should be considered in more detail, since its specific features appear to be essential for estimating the energetics of suggested mechanisms.

Internal rotation about the C(1)—O and C(1)—C(2) bonds in molecule **1** should be relatively free. Indeed, according to RHF calculations, there are three minima with rather close-lying energies on the potential curve of internal rotation about the C(1)—C(2) bond obtained for **1**; they correspond to an OC(1)C(2)C(3) dihedral angle of 0° (the planar form **1a**), 130° (**1b**), and 230° (**1c**). In the structures **1b** and **1c** the O atom deviates from the plane passing through the C(1), C(2), and C(3) atoms by 50°.



1a **1b** **1c**

Conversion of the planar form **1a** into the nonplanar form **1b** (or **1c**) occurs with overcoming of an energy barrier of 3.0 kcal mol^{-1}. The height of the barrier separating two nonplanar structures **1b** and **1c** is 1.4 kcal mol^{-1}. Rotation about other ordinary bonds also has little effect on the total energies of stable conformers and occurs with overcoming of low energy barriers.

Thus, there are several local minima on the PES constructed for molecule **1** with a spread in energy lying within the limits of 0.1 kcal mol^{-1}. Any of the structures corresponding to the minima can be equiprobably rearranged under the action of a base.

It should be expected that the rotation about the C(1)—O bond in molecules **2** and **3** also occurs with overcoming of low energy barriers. According to traditional concepts, molecules **2** and **3** can exist in three (*s-cis*, *s-trans*, and nonplanar *s-gauche*) conformations. Internal rotation can be hindered due to both the p,π-interaction of the lone electron pair of the O atom with π-electrons of the double bond and pure steric factors. It should be noted that the structure of this type of vinyl systems is a debated topic so far.[14]

According to RHF calculations, the *s-cis*-rotamer of compound **2** is the most energetically favorable (Fig. 1). The energy of the *s-gauche*-structure with a C(4)OC(1)C(2) angle of 145° is 1.1 kcal mol^{-1} higher. The energy barrier separating the *s-cis*- and *s-gauche*-rotamers is 3.6 kcal mol^{-1}. The planar *s-trans*-rotamer corresponds to a transition state between two equivalent *s-gauche*-positions of the methyl group. The Hesse matrix has one negative eigenvalue at this point. The height of the activation barrier to such a transition is only 0.3 kcal mol^{-1}. The inclusion of zero-point vibrational energy leads to the decrease in the energy difference between the rotamers down to 0.6 kcal mol^{-1}, the barrier to conversion between the *s-cis*- and *s-gauche*-forms decreases to 3.0 kcal mol^{-1}, and that to transition between two *s-gauche*-structures is only 0.2 kcal mol^{-1}.

Unfortunately, no experimental data on the barriers to internal rotation in the 1-methoxy-1-propene molecule are available. At the same time the shape of the potential curve of internal rotation is in good agreement with the concepts of intramolecular torsional motions of large amplitude observed experimentally for several rotameric forms of vinyl ethers.[14]

For structure **3** we considered stationary points on the PES corresponding to the rotamers with the *s-cis*-, *s-trans*-, and *s-gauche*-position of the methyl group (Fig. 2). As in the case of compound **2**, the *s-cis*- and *s-gauche*-structures of **3** correspond to minima on the PES; however, because of apparent steric hindrances the *s-gauche*-form with a C(4)OC(1)C(2) angle of 151° appears to be more stable (by 4.9 kcal mol^{-1}). The barrier

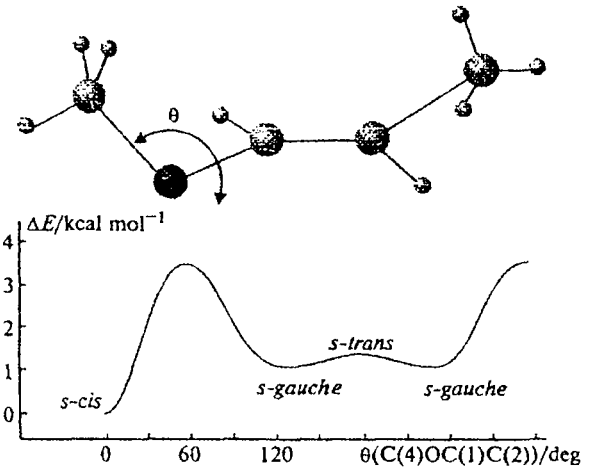


Fig. 1. Potential curve of internal rotation about the C(1)—O bond in the *E*-1-methoxy-1-propene molecule **2** (according to RHF/6-31+G* calculations).

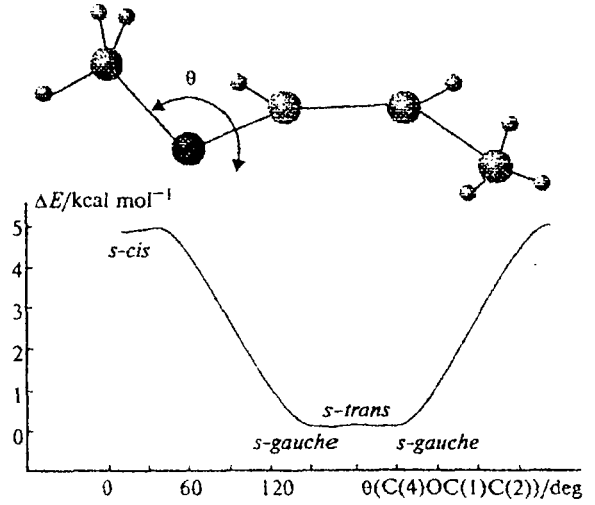


Fig. 2. Potential curve of internal rotation about the C(1)—O bond in the *Z*-1-methoxy-1-propene molecule **3** (according to RHF/6-31+G* calculations).

to transitions between these forms is 0.1 kcal mol^{-1}, while the inclusion of zero-point vibrational energy leads to a situation where the energy level of the transition state is lower than the first vibrational level of the *s-cis*-structure. The *s-trans*-form corresponds to the transition state between two *s-gauche*-structures of **3** while its energy is merely 0.1 kcal mol^{-1} higher than that of the *s-gauche*-form. Thus, calculations predict that molecule **3** exists entirely in the *s-gauche*-conformation characterized by intramolecular torsional motion of large amplitude characteristic of compounds in which the O atom is adjacent to the double bond.

It is significant that the total energies of the most stable rotamers of molecules **2** (*s-cis*) and **3** (*s-gauche*) calculated in the RHF approximation differ by only ~0.6 kcal mol^{-1}, the *E*-isomer of **2** having the lower energy. The total energies of *s-gauche*-forms of molecules **2** and **3** are also close, the structure **3** (*s-gauche*) being only ~0.6 kcal mol^{-1} preferable. Therefore the thermal effect of isomerization of **1** into any of these forms does not cause one to anticipate a preferred formation of a particular structure.

Mechanism of intramolecular proton transfer upon prototropic isomerization of 1-methoxy-2-propene

In the MP2/6-31+G* approximation we studied the profile of **1** → **2** rearrangement with participation of a hydroxide ion following the mechanism considered previously for the propene molecule, which involves the intermediate formation of a complex between the corresponding carbanion and the water molecule. There is a minimum corresponding to complex **6** between the [*E*-MeOCHCHCH$_2$]$^-$ anion (**9**) and the water molecule on the structure—energy diagram of the system under study (Fig. 3). This complex is, on the whole, structurally similar to the analogous complex with propene.[2] Introduction of a substituent (methoxy group) leads to a displacement of the coordinated water molecule toward the terminal C atom. The gas-phase formation energies of complex **6** (from isomer **1** and hydroxide ion) and the analogous complex formed in the course of prototropic isomerization of unsubstituted propene are also close (9.7 kcal mol^{-1} and 8.9 kcal mol^{-1}, respectively). The anion **9**, with a C(4)OC(1)C(2) angle of 114.4° in complex **6** and 121.1° in isolated structure **9**, is structurally similar to the *s-gauche*-form of **2**.

By shortening the C(1)—H distance followed by refinement using the GAMESS program we found the transition state **5** corresponding to proton migration from the sp^3-hybridized C atom toward the attacking hydroxide ion (Fig. 4). Transition state **7**, corresponding to the proton transfer from the water molecule to the terminal C atom, was localized analogously using the C(3)—H distance as the reaction coordinate.

By descending from point **5** along the reaction coordinate one arrives at complex **4** between the initial molecule **1** and the hydroxide ion; in this complex the C(3)C(2)C(1)O torsion angle corresponding to rotation about the C(1)—C(2) bond is 99.3° and the C(2)C(1)OC(4) angle characterizing rotation about the C(1)—O bond is 69° (see Fig. 4). Such a complex can be formed from structure **1c**. Noteworthy is the appreciable rotation of the methoxy group in the complex as compared to the structure **1c** (the C(3)C(2)C(1)O angle is 130°) and obvious distortion of the "cisoid" conformation characteristic of the allyl group. Analogous distortion found also for unsubstituted propene[2] is most likely due to involvement of not only the proton at the C(1) atom, but also that at the C(2) atom (see Fig. 4) in the coordination with the hydroxide ion.

The gas-phase formation energy of complex **4** from molecule **1c** and a hydroxide ion is 11.6 kcal mol^{-1},

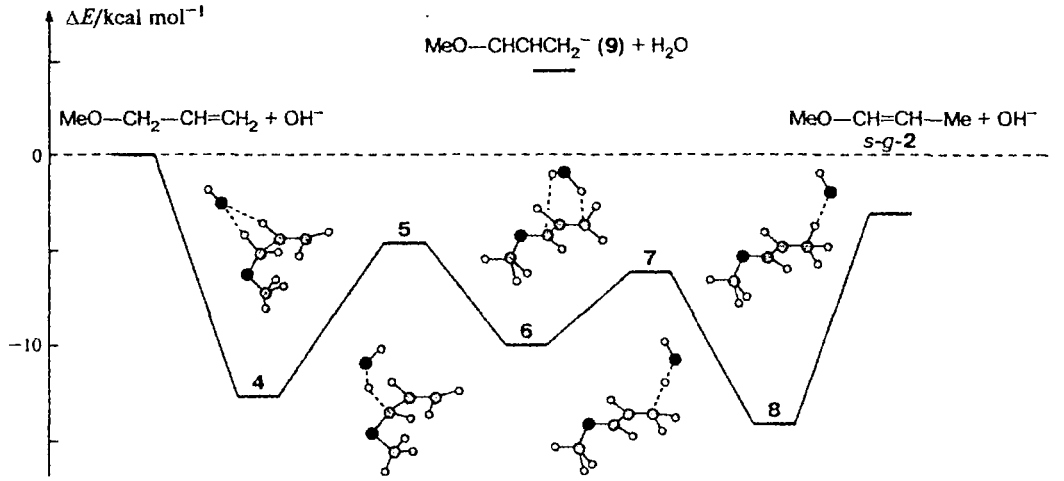


Fig. 3. Structure—energy diagram of the reaction of 1-methoxy-2-propene isomerization into *E*-1-methoxy-1-propene (the relative energies of the structures (ΔE) were calculated in the MP2/6-31+G* approximation).

which is 1.6 kcal mol^{-1} lower than for unsubstituted propene. The **4** → **6** transition is accompanied by an increase in the total energy of the system of 1.9 kcal mol^{-1} and requires overcoming of an activation barrier of 7.3 kcal mol^{-1} (*cf.* 1.3 and 7.6 kcal mol^{-1}, respectively, for the unsubstituted propene). Analogously, the energy of transition state **5** is 4.4 kcal mol^{-1} lower than those of the initial reagents (*cf.* 5.7 kcal mol^{-1} for propene).[1] Thus, the stages of proton abstraction from the C(1) atom and complex formation between the carbanion and the water molecule are close for propene and its methoxy derivative on both qualitative and quantitative levels.

By descending from point **7** along the reaction coordinate one arrives at complex **8** between the *s-gauche*-rotamer of molecule **2** (the C(2)C(1)OC(4) angle is 130°) and the hydroxide ion (see Fig. 3). The energy of its formation from the initial reagents is 13.3 kcal mol^{-1}. The **6** → **8** transition occurs with overcoming of a barrier of 4.0 kcal mol^{-1} and is accompanied by a decrease in the total energy of the system of 3.5 kcal mol^{-1}. Abstraction of the hydroxide ion from complex **8** is accompanied by an increase in the total energy of the system of 9.8 kcal mol^{-1}. On the whole, the double bond migration is exothermic (3.5 kcal mol^{-1}). Abstraction of a water molecule from complex **6** to form the anion **9** requires a much larger energy expenditure, estimated at 17.8 kcal mol^{-1}.

The obtained structure—energy diagram of the multiple bond migration (see Fig. 3) indicates that this reaction can also follow the mechanism of intramolecular proton transfer in the presence of a substituent with lone electron pairs. Moreover, in the case of methoxypropene this mechanism seems to be more (without considering solvation effects) energetically preferable as compared to proton transfer through the reaction medium.

The results obtained suggested that change in the methoxy group orientation should not strongly affect the reorganization mechanism of the hydrocarbon skeleton of the propene system. Indeed, the structure—energy diagram of the prototropic rearrangement of molecule **1** into the *Z*-isomer **3** obtained in the MP2/6-31+G* approximation (Fig. 5) is qualitatively similar to that of the formation reaction of the *E*-isomer of molecule **2** considered above. The reaction occurs *via* the formation of complex **10** between the initial methoxypropene **1** and the hydroxide ion attacking the proton at the sp^3-hybridized C(1) atom. This complex is transformed *via* transition state **11** into

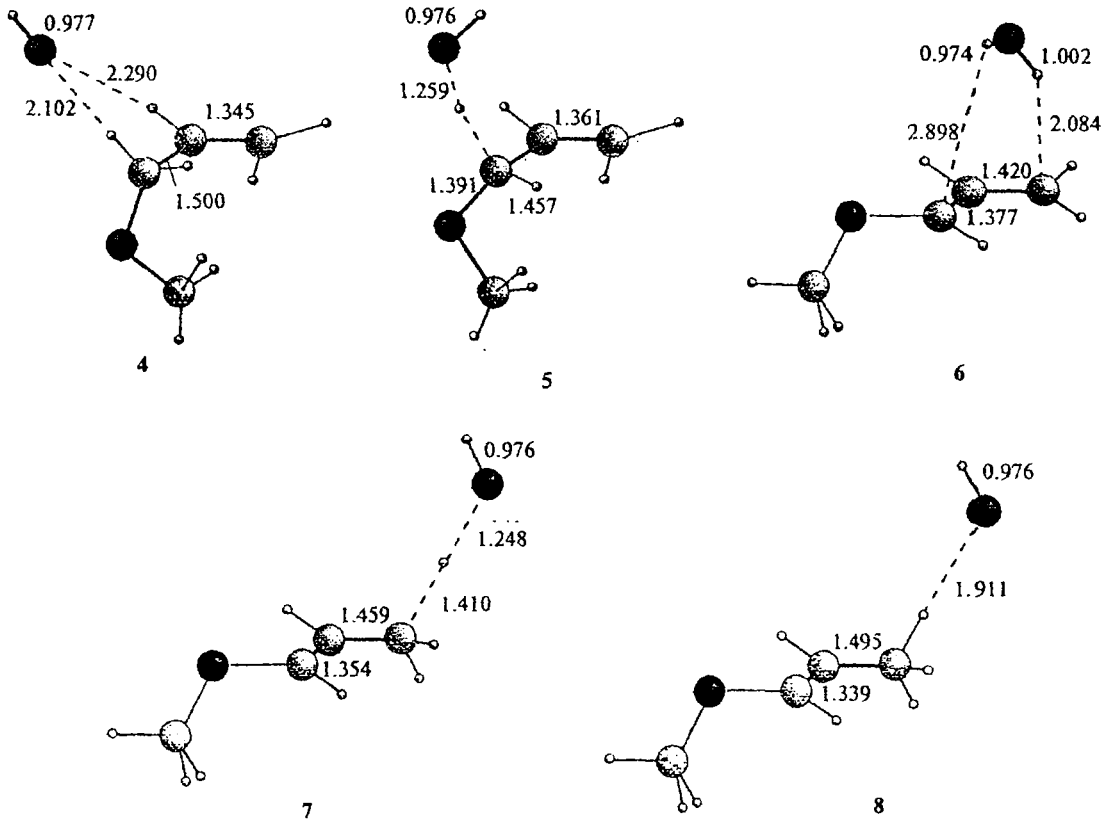


Fig. 4. Structures corresponding to stationary points on the structure—energy diagram of the reaction of 1-methoxy-2-propene isomerization into *E*-1-methoxy-1-propene (internuclear distances (*d*/Å) obtained from MP2/6-31+G* calculations are given).

complex **12** between the $[MeOCHCHCH_2]^-$ anion and the water molecule. In turn, complex **12**, *via* transition state **13** formed upon proton migration from the O atom to the C(3) atom, can undergo transformation into complex **14** between the molecule **3** and the hydroxide ion. Dissociation of **14** into isomer **3** and the hydroxide ion completes the rearrangement. As in the preceding cases, the energies of both transition states are lower than those of the initial reagents and reaction products.

At the same time, the O atom occupying a position immediately adjacent to the region in which the proton transfer occurs, is capable of having an appreciable effect on the geometry and stability of the intermediate structures (Fig. 6). Complex **10** with a formation energy of 15.8 kcal mol^{-1} is structurally close to the analogous complex of unsubstituted propene. However, the water molecule in complex **12** is no longer coordinated by the three-carbon system: the proton abstracted by the base from the C(1) atom appears to be closest to the O atom of the methoxy group. The formation energy of complex **12** from molecule **1** and the hydroxide ion is ~14.8 kcal mol^{-1}, which is 5 kcal mol^{-1} higher than for the analogous complex **6** of *E*-structure. It should be noted that the *Z*-form of the $[MeOCHCHCH_2]^-$ anion formed upon proton abstraction is 3.3 kcal mol^{-1} more stable than the *E*-anion **9**.

It is interesting to note that despite obvious similarity of transition states **13** and **7**, by descending from point **13** along the reaction coordinate one arrives at a minimum corresponding to complex **14** between a *Z*-1-methoxy-1-propene molecule and the hydroxide ion, which is mostly coordinated by the proton bonded to the C(2) atom. Nevertheless, further dissociation of this complex eventually leads to the formation of isomer **3** of compound **1**.

Finally, decomposition of complex **12** into the *Z*-$[MeOCHCHCH_2]^-$ anion and a water molecule requires an energy expenditure of 19.6 kcal mol^{-1}, which is 1.8 kcal mol^{-1} higher than the dissociation energy of analogous complex **6** of *E*-structure. At the same time proton abstraction accompanied by the formation of the *Z*-anion requires 4.8 kcal mol^{-1} relative to the energies of the initial reagents **1** and OH^-, whereas the formation of the *E*-anion requires 8.1 kcal mol^{-1}.

The estimates obtained suggest that the route resulting in the formation of isomer **3** is somewhat more energetically preferable irrespective of the reaction mechanism ("intramolecular" or traditional one involving a proton transfer through the medium). At the same time these energy differences can hardly be considered as substantial, in particular, taking into account the small difference in the overall thermal effect of the reaction. We believe that a more important factor favoring the preferred formation of the *Z*-form of **3** is the spatial structure of the propene fragment. To form the *Z*-structure in the reaction under consideration, molecule **1** should have the form **1a**, in which there are two protons suitable to the attack. On the contrary, the *E*-isomer can be formed from structure **1b** (or **1c**), containing only one appropriate proton.

Thus, in the case of 1-methoxy-2-propene the proposed mechanism of multiple bond migration with participation of a hydroxide ion by intramolecular proton transfer seems to be even more preferable than for unsubstituted propene. Both energy and structural characteristics of the process indicate a preferred formation of the *Z*-isomer; however, the reaction occurring with the formation of the *E*-form also cannot be ruled out, which is in agreement with the known experimental data.[6] We believe that the considered mechanism of

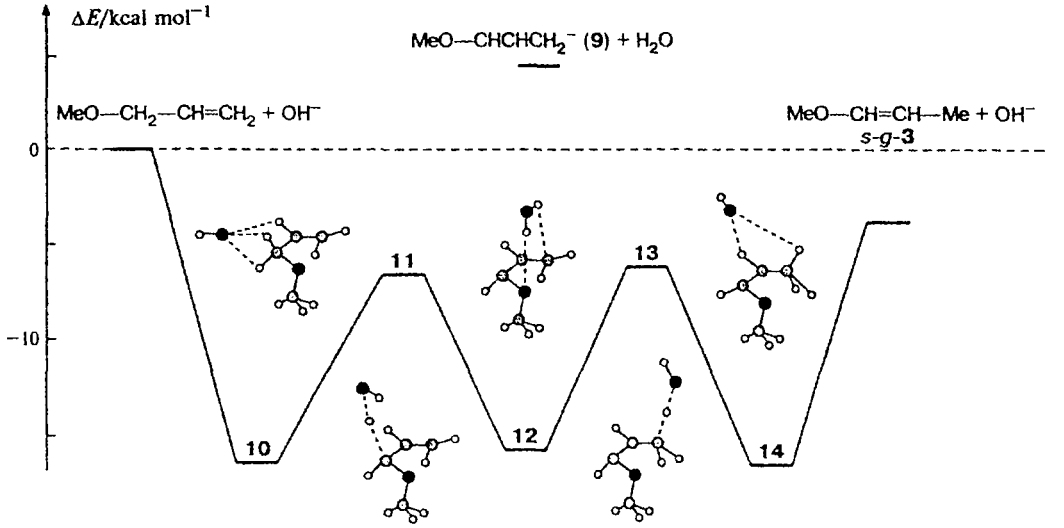


Fig. 5. Structure—energy diagram of the reaction of 1-methoxy-2-propene isomerization into *Z*-1-methoxy-1-propene (the relative energies of the structures (ΔE) were calculated in the MP2/6-31+G* approximation).

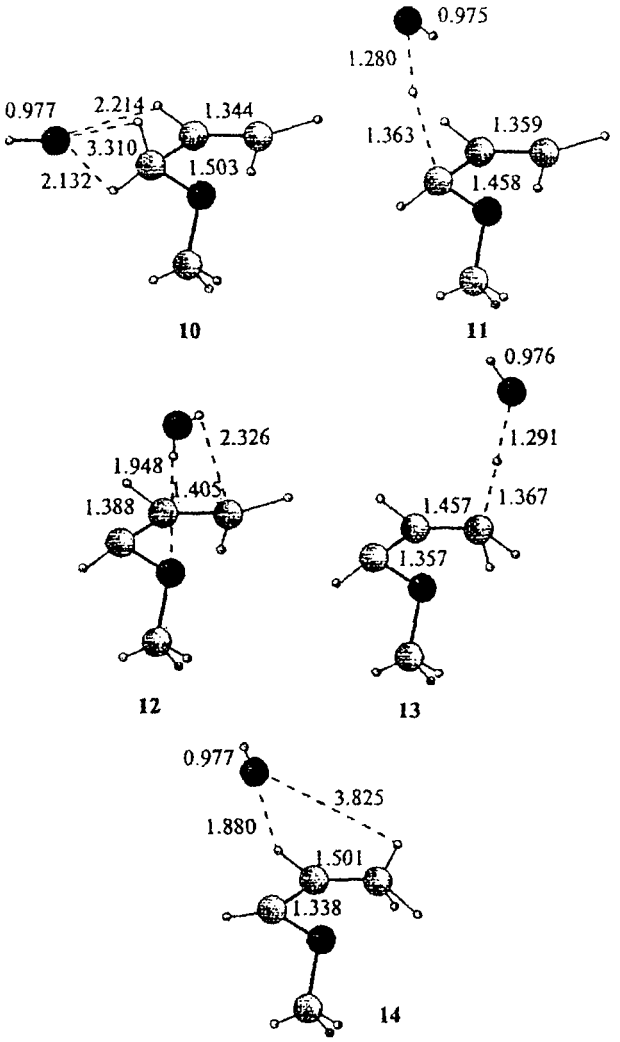


Fig. 6. Structures corresponding to stationary points on the structure—energy diagram of the reaction of 1-methoxy-2-propene isomerization into *Z*-1-methoxy-1-propene (internuclear distances (d/Å) obtained from MP2/6-31+G* calculations are given).

1,3-hydrogen shift with participation of a proton-containing base suggests the kinetically controlled formation of both *E*- and *Z*-products with predominance of the latter irrespective of the substituent nature and that the direction of the double bond migration will be completely determined by the energy difference between the initial reagents and final products.

This work was supported by the Russian Foundation for Basic Research (Project No. 98-03-33152a).

References

1. N. M. Vitkovskaya, V. B. Kobychev, E. Yu. Larionova, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 35 [*Russ. Chem. Bull.*, 1999, **48**, 35 (Engl. Transl.)].
2. N. M. Vitkovskaya, V. B. Kobychev, A. B. Trofimov, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1772 [*Russ. Chem. Bull.*, 1997, **46**, 1677 (Engl. Transl.)].
3. A. S. Atavin, V. I. Lavrov, O. N. Sidorova, and B. A. Trofimov, *Zh. Org. Khim.*, 1971, **7**, 235 [*J. Org. Chem. USSR*, 1971, **7** (Engl. Transl.)].
4. B. A. Trofimov, A. S. Atavin, V. I. Lavrov, and M. F. Shostakovskii, *Zh. Obshch. Khim.*, 1967, **37**, 743 [*J. Gen. Chem. USSR*, 1967, **37** (Engl. Transl.)].
5. *Comprehensive Organic Chemistry*, Eds. D. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, **1**.
6. D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York—London, 1965.
7. J. Saner and H. Prahl, *Chem. Ber.*, 1969, **102**, 1917.
8. A. Schouteeten and M. Julia, *Tetrahedron Lett.*, 1975, 607.
9. A. J. Hubert, *J. Chem. Soc.*, 1968, 2048.
10. R. A. Crellin and A. Ledwith, *Macromolecules*, 1975, **8**, 93.
11. M. Julia and A. Schouteeten, *Tetrahedron Lett.*, 1974, 3433.
12. V. D. Filimonov, V. A. Anfinogenov, and E. E. Sirotkina, *Zh. Org. Khim.*, 1978, **14**, 2607 [*J. Org. Chem. USSR*, 1978, **14** (Engl. Transl.)].
13. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupius, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
14. L. M. Sinegovskaya and B. A. Trofimov, *Usp. Khim.*, 1996, **65**, 1091 [*Russ. Chem. Rev.*, 1996, **65** (Engl. Transl.)].

Received August 24, 1998