QUANTUM-CHEMICAL STUDY OF REARRANGEMENT OF VINYL ALCOHOL INTO ACETALDEHYDE. INTRAMOLECULAR SIGMATROPIC [1,3] SHIFT OF HYDROGEN

Maria ŽÁKOVÁ and Jaroslav LEŠKA
Department of Organic Chemistry,
Comenius University, 816 31 Bratislava

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The rearrangement mechanism of vinyl alcohol into acetaldehyde in the isolated molecule has been studied with respect to two possible different ways: the rearrangement in the plane of the molecule and in the plane perpendicular to the molecule. According to the Woodward–Hoffmann rules the former way is considered to be an allowed antarafacial [1, 3] shift, and the latter way is a forbidden suprafacial shift. The reaction pathways have been studied by the method of reaction coordinate at the level of the semiempirical CNDO/2 and MINDO/3 methods by the technique of complete optimization. The reaction coordinates used for the study of reaction pathways in the plane of the molecule were the lengths of the bond being split between oxygen and hydrogen and that being formed between carbon and hydrogen and the angle formed by the three mentioned atoms (∢ OHC). The reaction coordinates used for the perpendicular plane were the bond length between hydrogen and carbon (being formed) and those describing the way above the bonds. All the reaction pathways have to cross barriers, which means that the suprafacial shift is forbidden, and the antarafacial shift is geometrically difficult. Surprisingly the barrier of the suprafacial shift is lower than that of the antarafacial one, which has been explained by interaction of the migrating hydrogen atoms with bonds. This explanation is supported by the bond distance between the migrating hydrogen and central carbon atom in the transition state as well as by formation of hydrogen bond between oxygen, migrating hydrogen and double bond, which is indicated by the charge transfer connected with a considerable dipole moment. Existence of the relatively high barriers indicates that a spontaneous hydrogen shift in vinyl alcohol is impossible.

Proton shifts in organic molecules represent frequently a step in mechanisms of organic reactions. Often the proton [1, 3] shift takes place in tautomeric processes out of which keto-enol rearrangement represents a classical example. It is a well-known fact that rearrangement of vinyl alcohol into acetaldehyde takes place spontaneously during preparation of acetaldehyde from acetylene, so that it is impossible to isolate vinyl alcohol. In spite of importance of this reaction, the rearrangement mechanism is not fully understood yet. According to the Woodward–Hoffmann rules[1] this rearrangement can hardly be intramolecular, because the suprafacial rearrangement is symmetry-forbidden, and the allowed antarafacial rearrangement is impossible due to geometry. Therefore it seems likely that the reaction medium and the intermolecular interactions taking place therein play a decisive role in this process. It is suprising that so far only few communications have dealt with this problem. Besides calculation of the isomerization energies[2], the transition states were investigated which are formed in two different ways of the intramolecular rearrangement induced by vibration motions either in or perpendicular to the plane of vinyl alcohol molecule. Bouma and Radom[3,4] carried out *ab initio* calculations of these transition states. Recently Klopman published[5] calculation results of the reaction pathway of the rearrangement of acetaldehyde into vinyl alcohol by an intramolecular mechanism assisted by water and catalyzed by acid and base. This communication[5] appeared when our investigations were in advanced state. However, our study is dealing with the mentioned rearrangement in the both directions and much more fully.

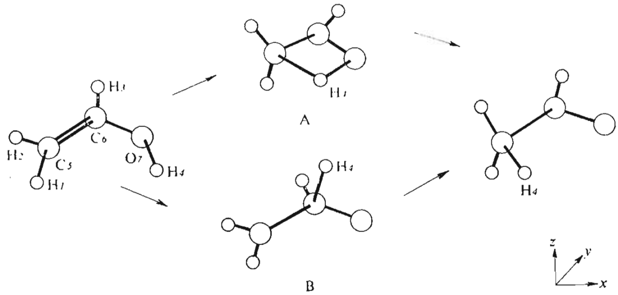
As plane conformation of vinyl alcohol has low symmetry, the hydrogen shift is not absolutely impossible in the isolated molecule, but it can be accomplished thermally over a barrier. Klopman[5] showed that this process in opposite direction proceeds over a barrier whose height indicates that a spontaneous hydrogen shift in acetaldehyde is impossible. In spite of that it seemed useful to investigate more fully also the rearrangements of the isolated molecules in the both directions. Recently, existence of molecules similar to vinyl alcohol (*e.g.* $CH_2{=}CHCN$) was proved in interstellar space, and according to Saito[6] vinyl alcohol could be present there, too. Therefore, not only for theoretical reasons, but also from the point of view of astrochemistry it could be interesting to study the intramolecular hydrogen shifts in isolated molecules even in their ground states.

CALCULATIONS

The calculations were carried out by the semiempirical CNDO/2 and MINDO/3 methods; only in some cases (for comparison) the reaction pathways were calculated simultaneously by the both methods. The calculation of the reaction pathways was preceded by optimization of molecular geometries of vinyl alcohol and acetaldehyde. Within accuracy limits of the semi-empirical methods used, the equilibrium geometries of the two molecules are identical with those given by Klopman[5], and, therefore, we do not give them here. The ground states of the both molecules (vinyl alcohol and acetaldehyde) are most stable in *cis* conformations, *i.e.* with zero torsion angles C=C—O—H and H—C—C=O, respectively. The energy differences between the mentioned conformations of vinyl alcohol and acetaldehyde obtained by the both methods are close to those given by Klopman[5], too.

For the calculations of reaction pathways we chose the simple but frequently used method of reaction coordinate[7-12] which is decidedly dependent on selection of the geometry parameters of the respective reaction coordinate which are changed in a defined manner during the reaction. A given value of the reaction coordinate will find a point on the reaction pathway by minimizing the total energy with respect to all other parameters. The highest point on the reaction pathway is close to the real transition state. For the optimization of geometry we used the variable metric optimization procedure at the level of the semi-empirical CNDO/2 and MINDO/3 methods[13,14].

The result of the calculation method depends on choice of the reaction coordinate. As the reaction course involves simultaneous splitting of O–H bond and formation of a new C–H bond, it would seem reasonable to choose for the reaction coordinate the bond being split or that being formed and the angle $H_4C_5C_6$ (Scheme 1) which is considerably different in the vinyl alcohol and acetaldehyde molecules. Furthermore,



SCHEME 1

it seemed logical to consider two substantially different pathways of hydrogen shift in vinyl alcohol, both of them being induced by vibration motions. The mentioned pathways are in the plane or perpendicular to the molecule. Structural changes along the reaction pathways are described below.

Hydrogen Shift in the Plane of the Molecule

Reaction coordinate R_{OH}. We used the CNDO/2 method. The reaction coordinate (*i.e.* the OH_4 bond) was lenghtened by small intervals 0·02 to 0·04 nm, and the energy was always minimized with respect to the other degrees of freedom. In the course of this process the O–H bond is gradually weakened and the distance C_5H_4 is shortened (Scheme 1). The whole dependence of energy on the reaction coordinate is given in Fig. 1.

It can be seen that, along the reaction pathway, the energy is increased up to a maximum corresponding to configuration of the transition state (TS). The found structure is planar (RC3), having C_{1h} symmetry, and is closer to the reactant than to the product (dipole moments of vinyl alcohol, acetaldehyde, and the transition state are $4{\cdot}87 \,.\, 10^{-30}$, $10{\cdot}78 \,.\, 10^{-30}$, and $4{\cdot}94 \,.\, 10^{-30}$ Cm, respectively, the distances $R_{OH} = 0{\cdot}158$ nm, $R_{CH} = 0{\cdot}226$ nm). The activation energy corresponding to this transition state is 291·6 kJ mol^{-1}. After reaching the maximum, the other geometry parameters are changed monotonously and relatively little, too. However, in the vicinity of the RC3 point even a small change of the reaction coordinate (0·01 nm) causes a great change in the other parameters; thus *e.g.* the C–C bond length is changed from 0·133 nm to 0·14 nm, the distance H_4-C_5 is changed from 0·226 nm to 0·123 nm. Furthermore the carbon atoms are rehybridized from sp^2 to sp^3 (the dihedral angle $OCCH_1$ is changed from 0·1° to 115·3°). The vinyl alcohol structure can be said to be dramatically collapsed at this point. The energy barrier is 291·6 kJ . . mol^{-1}.

Changes in electronic structure along the reaction pathway are characterized by continuous changes of charge densities $q(A)$ (Fig. 2). From the graph it can be seen that the charge values at the hydrogen atoms not directly involved in the reaction, *i.e.* $q(H_1)$, $q(H_2)$, $q(H_3)$, are not changed much. Steepness of the curves indicates that the charge transfer from oxygen to the migrating atom H_4 takes place at the beginning of the reaction, and near the point RC3 the atom H_4 is being bound to C_5 due to mild charge increase at the latter. Further reaction course is connected with the charge transfer from H_4 to C_5. Hence it is obvious that the migrating hydrogen atom carries a part of electron density with it, although it remains positively charged. This fact is due to its motion in the electronic system of the molecule. Changes of charges at all the atoms involved in the reaction correspond to energy changes along the reaction coordinate, and the region of abrupt change corresponds to that of energy barrier.

The considered mechanism exhibits chemical hysteresis. It means, that the reaction pathway is different, if the same reaction coordinate is used for the hydrogen rearrangement from acetaldehyde to vinyl alcohol (Fig. 1). Also in the case of the opposite

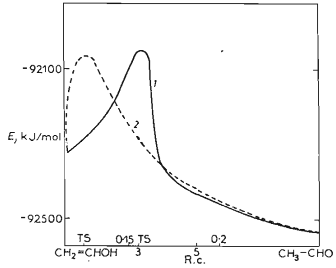


FIG. 1

Dependence of energy of the system on the reaction coordinate R_{OH}. (CNDO/2). Forward *1*, backward *2*

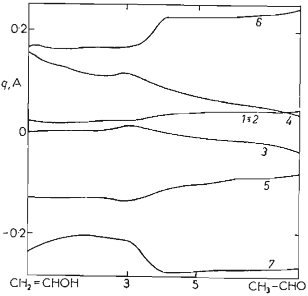


FIG. 2

Dependences of charge densities $q(A)$ on the reaction coordinate R_{OH}. (CNDO/2) The numbers at the right-hand side denote the atoms pathway the dramatic change of the geometry parameters and electronic structure of the molecule does not take place until after reaching the barrier, *i.e.* the dramatic collaps takes place afterwards. These results agree with those by Klopman[5]. Value of the energy barrier is 275·3 kJ mol^{-1} (351·5 kJ mol^{-1} according to Klopman[5] by the MINDO/3 method).

Reaction coordinate R_{CH}. For the sake of comparison we used side by side the CNDO/2 and MINDO/3 methods. The reaction coordinate (CH distance) was gradually shortened by 0·02 nm (by 0·01 nm in the vicinity of TS). The shortening of the CH distance results in overall deformation of the molecule; the C–C and O–H bonds are lengthened, the CCH_1 and CCH_2 angles are decreased. According to the CNDO/2 method the structure near TS is planar and more resembling the reactants ($R_{OH} = 0·127$ nm, $R_{CH} = 0·142$ nm, dipole moment $8·01 . 10^{-30}$ Cm), according to the MINDO/3 method the TS structure is nearer to products ($R_{CH} = 0·12$ nm, a partial rehybridization of carbon orbitals from sp^2 to sp^3 takes place, which is shown by the value of angle $OCCH_1 = 18·7°$), the distance between the migrating hydrogen and oxygen being still bonding ($R_{OH} = 0·110$ nm). The same follows also from the dependences of energy on the reaction coordinate (Fig. 3) which have similar shape, however, TS is closer to products according to MINDO/3. After crossing the TS all the geometry parameters are changed abruptly and approach the values

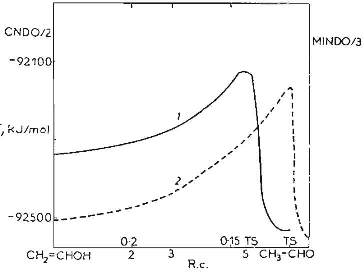


FIG. 3

Dependence of energy of the system on the reaction coordinate R_{CH}. CNDO/2 *1*, MINDO/3 2

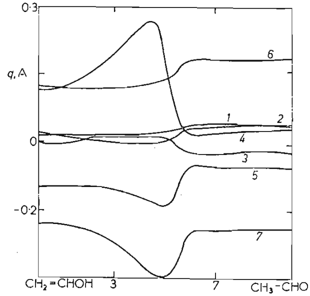


FIG. 4

Dependences of charge densities q(A) on the reaction coordinate R_{CH} (CNDO/2) of acetaldehyde. The activation energy of the rearrangement is 218·9 and 341·5 kJ . . mol^{-1} according to CNDO/2 and MINDO/3, respectively.

Dependence of charge density $q(A)$ on the reaction coordinate is given in Figs 4 and 5. The $q(H)$ values of hydrogen atoms not directly involved in the reaction are not very much changing here, too. Shape of the curves in the both diagrams indicates that a great charge transfer from H_4 to oxygen takes place until the transition state, and near the point RC5 the atom H_4 is being linked to C_5 on which the charge had increased. The dependence of $q(A)$ on the reaction coordinate agrees with the corresponding energy dependence, the region of abrupt charge change corresponding to energy barrier.

If this transition is compared with the previous case, it can be stated: *i*) the energy barrier is lower in this case by 72·7 kJ mol^{-1}, *ii*) in the both cases the structure of the molecule is relatively little changed up to reaching TS, and first then the dramatic collaps takes place during which the geometry parameters are changed abruptly, *iii*) in this case a greater charge re-distribution takes place near the TS, the charge at the migrating hydrogen being substantially more decreased (and at oxygen increased). Greater charge changes take place also at carbon atoms, which agrees with chemist's intuition concerning changes of electron structure during the rearrangement.

Reaction coordinate $\sphericalangle H_4C_5C_6$. Starting from the value $\sphericalangle H_4C_5C_6 = 47°$ (which corresponds to the value in vinyl alcohol) we increased the angle gradually

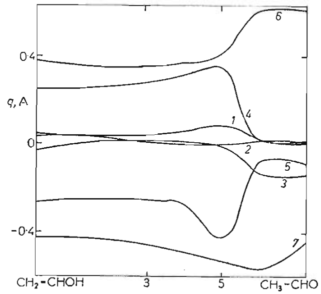


FIG. 5

Dependences of charge densities $q(A)$ on the reaction coordinate R_{CH} (MINDO/3)

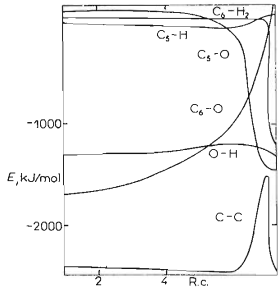


FIG. 6

Dependence of biatomic contributions E_{AB} to the total energy of the system on the reaction coordinate $\sphericalangle H_4C_5C_6$ (MINDO/3) by 10° up to 110°. The energy was minimized by the MINDO/3 method with respect to the other degrees of freedom. It was presumed that increasing of the angle will be connected with lengthening and weakening of OH bond and formation of a new CH bond. The calculation results showed that with increasing $\measuredangle$ HCC the value of $\measuredangle$ CCO is decreased and the $R_{C_5H_4}$ distance shortened until the TS (0·157 nm). However the OH bond length remains roughly unchanged, and after crossing the TS the whole OH group is shifted to the C_5 carbon. In the TS (which is reached at $\measuredangle H_4C_5C_6 = 97°$) the atoms H_1 and H_2 are deviated out of *xy* plane (the plane determined by CCO atoms). After crossing the TS the atom H_2, which was below the *xy* plane, is shifted to the second carbon atom. Thus a vinyl alcohol molecule is formed which is rotated around the *y* axis by 180° as compared with the original molecule. Activation energy of this rearrangement is 424·7 kJ mol^{-1}.

This result is also confirmed by the dependence of biatomic contributions to the total energy (E_{AB}) on the reaction coordinate (Fig. 6). From the diagram it can be seen that energy of O–H and C_5–H bonds is not changed, and the greatest changes are in the values $E_{C_6-O_7}$ and $E_{C_5-O_7}$ which indicate splitting and formation of C–H bond.

In spite of the fact that the result of the reaction did not make itself felt, a chemical process (dehydration and hydration or "rehydration") did take place which can be interesting not only from theoretical point of view but also from the point of view of possible applications. If some atoms of vinyl alcohol molecule were labelled with isotopes, then the "rehydration" would produce a new molecule differing from the original one.

As the described procedure does not lead to the rearrangement, we used a procedure similar to the PLM technique (Principle of Least Motion$^{15-17}$), the reaction coordinate being the angle $\measuredangle H_4C_5C_6$ within the interval 47° to 116° at a fixed value of C–H bond. At a given value of the angle and C–H bond length the total energy of the system was minimized with respect to the other independent internal coordinates. Within the range of the angle from 47° to 81° no large changes in the individual geometry parameters are observed. For the value $\measuredangle$ HCC = 85° the CO bond length is increased by 0·005 nm, and the C–C bond length is decreased by 0·001 nm. The increasing energy (Fig. 7) reaches its maximum value at the angle 85° and C–H bond length 0·128 nm. The respective structure RC6 represents the TS of the thus calculated reaction pathway. After crossing the TS the values of total energy of the system are changed abruptly, the same being true of the geometry parameters (the jump in energy 350 kJ mol^{-1}, in bond lengths 0·016 to 0·018 nm, and in angles up to 80°). The dependence of charge densities of the atoms on the reaction coordinate (Fig. 8) shows abrupt changes of densities in the region corresponding to the energy barrier.

If the result of this procedure is compared with that using only the C–H bond being formed for the reaction coordinate, then it follows: (*i*) that the potential barrier is higher by 11·8 kJ. mol^{-1}, which can be ascribed to the fact that a smaller number of internal coordinates of the system are optimized. (*ii*) that in the both cases there is a partial rehybridization in the TS at the C_5, C_6 atoms from sp^2 to sp^3 (the H_1 and H_2 atoms are out of the plane given by the atoms CCO), (*iii*) al the geometry parameters, after reaching the TS, are more markedly changed in the second case, (*iv*) in the second case a greater charge transfer is from C_5 to C_6, and, on the contrary, in the first case greater charge transfers are from H_4 to C_5 and from C_6 to C_7.

Chemical hysteresis is clearly seen in Fig. 7 for the second procedure, too. The point corresponding to the TS in the reverse rearrangement is shifted to $\sphericalangle H_4C_5C_6 = 60°$, and the energy barrier is lower by 147·6 kJ mol^{-1}. Furthermore, in the reverse reaction pathway the change in geometry parameters is not so large. For the forward and backward reactions *e.g.* the C–O bond length reaches the maximum values 0·138 and 0·133 nm, respectively, the CCO angle has the values 108° and (only) 86°, respectively. All this indicates greater stability of the TS of the backward reaction.

Hydrogen Shift in the Plane Perpendicular to the Plane of the Molecule

Reaction coordinate R_{CH}. The calculation was carried out by the CNDO/2 method starting from *trans* vinyl alcohol. The migrating hydrogen was shifted above the imaginary connecting line between its position in *trans* conformer of vinyl alcohol

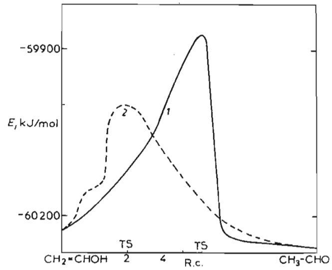


FIG. 7

Dependence of energy of the system on the reaction coordinates $\sphericalangle H_4C_5C_6$ and R_{CH} (MINDO/3); forward *1*, backward *2*

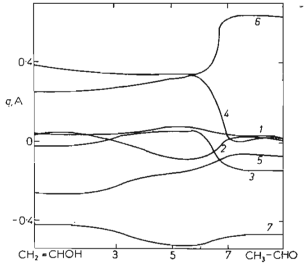


FIG. 8

Dependences of charge densities q(A) on the reaction coordinates $\sphericalangle H_4C_5C_6$ and R_{CH} (MINDO/3) and its new position in acetaldehyde. The z coordinate of the migrating atom and the other geometry parameters were new optimized in each point of the reaction pathway. The transition state is in the vicinity of C_6 atom. Although the O—H and C—H bond lengths are relatively large (0·204 and 0·185 nm, respectively), the distance between the migrating hydrogen and C_6 atom has bonding character (0·123 nm). The activation energy of this process is 232·5 kJ mol^{-1}. However, this straight pathway is not the most favourable one, and the really best pathway is considerably complex (as it is shown in the following case).

Reaction coordinate is the motion over the bonds. In this case we used both the CNDO/2 and the MINDO/3 methods for comparison. In the model considered the migrating hydrogen atom moves over the bonds. At the beginning of the reaction the OH group is rotated around the C–O bond; the most convenient position is at the dihedral angle CCOH 75°. Energy of this conformation is lower than that of the planar one by only 4·0 kJ mol^{-1}. From this relatively convenient position the hydrogen atom shifts further parallel to the C—O bond, being kept at a bonding distance. It is obvious that before the migrating hydrogen atom reaches the central carbon atom, the methine hydrogen atom (H_3) sinks below the plane of the molecule. There is a very short distance between the migrating hydrogen atom and central carbon C_6 (0·125 and 0·118 nm according to CNDO/2 and MINDO/3, respectively). The hydrogen atom moves further parallel to the axis of C–C bond towards the carbon C_5. Simultaneously the CH_2 group rotates around the bond axis to reach the equi-

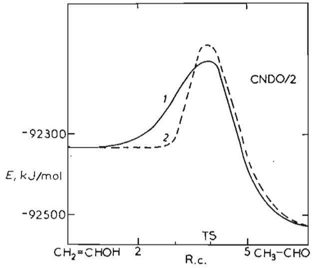


FIG. 9

Dependences of energy of the system on the reaction coordinate determined by direction of the bonds (CNDO/2); forward *1*, backward 2

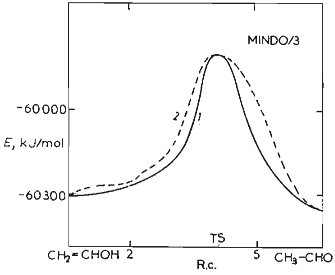


FIG. 10

Dependence of energy of the system on the reaction coordinate determined by direction of the bonds (MINDO/3); forward *1*, backward 2 librium position. Dependences of the energy of this system on the reaction coordinate are given in Figs 9 and 10. The both methods give the transition state in the region above the carbon atom C_6.

It must be mentioned that in this case a small change of the reaction coordinate near the TS is not accompanied by any large change of the other geometry parameters. Comparison of the energy barriers with those of the previous cases shows that the barrier is lowest in this case, being 217·7 and 337·3 kJ mol^{-1} according to CNDO/2 and MINDO/3, respectively, which is smaller by 1·2 and 4·2 kJ mol^{-1}, respectively, as compared with the value of the model R_{CH}. These findings can be explained by an idea that the hydrogen shifts above the bonds represent stepwise symmetry-allowed [1, 2] shifts. This idea also forms the basis for calculation[18] of experimental energy of the tautomerism. Another explanation, perhaps more acceptable, is based on the idea that energy of the rearrangement is lowered by favourable interactions of the migrating hydrogen with the bonds enabled by the presence of an electronegative atom (oxygen), which is supported by other observations.

Dependences of charge density along the reaction pathway are given in Figs 11 and 12. A certain periodicity of the dependences of $q(4)$, $(q5)$, $q(6)$, $q(7)$ in the CNDO/2 method corresponds well to structural periodicity along the bonds. Similar, even though not so marked at $q(4)$ and $q(6)$, is the periodicity of these dependences

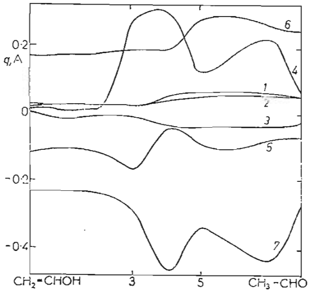


FIG. 11

Dependences of charge densities q(A) on the reaction coordinate determined by direction of the bonds (CNDO/2)

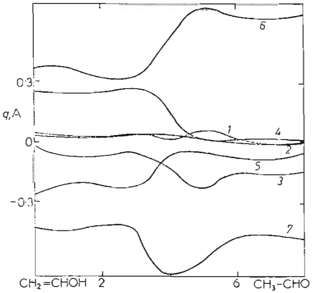


FIG. 12

Dependences of charge densities q(A) on the reaction coordinate determined by direction of the bonds (MINDO/3) in the MINDO/3 method. In this method the dependences of $q(4)$ and $q(6)$ show the shapes of mirror symmetry. It is interesting that the CNDO/2 method gives large changes in charge at the migrating hydrogen atom and oxygen in the region of double bond, which could indicate formation of a hydrogen bond between oxygen and the double bond. Also the diagrams in Figs 11 and 12 show a greater charge density at $q(4)$ than at $q(6)$ in the region of the transition state, which is similar to all the previous cases and corresponds to the chemist's intuition concerning shift of bonding electron pairs during tautomeric rearrangements.

In this case, too, the backward reaction pathways were calculated. As it can be seen from Figs 9 and 10 these pathways are not much different, the transition states being precisely at the same value of the reaction coordinate, and the chemical hysteresis in the overall course of the reaction pathway is much smaller than in the previous cases. This fact can be explained by greater interactions between the migrating hydrogen atom and the bonds, these interactions being decisive for the course of the reaction pathway. The MINDO/3 method gives for the TS of the backward pathway practically the same energy value and the same structural parameters. Only the CNDO/2 method gives a different energy value for the TS (greater by 37·1 kJ mol^{-1}) and different structural parameters. However, even here there is a bonding distance between the migrating hydrogen atom and the C_6 carbon atom (0·125 nm). The O–H and C–O bond lengths are greater by 0·021 and 0·012 nm, respectively, the CCO angle has a lower value by 2°. The other angles differ at most by 8°. Table I gives a list of values of some structural parameters of the transition states for the three most important reaction pathways.

CONCLUSIONS

First of all it must be stated that the MINDO/3 method reflects structural relations of the transition states less sensitively, which follows from the given data, and, therefore, it seems less suitable for study of reactions. This agrees with the criticism in refs[12,19]. Hence the data about the transition states obtained by the CNDO/2 method are considered more reliable and are further discussed below.

Furthermore it must be stated that it can seem rather improper to apply the rules of conservation of orbital symmetry to a little symmetrical rearrangement of vinyl alcohol to acetaldehyde. However, with respect to the skeleton formed by the CCO atoms in which the rearrangement takes place it is acceptable to consider the rearrangement of hydrogen in plane of the molecule (*A*) to be symmetry-allowed antarafacial and that taking place perpendicular to that plane (*B*) to be forbidden suprafacial.

The calculated values of activation energy of the models of the reaction pathway indicate that the symmetry-forbidden rearrangement in perpendicular plane to the molecular plane is the rearrangement with the lowest activation energy. This at first

TABLE I

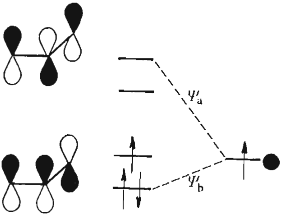
Values of some geometry parameters[a] in the calculated transition states for the individual types of the reaction pathways

Reaction coordinate	Method	R_{OH_4}	R_{CH_4}	R_{CC}	R_{CO}	$\sphericalangle$ CCO	$\sphericalangle$ COH_4	$\sphericalangle$ CCH_1	$\sphericalangle$ CCH_4	$\sphericalangle$ $OCCH_1$	$\sphericalangle$ $OCCH_2$	E kJ mol^{-1}
R_{OH}	CNDO/2	0·158	0·226	0·132	0·135	123·2	95·0	125·2	67·4	0·1	180·0	291·6
R_{CH}	CNDO/2	0·127	0·142	0·134	0·136	108·7	72·9	133·1	69·1	0·0	170·9	218·9
R_{CH}	MINDO/3	0·110	0·120	0·135	0·132	—	73·6	135·9	—	18·7	185·9	341·5
Along bonds	CNDO/2	0·181	0·178	0·140	0·134	126·8	43·8	122·9	44·4	7·5	185·8	217·7
Along bonds	MINDO/3	0·174	0·183	0·140	0·127	127·7	—	125·7	—	14·4	178·9	337·3

[a] The bond lengths are in nm, the bond angles are in degrees.

sight surprising result is explained by the idea of mutual interactions between the migrating hydrogen and bonds of the CCO skeleton which is especially marked, if the rearrangement takes place immediately above the bonds. Also the values of geometry parameters (the CCO angle and C–C and C–O bond lengths) of the transition state *B* are closer to acetaldehyde than those of the TS in *A*.

The transition states differ in other properties, too. Thus the transition state *B* is strongly polar having the dipole moment $19{\cdot}3 \,.\, 10^{-30}$ Cm, whereas that of *A* has the value $8{\cdot}0 \,.\, 10^{-30}$ Cm. The polarity is due to great difference in electronic density mainly at C_6 and oxygen which is probably caused by the charge transfer mediated by a hydrogen bridge formed by the migrating hydrogen. Also the energy gap between the HOMO and LUMO orbitals is smaller in the case *B* (by up to 458 kJ . . mol^{-1}). In such case (in accordance with Berson and Salem[20,21]) the transition state can be considered to consist of separated fragments hydrogen + allyl, and stability of the forbidden transition state in sigmatropic rearrangements is enabled by interaction of the hydrogen with the allyl MO's with lower and higher energies ψ_a, ψ_b (Scheme 2).



SCHEME 2

The energy preference of the suprafacial rearrangement *B* of the hydrogen to the antarafacial one *A* is also confirmed by results of an *ab initio* calculation of energies of the transition structures obtained by the CNDO/2 method which we carried out by a modified version[22] of the Gaussian 70 in the extended 4−31G basis[23]. Energies of these states at the reaction coordinates R_{OH}, R_{CH} and above the bonds (*i.e.* −305 783·3, −326 158·9, and −326 963·2 kJ mol^{-1}, respectively) determine quite clearly the preference order in accordance with the CNDO/2 data. These values also confirm that a spontaneous intramolecular rearrangement of hydrogen in vinyl alcohol is impossible.

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