Physical Chemistry

Multiple bond migration with participation of a protophilic agent

1. An *ab initio* quantum-chemical study of 1,3-hydrogen shift in propene and propyne 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/4-31G) method. Stationary points corresponding to stable complexes between the molecules under study and the hydroxide ion and between the corresponding carbanions and water were found on the potential energy surfaces of the proton transfer reactions. There are no transition states with energies exceeding the energies of the initial reagents or those of the end products on the reaction coordinate. Therefore, the expenditure of energy to overcome the barriers is completely compensated by the energy gain due to the formation of intermediate complexes. The direction of multiple bond migration by this mechanism is almost completely determined by the ratio of the energies of the initial reagents and the end products. Account of the electron correlation and the extension of the basis set do not lead to radical changes in the results.

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

Reactions involving migration of a multiple bond and base-catalyzed isomeric transformations with intermediate formation of carbanions are known to be characteristic of unsaturated compounds, in particular, alkenes, alkynes, and their derivatives containing a heteroatom in addition to the multiple bond.[1–6] In this case the multiple bond usually migrates toward the heteroatom,[5,6] which is explained by a decrease in the energy due to conjugation between the lone electron pair of the heteroatom and the π-system. It is assumed that these processes can play an important role in synthesizing substituted pyrroles,[7–8] pyridines,[9–11] nitrons,[12] and *N*-vinylacrylamides[13] from *O*-vinyl, *O*-(2-propenyl)-, and *O*-(2-propynyl)ketoximes, which are of considerable current use.

A peculiarity of reactions of this type is that they proceed in superbase media (solutions of hydroxides or alkoxides of alkali metals in DMSO), which are charac-

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terized by an increased activity of the base anion. Therefore, the quantum-chemical study of mechanisms of isomerizations and rearrangements in various unsaturated structural elements of organic and organoelement molecules in the presence of an anion is of fundamental importance not only for theoretical chemistry but also for organic synthesis.

Migration of the multiple bond in the propene molecule

Migration of the multiple bond in an isolated molecule of propene *via* a 1,3-hydrogen shift has been studied in considerable detail using different quantum-chemical approaches. It has been shown in the framework of the simple method of molecular orbitals (MO) that the suprasurface migration of the H atom is symmetry-forbidden, while the antarasurface transfer is symmetry-permitted.[14] At the same time, more accurate calculations[15] indicate that the energy barriers for both reaction pathways are comparable and exceed the energy of the C—H bond cleavage. Moreover, reaction mechanisms based on proton abstraction by a protophilic species of the reaction medium have long been discussed;[1,2,16] however, no quantum-chemical description of such a type of process performed for estimating its energy characteristics (as compared to those of multiple bond migration in the isolated molecule) has been reported to date.

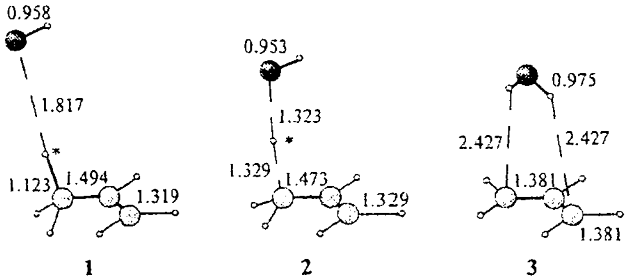
The propene molecule is by far the simplest system, for which the role of an external species in the transfer of the H atom must be considered. An analysis of the double bond migration involving a nucleophilic species makes it possible to estimate the possibility for this process to occur in the system in question and provides the basis for further studying multiple bond migration in the acetylene derivatives and the influence of substituents containing heteroatoms on the direction of the reaction.

We calculated several profiles of the potential energy surface (PES) of reaction

$$C(1)H_3{-}C(2)H{=}C(3)H_2 + OH^- \longrightarrow C(1)H_2{=}C(2)H{-}C(3)H_3 + OH^- \qquad (1)$$

in the framework of the Hartree—Fock method in the valence-split 4-31G* basis set using the GAMESS program[17] with full optimization of all structural parameters. The hydroxide ion, which has an increased concentration and activity in base and superbase media of the MOH/DMSO (M = Li, Na, and K) type, was chosen as protophilic species. It should be noted that since the thermal effect of the reaction is equal to zero, the possibility for the multiple bond to migrate is completely defined by the presence and height of the energy barriers controlling the process in question.

In the first stage of this reaction, the OH^- ion attacks the Me group of the propene molecule to form stable complex **1** (Fig. 1). The structural parameters of the interacting subsystems (OH^- and $MeCH{=}CH_2$) in this complex remain nearly unchanged, the negative charge is concentrated on the OH^- group (Table 1), while the positive charge of the attacked H atom substantially increases. Cleavage of the C—H* bond and formation of the H*—O bond occur simultaneously to give even more stable complex **3**, which can be characterized as an adduct of the $[CH_2CHCH_2]^-$ anion and H_2O molecule (see Fig. 1). The negative charge in this complex is concentrated on the C(1) and C(3) atoms, while the water molecule is nearly electroneutral.



1 **2** **3**

Fig. 1. Structures corresponding to the stationary points on the PES of reaction (1) (internuclear distances are given in Å).

Table 1. The Mulliken atomic charges (*q*) calculated in the 4-31G* basis set

Compound, ion	C(1)	C(2)	C(3)	H*	O	H
	q/au					
Propene	−0.49	−0.14	−0.39	0.17		
1	−0.56	−0.09	−0.42	0.34	−1.09	0.24
2	−0.61	−0.04	−0.46	0.42	−1.04	0.29
3	−0.60	−0.01	−0.60	0.43	−0.96	0.43
OH^-					−1.19	0.19
H_2O				0.43	−0.86	0.43
Propyne	−0.51	0.10	−0.42	0.20		
4	−0.59	0.14	−0.52	0.36	−0.95	0.25
5	−0.65	0.17	−0.56	0.42	−1.04	0.29
6	−0.65	0.15	−0.63	0.44	−0.95	0.37
7	−0.65	0.13	−0.62	0.44	−0.95	0.40
8	−0.60	0.05	−0.55	0.44	−0.95	0.38
Allene	−0.48	0.17	−0.48	0.20		

There is a stationary point corresponding to transition state **2** between the two minima on the PES. An analysis of the spatial and electronic structures of transition state **2** indicates that its OH^- group is mainly associated with the hydroxide ion, since it has the negative charge (−0.75 au), and the O—H bond length is shortened to 0.953 Å, analogously to complex **1**. In the fragment corresponding to the propene molecule, all geometric parameters are little changed, except for the

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* Hereafter the migrating hydrogen atom is indicated by an asterisk.

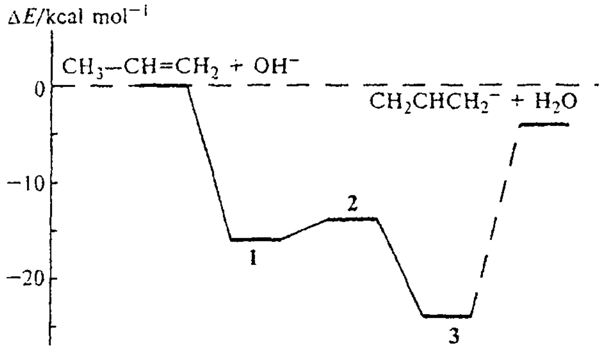

Fig. 2. Relative energies of the structures (ΔE) characterizing the profile of reaction (1).

C(1)—H* distance. The C(2)—C(1)—H* bond angle is close to the tetrahedral angle, and the H* atom is located at the midpoint of the straight line connecting the C(1) and O atoms and has a positive charge of 0.42 au.

The energy gain for the formation of complex **1** with respect to the initial reagents is 16.3 kcal mol^{-1}. Its transformation into a more stable form **3** is associated with overcoming a barrier of 3.5 kcal mol^{-1} and a further decrease in the energy by 8.0 kcal mol^{-1} relative to structure **1** (Fig. 2).

Thus, the hydroxide ion attacks the propene molecule to form a stable (24.3 kcal mol^{-1}) symmetric complex between the $[CH_2CHCH_2]^-$ carbanion and H_2O. Then, the water molecule can be eliminated with increasing energy of the system by 20.3 kcal mol^{-1}, and the resultant thermal effect of the reaction

$$\mathrm{Me{-}CH{=}CH_2 + OH^- \longrightarrow [CH_2CHCH_2]^- + H_2O} \qquad (2)$$

is equal to 4.0 kcal mol^{-1}. In further stages, the carbanion is capable of abstraction of the H^+ ion from the molecules of the proton donors present in the reaction medium; its attachment to any of the terminal carbon atoms occurs with equal probability.

At the same time, in order for the multiple bond migration to occur, it is not necessary for the water molecule to pass into the medium, since the transformation of symmetric complex **3** into form **1** is associated with overcoming a barrier of 11.5 kcal mol^{-1}; in this case any of the H atoms of the water molecule is capable of binding to the nearest C atom. Further elimination of the OH^- group from complex **1** requires an energy expenditure of 16.3 kcal mol^{-1}. These barriers are lower than the energy required for the water molecule to pass into the medium, especially as the coordination of water by the carbanion again results in the formation of structure **3** (see Fig. 2).

The results obtained indicate that in the gas phase the acidity of propene is higher than that of water. The ratio of acidities in solutions is substantially different: the pK_a of water is 15.7 while those of hydrocarbons lie in the 30 to 40 range.[18] At the same time, propene is a stronger acid than water in the gas phase.[19]

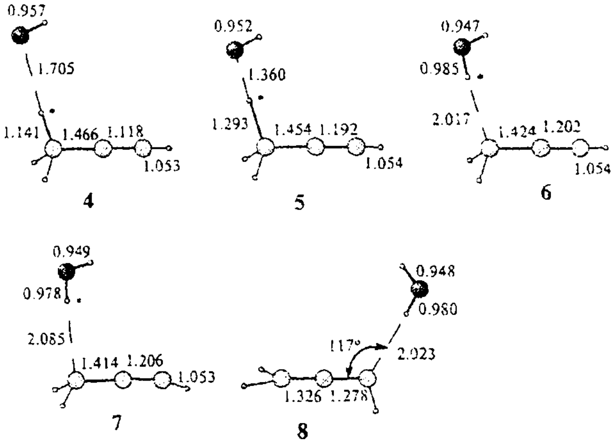

Fig. 3. Structures corresponding to the stationary points on the PES of reaction (3) (internuclear distances are given in Å).

The multiple bond migration by the described mechanism involving the H atom of the hydroxide ion is characterized by lower energy barriers than the usually considered migration followed by passage of the water molecule into the medium.[2,16] It seems likely that this mechanism is the most probable for the gas phase or nonpolar solvents incapable of active solvation of the water molecule. There are no transition states with energies exceeding the energies of the initial reagents or those of the end products on the coordinate of reaction (1) (see Fig. 2), and expenditure of energy to overcome the barriers is completely compensated by the energy gain at the expense of the complex formation.

Migration of triple bond in the propyne molecule

Migrations of the triple bond in alkynes in the presence of bases are well known. They proceed *via* the intermediate formation of allenes, which in some instances appear to be the only products of isomerization.[5,6] We considered the multiple bond migration in the propyne molecule by the action of the OH^- base by analogy with the 1,3-hydrogen shift in propene:

$$\mathrm{C(1)H_3{-}C(2){\equiv}C(3)H + OH^- \longrightarrow}$$
$$\mathrm{\longrightarrow C(1)H_2{=}C(2){=}C(3)H_2 + OH^-.} \qquad (3)$$

In the initial stage of the reaction, the OH^- ion attacks the H atom of the methyl group to form complex **4**, in which the anionic species is coordinated to the attacked H* atom (Fig. 3), as in the case of propene. The stronger negative inductive effect of the ethynyl group as compared to that of the vinyl group causes a larger degree of the electron density transfer from the OH^- ion (see Table 1), which results in shortening the O—H* distance and increasing the stability of complex **4**

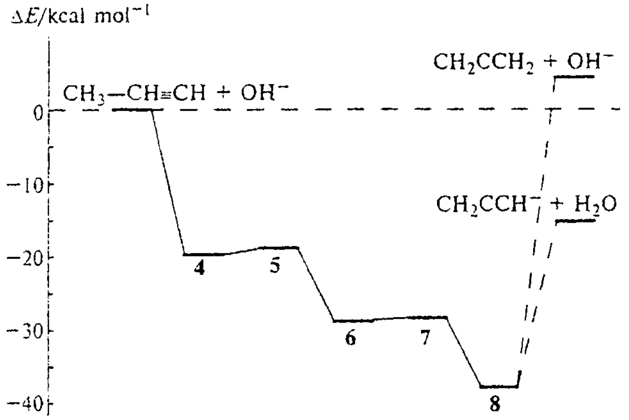

Fig. 4. Relative energies of the structures (ΔE) characterizing the profile of reaction (3).

(with an energy gain of 20.2 kcal mol^{-1}) as compared to those of its analog **1** (Fig. 4). As a whole, complex **4** can be characterized as an associate of the propyne molecule and the hydroxide ion.

Abstraction of the attacked proton from structure **4** is associated with overcoming a low energy barrier of 1.4 kcal mol^{-1}. An analysis of the geometry of transition state **5** shows that it is similar to complex **4** and is brought about by lesser changes in the C—H* and O—H* distances than those in transition state **2** in the reaction with the propene molecule. The OH^- groups in transient structures **5** and **2** retain their negative charges to a large extent (−0.75 au).

Further migration of the H* atom toward the hydroxide anion results in complex **6** between the $^-CH_2—C≡CH$ anion and the water molecule. Its energy is 29.6 kcal mol^{-1} lower than those of the initial reagents. The C(1)—C(2)—C(3)—H fragment holds its linearity in this complex, while the bond lengths in the above fragment are close to the internuclear distances in the isolated propyne molecule. The water molecule in structure **6** is coordinated to the C(1) atom and has a small negative charge (−0.14 au). The remainder of the negative charge is distributed between the C(1) and C(3) atoms of the carbanion (see Table 1).

An even more low-lying minimum on the PES corresponds to complex **8**, in which the H_2O molecule had changed its position and is now coordinated to the C(3) atom of the carbanion having a hydrocarbon fragment structure different from that in complex **6** (see Fig. 3). The water molecule is only capable of coordinating to one of the terminal carbon atoms without formation of a symmetric complex analogous to compound **3**, similarly to reaction (1). In complex **6**, the H_2O molecule stabilizes the carbanion, which is formed by the abstraction of a proton from the Me group of propyne and retains the structure of the propyne molecule. The calculation performed in the single-determinant approximation predicts a very low barrier of 0.2 kcal mol^{-1} for the **6** → **8** rearrangement *via* transition state **7**. It should be noted that in the case of the isolated $[CH_2CCH]^-$ anion only the allene structure ($CH_2=C=CH^-$) corresponds to the true minimum on the PES, whereas the structure of complex **6** does not correspond to the stationary point at all.

In complex **8**, the H_2O molecule retains a small negative charge (−0.13 au) and is coordinated to the C(3) atom, while the structure of the hydrocarbon fragment is identical to that of the isolated $CH_2=C=CH^-$ anion. As in molecule **6**, the negative charge in molecule **8** is distributed between the C(1) and C(3) atoms. Complex **8** is 6.0 kcal mol^{-1} more stable than **6** and 35.6 kcal mol^{-1} more stable than the initial reagents, MeC≡CH and OH^-. The decomposition of compound **8** into the allene molecule and the OH^- anion requires 37.9 kcal mol^{-1}, while that into the $CH_2=C=CH^-$ anion and H_2O requires only 20.6 kcal mol^{-1}. It is of interest to note that the PES of addition of OH^- to allene as well as that of elimination of H_2O from complex **8** contain no stationary points corresponding to the binding of $CH_2=C=CH_2$ with the hydroxide ion.

As a whole, reaction (3) is endothermic (2.3 kcal mol^{-1}). The energy profile obtained (see Fig. 4) can also be considered for the reverse reaction. The hydroxide anion attacks the allene molecule with a barrierless abstraction of the proton to form complex **8** with the release of 37.9 kcal mol^{-1}. This energy is quite sufficient to form propyne *via* structures **6** and **4**. It is just the direction of the reaction that is observed experimentally.[16]

The discussed mechanism of migration of the multiple bonds in the three-carbon fragment shows that the energies of all intermediate complexes and transition states are substantially lower than those of the initial reagents and the end products. Therefore, the differences in the energies of the initial reagents and the end reaction products should play a determining role, though introduction of the substituents can also affect the direction of migration.

Evaluation of the role of the electron correlation and basis set

Proton migrations according to the mechanisms discussed above occur in the presence of negatively charged species. It is well known that a correct calculation of the latter is a methodically complicated problem because of their electron saturation and usually requires considering the effects of the electron correlation and introducing additional diffuse functions into the basis set. To test the quality of the results obtained in the Hartree—Fock approximation using the 4-31G* basis set, several neutral (H_2O, MeCCH, and CH_2CCH_2) and negatively charged (OH^- and CH_2CCH^-) structures playing a key role in the transformations discussed above were calculated at a more precise theoretical level.

Table 2. The bond lengths (*d*) obtained by the RHF/4-31G* (HF) and CCSD/aug-cc-pvDZ (CCSD) methods

Compound, ion	Bond	*d*/Å		
		HF	CCSD	Experiment
H_2O	O—H	0.965	0.964	0.957[22]
OH^-	O—H	0.948	0.971	0.971±0.005[23]
$H_3C—C≡CH$	C—C	1.466	1.480	
	C≡C	1.184	1.225	1.202±0.005[18]
$H_2C=C=CH_2$	C=C	1.292	1.327	1.310±0.005[18]
$H_2C(1)=C(2)=C(3)H^-$	C(1)=C(2)	1.326	1.370	
	C(2)=C(3)	1.278	1.304	

The correlation-consistent polarized-valence two-exponential aug-cc-pvDZ basis set[20] with diffuse functions ([4s3p2d] on the atoms of elements of the second period and [3s2p] on the H atoms) and a variant of the method of coupled clusters with single and double excitations (CCSD) incorporated into the GAUSSIAN-94 program were used.[21] Full optimization of geometric parameters was performed for all structures. The labor consumption of the calculations performed is well illustrated by the example of the propyne molecule, for which optimization in the approximation described above took 43 h 20 min of CPU time on an IBM-RS/6000 M.580 (Power 2) workstation.

A comparison of the results shows that the internuclear distances obtained from calculations in the RHF/4-31G* approximation are shorter while those obtained from calculations using the variant of the CCSD/aug-cc-pvDZ method are somewhat longer than experimental values (Table 2). The calculated energies of proton abstraction are much more different. From the aforesaid, the largest error could be expected for the hydroxide ion, since in this case the inadequacy of the basis set and neglect of the electron correlation hamper effective delocalization of the negative charge. In fact, taking into account these factors decreases the energy of the proton abstraction from the water molecule; however, the energy of the proton elimination from propyne to form an allene anion decreases to the same extent (Table 3).

Thus, the test performed has demonstrated conclusively that the relative energies of the initial reagents and the end products are well reproduced at the qualitative level in the framework of the theoretical model used in this work (RHF/4-31G*). Additionally, it might be expected that the relative energies of the intermediate complexes on the potential energy surfaces of reactions (1) and (3) are reliably reproduced, and the mechanism of migration of the multiple bonds in the propene and propyne molecules suggested on the basis of the SCF calculations in the 4-31G* basis set is entirely correct.

Table 3. Total energies (*E*) obtained by different methods with full optimization of geometric parameters

Compound, ion	*E*/au	
	RHF/4-31G*	CCSD/aug-cc-pvDZ
H_2O	−75.93900	−76.26863
OH^-	−75.24895	−75.63583
$CH_3—C≡CH$	−115.74810	−116.31660
$CH_2=C=CH_2$	−115.74440	−116.31610
$CH_2=C=CH^-$	−115.08192	−115.69103

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