INTERACTION OF VINYL ALCOHOL MOLECULES*

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The interaction has been studied between two vinyl alcohol molecules giving two acetaldehyde molecules, two models being considered: The first model locates the vinyl alcohol molecules in one plane and mutually rotated by 180°. The symmetry-forbidden HOMO–LUMO interaction between the molecules in this model become allowed through free rotation of the molecules around their CC bonds whereby hydrogen transfer is facilitated. The second model locates the vinyl alcohol molecules in two parallel planes, the allowed HOMO–LUMO interaction causing stabilization of the associate. Energy minimization of the supersystem in the both models by the technique of full optimization (at the level of CNDO/2 method) leads to a barrier-free transformation of vinyl alcohol into acetaldehyde.

Our previous communication[1] showed that energy barrier to intramolecular rearrangement of vinyl alcohol into acetaldehyde was considerably lowered by interaction of the activated complex with molecules of the reaction medium. In this paper we want to show that there exists a way of spontaneous rearrangement of vinyl alcohol to acetaldehyde, considering interaction of two vinyl alcohol molecules in two different mutual orientations.

First let us consider two vinyl alcohol molecules located in one plane and mutually rotated by 180° (Fig. 1). Positions of hydrogen atoms of OH groups with respect to orientation of the $2p_z$ orbitals forming double bond resemble those in the isolated molecules. However, situation is much more favourable for transfer of hydrogen atom from oxygen atom of one molecule to carbon atom of the other molecule, as compared with the situation in an isolated molecule. This advantage makes itself felt in two points: (*i*) the considered hydrogen atoms can approach the corresponding carbon atoms much nearer without necessary deformations and stress, (*ii*) the antarafacial shift of hydrogen atoms is facilitated by free rotation of the molecules (according to arrows in Fig. 1) to the positions needed for the transfer. Therefore, minimization of energy of the supersystem in Fig. 1 with respect to all degrees of freedom (except for the reaction coordinate) has the consequence that the molecules at suitable distance, first of all, begin to rotate around CC bonds, and, with proceeding

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rotation, they simultaneously approach each other. The whole process is accompanied by hydrogen transfer from OH groups to carbon atoms of the partner molecules.

The calculations were carried out by the CNDO/2 method, since it gives reliable interaction energies of dimers (Kollman and Allen)[2]. In the starting supersystem configuration the vinyl alcohol molecules stood at the distance $R = 0.4$ nm, the repulsion energy being 15.9 kJ mol^{-1}, which can be understood with the help of the frontier orbital theory by Fukui. From Fig. 2 it can be seen that the HOMO–LUMO interaction is symmetry-forbidden. Distance between double bonds of the vinyl alcohol molecules was chosen as the reaction coordinate: decreasing its value, the supersystem gets rid of repulsion interaction energy by rotation of the molecules out of the plane. The whole process results in two associated acetaldehyde molecules with the interaction energy of 11.5 kJ mol^{-1}.

The interaction ceases to be symmetry-forbidden, if the two vinyl alcohol molecules are located in two parallel planes (Fig. 3) which is manifested in stabilization energy of the supersystem. We chose two reaction coordinates: distance R (C_9H_5) and distance between double bonds of the molecules.

In the first case, starting from the distance 0.330 nm and minimizing the supersystem energy along the reaction coordinate (gradual shortening by 0.010 nm), the molecules, first of all, are mutually shifted and form a non-symmetrical configuration. Total energy of the supersystem continuously decreases with decreasing reaction coordinate (Fig. 4). Simultaneously, the molecules of supersystem change their geometries, the change being slight at the beginning and abrupt from a certain
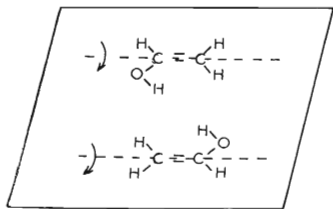

Fig. 1

Model of two interacting vinyl alcohol molecules in one plane
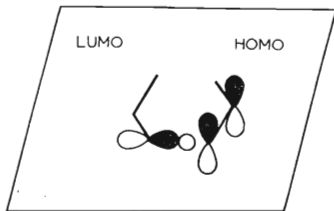

Fig. 2

Schematic representation of the HOMO and LUMO of two vinyl alcohol molecules in one plane

point. Also the charge is redistributed. Result of the whole process is two associated acetaldehyde molecules in *trans* conformation with interaction energy of 28·6 kJ . . mol^{-1}. Energy of the supersystem decreases monotonously through very flat relative maxima (Fig. 4). The point at the reaction pathway with $R(C_9H_5) = 0·1$ nm can be considered quasi-activated complex, since thereafter the vinyl alcohol molecules change their geometries very rapidly towards those of acetaldehyde. The supersystem is stabilized at the distance $R(C_9H_5) = 0·128$ nm. Also the dependences of atomic charges $q(A)$ *vs* reaction coordinate (Fig. 5) show abrupt changes near this quasi-activated complex. Electron densities at hydrogen atoms of OH groups decrease at first, and then they increase steeply with increasing shift. The densities at oxygen atoms as well as those at the carbon atoms to which hydrogen atoms are shifted exhibit an opposite change. Densities at the hydrogen atoms not directly involved in the process are changed but slightly. Charges at corresponding atoms of the vinyl alcohol molecules are not the same at the mentioned value of the reaction coordinate due to non-symmetrical configuration of the supersystem.

In the second case the reaction coordinate is represented by the distance between two parallel planes in which the molecules are placed. The molecules can move to each other, remaining in their parallel planes along the whole reaction coordinate. We started from the distance between the planes 0·400 nm and lowered it by 0·030 nm steps. The supersystem was fully optimized at every point of the reaction coordinate. In this case, too, the supersystem energy slowly decreases at first, and near the value
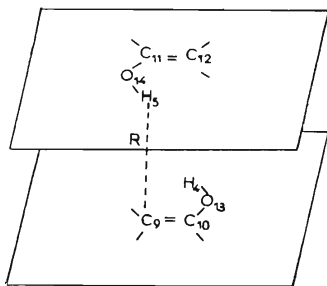

Fig. 3

Model of two interacting vinyl alcohol molecules placed in two parallel planes
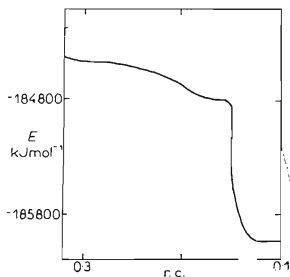

Fig. 4

Dependence of energy of two vinyl alcohol molecules placed in two parallel planes on the reaction coordinate $R(C_9H_5)$

0·300 nm at the reaction coordinate an abrupt energy change is encountered which is accompanied by abrupt change of geometry parameters of the vinyl alcohol molecules. Again, this point of abrupt change can be assigned to the quasi-activated complex, since further energy decrease is steep until equilibrium configuration of the supersystem is attained. In this phase of reaction the hydrogen atoms are definitively removed from oxygen atoms and attached to the carbon atoms of the partner molecules. The whole reaction pathway has similar shape as in Fig. 4. At the value 0·320 nm of the reaction coordinate the hydrogen shifts are finished, and two acetaldehyde molecules are obtained which, this time, stand in *cis* conformation at the distance 0·300 nm between the CC bonds. Stabilization energy of the associate is $-11·6$ kJ . . mol^{-1}. Charges at the corresponding atoms of the two molecules are the same along the whole reaction path (Fig. 6) due to symmetrical shape of the supersystem throughout the whole process. Here also, abrupt charge changes at atoms take place near the quasi-activated complex, and qualitatively they exhibit similar shape of changes of atomic charges at the corresponding atoms as in the first case.

We also tried to use the MINDO/3 method for the calculation, but it gave repulsive interaction between two vinyl alcohol molecules placed in two parallel planes. Only after forced overpowering of the unreal barrier the same result is obtained
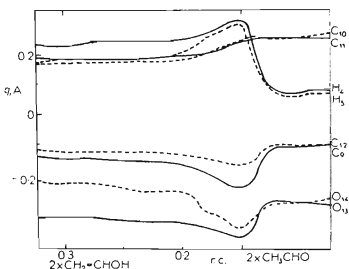

Fig. 5

Dependence of atomic charges $q(A)$ of two vinyl alcohol molecules on the reaction coordinate $R(C_9H_5)$. ——— Atomic charges of the reference vinyl alcohol molecule (bottom), – – – – – atomic charges of the vinyl alcohol molecule which reacts with the reference molecule
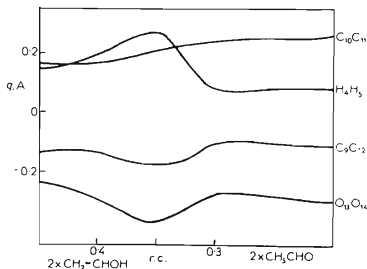

Fig. 6

Dependence of atomic charges $q(A)$ of two vinyl alcohol molecules on the reaction coordinate (distance between two parallel planes)

as by the CNDO/2 method. This repulsive interaction between molecules calculated by the MINDO/3 method was criticized earlier[3,4].

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