Multiple bond migration with participation of a protophilic agent

2.* Distinctions in mechanisms of multiple bond migration in propene and propyne molecules with participation of hydroxide ion

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The pathways of migration of the multiple bond in propene and propyne molecules involving the hydroxide ion were investigated by the *ab initio* (RHF/6-31+G* and MP2/6-31+G*) methods. Stationary points corresponding to stable complexes between the molecules under study and the hydroxide ion and between corresponding carbanions and water molecule were found on the potential energy surfaces of the proton transfer reactions. In the presence of hydroxide ion, migration of the multiple bond can occur by an "intramolecular" mechanism of the proton transfer involving the proton of hydroxide ion bound in the complex with propene or propyne molecule. For the propene system, such a mechanism seems to be quite realistic and more preferable energetically than a traditional two-stage mechanism with a passage of the proton into the medium. For the system with the triple bond, an equal expenditure of energy is required to follow any mechanism (without taking into account the effects of solvation and the interaction with a cation), whereas the formation of the stable $[H_2C=C=CH \cdot H_2O]^-$ complex can prevent further transfomations.

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

Prototropic isomerization reactions of unsaturated compounds accompanied by the migration of multiple bonds are well known. Usually, such transformations are described[2,3] as two-stage transformations with intermediate formation of carbanions. In this case the direction of the multiple bond migration depends on the relative stability of the anions, ease of their mutual transformations, and the electron distribution determining the reprotonation position.

An alternative single-step mechanism of prototropic rearrangement[4] involving a proton abstraction from one part of the system accompanied by simultaneous addition of another proton to the other part of the system is much rarely discussed. Three species simultaneously participate in the elementary act of the proton transfer.

In any case, the 1,3-hydrogen shift in the systems under consideration requires participation of a protophilic agent. For an isolated propene molecule quantum-chemical calculations[5] by the multi-configuration (MC) SCF and configurational interaction (CI) methods predict the activation barriers that exceed the energy of cleavage of the C—H bond for both the symmetry-forbidden *supra*-surface and symmetry-allowed *antara*-surface pathway of migration of the hydrogen atom.[6]

Previously,[1] we performed an *ab initio* study (in the 4-31G* basis set) of the multiple bond migration in propene and propyne molecules with participation of hydroxide ion occurring as a "single-stage" process with the intermediate formation of a complex of corresponding carbanion with water molecule. It cannot be ruled out that quantitative estimates obtained in the 4-31G* basis set can be substantially changed upon introducing diffuse functions into the basis set. Thus, the relative energies of initial reagents and end products calculated in the extended basis set taking into account correlation effects in the framework of the method of coupled clusters[1] are, on the whole, reproduced satisfactorily in the 4-31G* basis set, whereas they differ appreciably for hydroxide ion and water molecule.

The aim of this work was to refine the reaction profile of 1,3-hydrogen shift in propene and propyne molecules in the presence of hydroxide ion and to compare the opportunities for the migration of double and triple bonds to occur due to the double proton transfer.

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* For Part 1, see Ref. 1.

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Calculation procedure

Previously, we have carried out preliminary studies of pathways of multiple bond migration in the presence of hydroxide ion with the intermediate formation of a water molecule in the framework of the restricted Hartree—Fock (RHF) method in the 4-31G* basis set. The insufficiency of this basis set is clearly demonstrated by estimated energies of the proton abstraction from a water molecule (Table 1). The proton affinities of hydroxide ion calculated in different approximations were compared with the data of calculations in the aug-cc-pvDZ basis set[7] with inclusion of correlation effects in the framework of the method of coupled clusters.[1] The absence of diffuse functions in the 4-31G* basis set introduces a large error into the description of the hydroxide ion, which results in a substantial overestimating the protonation energy.

The introduction of diffuse functions on the oxygen atom (6-31+G*) into the basis set appreciably improves the estimate of the proton affinity of the hydroxide ion. The inclusion of correlation energy at the second-order Møller—Plesset (MP2) level of perturbation theory gives results which are in good agreement with those obtained by the CI method (see Table 1) and estimated from experimental data.[8] The values of geometric parameters calculated by the RHF and MP2 methods differ appreciably and noticeably deviate from the experimental ones;[9,10] therefore the equilibrium geometries found in the RHF approximation cannot be used in the MP2 calculations.

The sections of the potential energy surfaces (PES) of the reactions in question were obtained within the framework of the RHF method using the 6-31+G* basis set and with inclusion of correlation effects at the MP2 level of perturbation theory using the GAMESS program[11] on a Pentium II computer with the LINUX operating system and on a SunSparc-1000 workstation. First, search of the energy minima on the PES of corresponding carbanion complexes with H_2O molecule was performed. The geometry at stationary points was refined by the gradient optimization method using the GAMESS program at a standard deviation of 10^{-4} au B^{-1} taking the geometric parameters obtained in the 4-31G* basis set as initial approximation. Preliminary search for the saddle points was performed by stepwise change of one of the geometric parameters which changed to the greatest extent on going from one structure to another. The refinement of the geometry of transition states was carried out using standard tools of the GAMESS program. For all given transition states, the Hesse matrices have one negative eigenvalue at the critical points found. Then, a descent was performed along the gradient line from the saddle point found to the next minimum.

Table 1. Energies of proton abstraction (ΔE)[a] and geometric parameters of H_2O molecule and OH^- ion (bond lengths (d) and the H—O—H bond angles) calculated by different methods

Parameter	RHF/ 4-31G*	RHF/ 6-31+G*	MP2/ 6-31+G*	CCSD/aug-cc-pvDZ +CI	Experiment
ΔE/kcal mol^{-1}	433.0	402.4	389.9	397.1	386[b]
$d(O-H)_{H_2O}$/Å	0.948	0.948	0.971	0.964	0.957[9]
H—O—H/deg	105.3	106.5	105.5	104.1	104.5[9]
$d(O-H)_{OH^-}$/Å	0.965	0.952	0.977	0.971	0.971[10]

[a] $\Delta E = E_{H_2O} - E_{OH^-}$.

[b] Calculated using data taken from Ref. 8.

The estimates of geometry at stationary points obtained from RHF and MP2 calculations differ substantially; therefore, the geometric parameters of the structures in question were optimized in each of these approximations. The zero-point vibrational energies were estimated only in the RHF approximation for a temperature of 295 K using a standard scale factor of 1.0. The results obtained were used to correct the values of relative enthalpies (ΔH^{295}) calculated by the MP2 method.

Results and Discussion

Migration of the double bond

The energy profile of the proton transfer reaction in the propene molecule makes it possible to describe the process of the double bond migration by the following stages. In the initial stage of the reaction, hydroxide ion attacks the H atom of the propene methyl group to form a complex between OH^- and $MeCH=CH_2$. Both RHF and MP2 calculations in the 6-31+G* basis set predict that this complex has the structure **1** with C_s symmetry (Fig. 1), where the O atom of hydroxide ion is coordi-

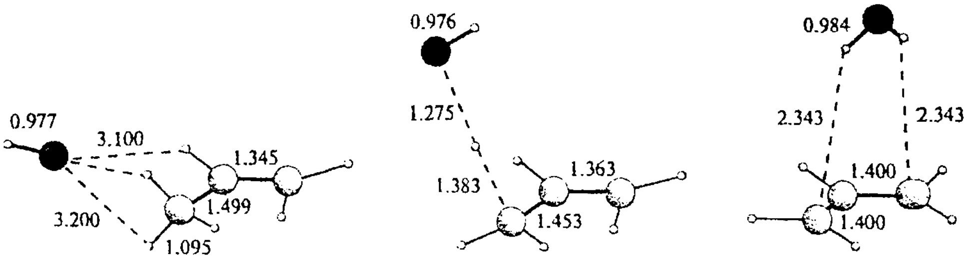

Fig. 1. Structures corresponding to stationary points on the PES of the reaction of propene isomerization. Internuclear distances (d/Å) calculated by the MP2/6-31+G* method are given.

nated by three H atoms, two of which are the methyl group hydrogen atoms and one H atom is bonded to the central C atom. The bond lengths, bond angles, and charge distribution in both propene and OH^- in complex **1** remain virtually unchanged. It should be noted that another structure of the complex formed upon attacking the $MeCH=CH_2$ molecule by the OH^- anion was obtained in the 4-31G* basis set; this structure is characterized by a higher binding energy (Table 2) and the location of the O atom on the extension of one of the methyl C—H bonds.

Further transformation of complex **1** occurs with cleavage of one of the C—H bonds of the methyl group and simultaneous formation of the H—O bond (transition state **2**, see Fig. 1). It is noteworthy that the structures of this state obtained from all three calculations performed at different levels are similar and the only difference is that, according to the calculations in the 4-31G* basis set, the abstracting proton of the methyl group is less shifted toward the hydroxide ion. According to the RHF/6-31+G* calculations, the energy of the transition state is 3.8 kcal mol^{-1} higher than those of the initial reagents (OH^- and $MeCH=CH_2$), whereas the inclusion of zero-point vibrational energy decreases it by 2.6 kcal mol^{-1}. At the same time, the inclusion of correlation effects leads to its substantial decrease (see Table 2) so that the transition state appears to be more stable than the initial reagents; the zero-point vibrational energy correction calculated in the RHF approximation is responsible for the further decrease in the relative energy of the saddle point.

Moving further along the reaction coordinate, the system arrives at a stable symmetric complex **3**, whose structure and charge distribution make it possible to characterize it as an adduct of the $[CH_2CHCH_2]^-$ anion with the H_2O molecule (structures with the same C_s symmetry were obtained in all three calculations performed at different levels of theory). In this complex, the geometric parameters of the isolated allyl anion remain virtually unchanged, whereas the O—H bond in the coordinated water molecule is somewhat lengthened (by ~0.01 Å). The negative charge is localized on the hydrocarbon fragment. Calculations in the 4-31G* basis set appreciably overestimate the energy of formation of this complex as compared to that obtained by the MP2/6-31+G* method, whereas calculations in the RHF/6-31+G* approximation underestimate this energy to a certain extent (see Table 2).

Table 2. Relative energies (ΔE/kcal mol^{-1}) and enthalpies (ΔH^{295}/kcal mol^{-1}) of the systems characterizing the profile of the $Me-CH=CH_2 + OH^- \rightarrow H_2C=CH-Me + OH^-$ reaction calculated by different quantum-chemical methods

System	4-31G*,	RHF/6-31+G*		MP2/6-31+G*	
	ΔE	ΔE	ΔH^{295}	ΔE	ΔH^{295}
$MeCH=CH_2$ + + OH^-	0	0	0	0	0
$[CH_2CHCH_2]^-$ + + H_2O	−4.0	+5.6	+3.4	+6.9	+4.7
1	−16.3	−9.6	−8.8	−13.3	−12.4
2	−12.8	+3.8	+1.2	−5.7	−8.3
3	−24.3	−8.9	−8.5	−12.0	−11.6

Further, the abstraction of a water molecule accompanied by an increase in the energy of the system is possible: according to the data of the MP2 method, for the reaction

$$Me{-}CH=CH_2 + OH^- \longrightarrow [CH_2CHCH_2]^- + H_2O$$

this value is 6.9 kcal mol^{-1}. Further, the $[CH_2CHCH_2]^-$ carbanion that formed is capable of eliminating the H^+ from proton-donor molecules in the reaction medium; in this case its addition to any terminal carbon atom is equiprobable. At the same time, migration of the multiple bond can also occur without abstracting the water molecule as a result of decomposition of the complex into propene and hydroxide ion (Fig. 2). In the symmetric system **3**, the proton can be equiprobably bonded to any terminal carbon atom.

It should be pointed out that the RHF/6-31+G* approximation underestimates the energy of complexation and overestimates the height of the activation barrier. The inclusion of correlation effects at the second-order level of perturbation theory substantially decreases the energy of transition state and affects the energy minima on the PES to a lesser extent (see Table 2). This is evidence for the impossibility of a correct description of the multiple bond migration without inclusion of electron correlation. Taking into account the zero-point vibrational energy decreases the barrier to the intramolecular rearrangement of complex **1** into complex **3** by 3.4 kcal mol^{-1}.

Appreciably affecting quantitative characteristics, the improvement in quality of calculations does not change

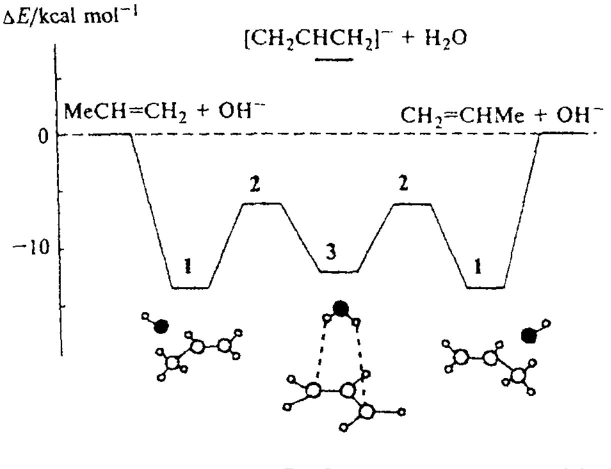

Fig. 2. Relative energies (ΔE) of the structures characterizing the profile of the reaction of propene isomerization (calculated by the MP2/6-31+G* method).

the main conclusion we have drawn previously:[1] migration of the double bond in the presence of hydroxide ion can occur through a complex of the three-carbon system with water molecule formed from the attacking hydroxide ion and one of the protons of the propene methyl group, *i.e.*, formally, without exchange between the migrating proton and the medium ("intramolecularly"). It is commonly accepted that the detection of deuterium in a prototropically isomerizing unsaturated compound when performing base-catalytic isomerization in a deuterated medium can serve as experimental evidence for the intermolecular nature of the process (abstraction of the proton and capture of the deuterium cation of the medium by the carbanion formed). Our results indicate that the enrichment of propene with deuterium in the case of its isomerization in a deuterated medium will also occur in the case of the described "intramolecular" mechanism owing to the hydroxide ion in which the hydrogen atom will be replaced by deuterium in a deuterium-mobile medium.

Table 3. Relative energies (ΔE/kcal mol^{-1}) and enthalpies (ΔH^{295}/kcal mol^{-1}) of the systems characterizing the profile of the $Me-C\equiv CH + OH^- \rightarrow H_2C=C=CH_2 + OH^-$ reaction calculated by different quantum-chemical methods

System	4-31G*	RHF/6-31+G*		MP2/6-31+G*	
	ΔE	ΔE	ΔH^{295}	ΔE	ΔH^{295}
$Me-C\equiv CH$ + OH^-	0	0	0	0	0
$[H_2C=C=CH]^-$ + H_2O	−15.0	−2.7	−4.5	+2.4	+0.6
$H_2C=C=CH_2$ + OH^-	+2.3	+1.8	+1.4	+4.0	+3.6
4	−20.2	−11.0	−10.3	−13.4	−12.7
5	−18.9	−2.6	−5.1	−8.9	−11.4
6	−35.6	−18.2	−17.6	−15.9	−15.3
7	—	−5.6	−8.1	−9.1	−11.6
8	—	−10.0	−9.7	−10.2	−9.9

Migration of the triple bond

By analogy with 1,3-hydrogen shift in propene, we studied the process of the multiple bond migration in the propyne molecule under the action of OH^- (Table 3). It is obvious that in the unsubstituted $MeC\equiv CH$ molecule, the "acidic" proton at the sp-hybridized C atom rather than the methyl group proton should be attacked preferably by a base. In fact, according to MP2 calculations, the energy of the $[MeC\equiv C]^-$ anion is 6.3 kcal mol^{-1} lower than that of the $[CH_2CCH]^-$ anion. In this case the migration of the triple bond can be associated, in particular, with intramolecular rearrangement of the anion that formed; however, a special investigation of this process is required. Here, we will consider a propyne molecule as the simplest model of a three-carbon system with a triple bond assuming that the base abstracts a proton from the sp^3-hybridized C atom with further reprotonation of the carbanion.

As in the case of propene, the attack of the OH^- ion on the H atom of the methyl group results in the formation of complex **4** (with C_s symmetry) between propyne and the hydroxide ion (Fig. 3). Unlike complex

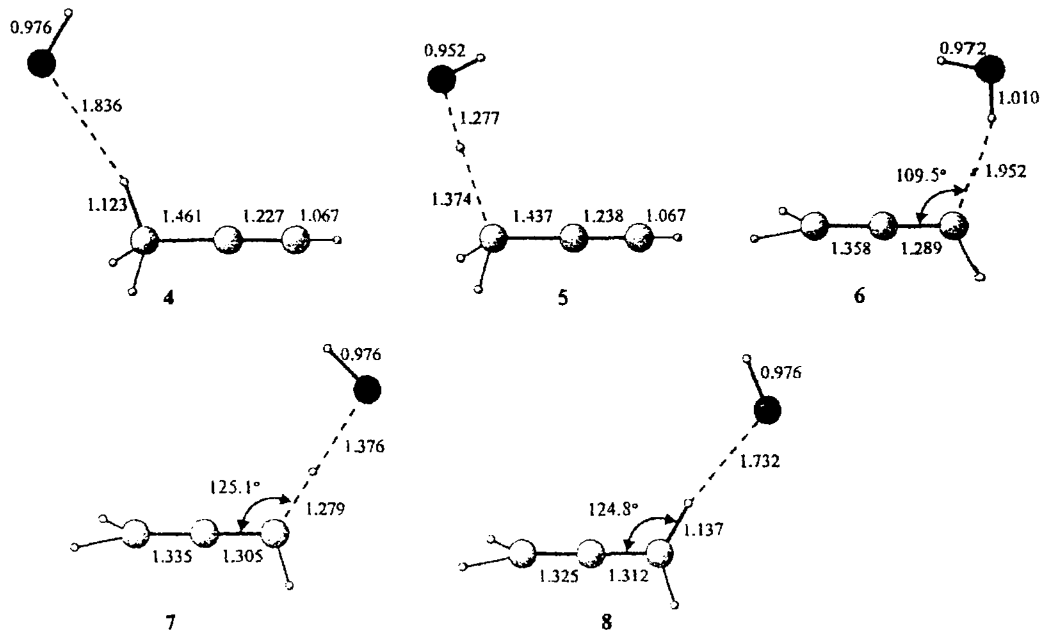

Fig. 3. Structures corresponding to stationary points on the PES of the reaction of propyne isomerization. Internuclear distances (*d*/Å) calculated by the MP2/6-31+G* method are given.

1, in the structure **4** the attacking hydroxide ion is coordinated by only one hydrogen atom. As a result, a stronger interaction of the attacked proton with hydroxide ion is observed, which manifests itself in appreciable shortening of the H···O distance and lengthening of the C—H bond by 0.030 Å. This complex is transformed into the even more stable complex **6** between the $[CH_2CCH]^-$ anion and water molecule *via* the transition state **5**.

According to calculations in the 4-31G* basis set,[1] the H_2O molecule can be coordinated to one of the terminal carbon atoms with a low barrier to migration from the C(1) atom to the C(3) atom. It has been pointed out[1] that in the case of an isolated $[CH_2CCH]^-$ anion only the allene type structure $CH_2=C=CH^-$ corresponds to the true minimum on the PES, whereas there is no stationary point of any sort corresponding to a complex with a water molecule coordinated to the C(1) atom. In the framework of the RHF/6-31+G* and MP2/6-31+G* methods, by descending along the reaction coordinate from transition state **5** one can arrive only at complex **6** (coordination to the C(3) atom). If in the case of the double bond migration the passage from a complex with hydroxide ion to an adduct with water molecule is accompanied by an increase in the energy of the system, the deepest minimum on the PES corresponds to complex **6**. The binding energy of this complex calculated by the RHF/6-31+G* method is ~18 kcal mol^{-1} and that obtained with inclusion of correlation effects is somewhat lower (see Table 3).

The geometric parameters of the fragments of structure **6** calculated by MP2/6-31+G* method are close to those of isolated $[CH_2CCH]^-$ anion and H_2O molecule. Thus, the equilibrium C(1)—C(2) and C(2)—C(3) distances in complex **6** (see Fig. 3) differ slightly from the corresponding values in isolated $[CH_2CCH]^-$ anion (1.367 and 1.281 Å, respectively). In the coordinated water molecule, one of the O—H bonds is somewhat lengthened, whereas the other O—H bond remains unchanged. The H—O—H bond angle decreases from 105.5° to 101.5° upon complex formation. The negative charge is completely localized on the three-carbon fragment.

Further transformations of complex **6** can occur following two different routes: by decomposition into the $[CH_2CCH]^-$ anion and H_2O molecule or due to elimination of hydroxide anion to form an allene molecule. The first route requires no overcoming of activation barriers. According to the RHF calculations, the process is exothermic and the products of this decomposition are more stable than initial propyne and hydroxide ion, whereas MP2 calculations characterize the process as endothermic one.

The second route, resulting in the formation of allene from the initial propyne, is associated with an energy increase (see Table 3). Decomposition of complex **6** into the allene molecule and OH^- ion requires a larger expenditure of energy than its decomposition into the $[CH_2CCH]^-$ anion and H_2O molecule; however, the MP2 method predicts a rather small (~1.5 kcal mol^{-1}) energy difference for these transformation channels. At the same time, the stage of the allene formation seems to be necessary for the triple bond migration to occur so this route of decomposition of complex **6** should be considered in more detail.

The transition state **7** is generated in the case of the cleavage of the O—H bond and simultaneous formation of the C—H bond; in this state the migrating H atom lies on the straight line connecting the C and O atoms and its shift along this line is the only significant component of the transition vector. By descending further along the reaction coordinate one can arrive at complex **8** in which the hydroxide ion is coordinated to one of the allene hydrogen atoms. Such a coordination somewhat degrades the equivalency of the C=C bonds (the length of this bond in the isolated allene molecule calculated in the MP2/6-31+G* approximation is 1.316 Å). A charge of 0.07 *e* is transferred from the coordinated OH^- ion to the allene fragment.

The estimates of the stability of this complex obtained from calculations at different levels of theory are different. The difference of the total energies of complexes **8** and **7** obtained in the RHF/6-31+G* approximation is 4.4 kcal mol^{-1}; however the inclusion of zero-point vibrational energy decreases it to 1.6 kcal mol^{-1}. In the framework of the MP2 method the activation barrier to transformation of complex **8** into complex **6** is merely 1.1 kcal mol^{-1}, whereas the zero-point vibrational energy corrections found in the RHF/6-31+G* approximation indicate that this barrier is not higher than the energy of its first vibrational level. It is quite probable that no formation of complex **8** occurs in the course of the reaction. The system retains its C_s symmetry when moving along the reaction coordinate all the way from complex **4** to complex **8**.

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The above results make it possible to compare different mechanisms of the migration of the double and triple bond. Further, we will use the energy estimates obtained in the framework of the MP2/6-31+G* method.

In accordance with the traditional two-stage mechanism, the C—C=C → C=C—C rearrangement of the propene system in the presence of hydroxide ion is associated with an increase in the energy of the system relative to the energies of the initial reagents upon the formation of H_2O molecule and $[CH_2CHCH_2]^-$ anion. This increase was estimated by the MP2/6-31+G* method at 6.9 kcal mol^{-1} (see Table 2 and Fig. 2). Since the simultaneous presence of propene and OH^- in the reaction medium should result in the formation of complex **1**, the "internal" barrier to the two-stage double bond migration is 20.2 kcal mol^{-1}.

The considered mechanism of the two-proton double bond migration in the propene molecule is related to the appreciably lower internal barriers (7.6 kcal mol^{-1} and

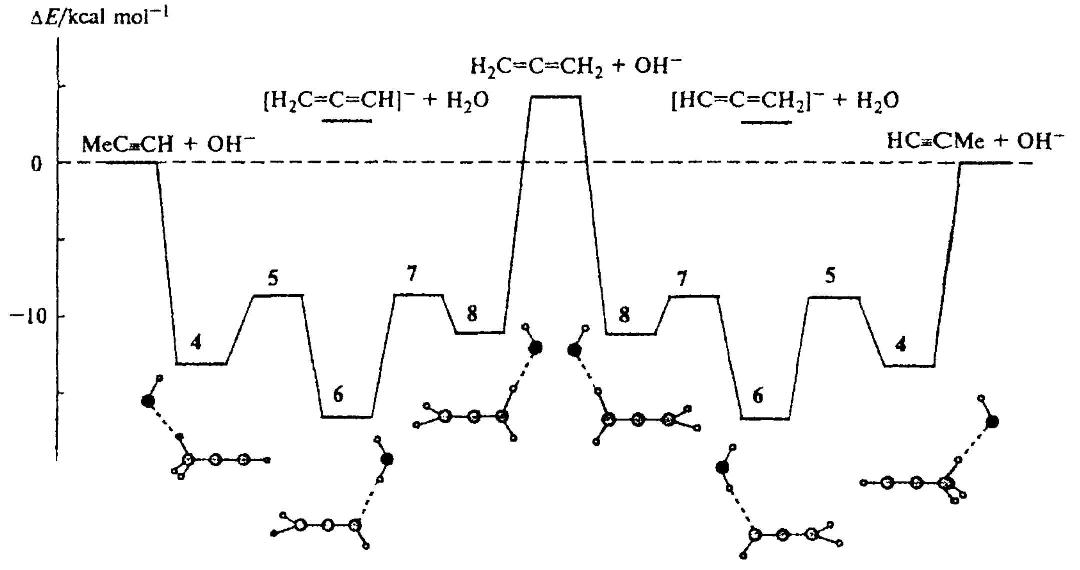

Fig. 4. Relative energies (Δ*E*) of the structures characterizing the profile of the reaction of propyne isomerization (calculated by the MP2/6-31+G* method).

6.3 kcal mol^{-1}); in this case the transition state **2** is 5.7 kcal mol^{-1} more stable than the initial one (MeCHCH$_2$ and OH$^-$). Thus, this mechanism appears to be quite realistic and energetically more preferable.

In the propyne system, the transformation Me—C≡CH → HC≡C—Me involves the stage of formation of the allene structure CH$_2$=C=CH$_2$, which is accompanied by an energy increase of 4.0 kcal mol^{-1}. This is more than sufficient for the proton abstraction to occur and to form the [CH$_2$CCH]$^-$ anion and H$_2$O molecule (2.4 kcal mol^{-1}) in the case of a two-stage mechanism and is much more larger than the energies of transition states in the case of intramolecular migration (Fig. 4). This circumstance does not allow one to judge the preference of one or another mechanism of triple bond migration in an unsubstituted propyne (though the presence of substituents stabilizing the allene structure can significantly affect these estimates). Taking into account the possible instability of complex **8** between the formed allene molecule and hydroxide ion, one can assume that the proton attached to the protophilic species can even hinder the migration of the triple bond due to preferable formation of a stable complex of the type **6**. At the same time, considering isomerization of the allene structure into acetylene, one can conclude that the proposed single-stage mechanism is more probable in this case.

The energy profiles investigated suggest that the presence of a proton-containing protophilic species in the reaction medium favors the migration of the double bond to a greater extent than that of the triple bond. Moreover, the proton at a protophilic reagent, facilitating the double bond migration in the propene molecule, hinders the triple bond migration in the propyne molecule.

Only two-stage mechanism can be realized for a protophilic species containing no proton capable of participating in a concerted transfer (*e.g.*, for alkoxide ion). The values of the energy characteristics of this mechanism of the processes of double and triple bond migration with participation of hydroxide ion are close, though deprotonation of propyne occurs more easily. This is in agreement with the traditional concepts of the relative mobility of the protons adjacent to double and triple bonds and of the stability of corresponding carbanions.

The investigation performed takes no account of a number of the factors capable of affecting the isomerization process, *viz.*, differences in the acidity of hydroxides and alkoxides, solvation effects, the nature of the cation (though the isomerization rates in the series LiOH, NaOH, and KOH differ appreciably). At the same time, the results obtained indicate the possibility of a nontraditional mechanism of the prototropic rearrangement in the alkene and alkyne molecules; in this case the participation of a base proton can differently affect the migration of the double and triple bond.

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