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# Application of Computational Methods Mm2 and Gussian for Studing Unimolecular Decomposition of Vinil Ethers based on the Mechanism of Hydrogen Bonding

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***Abstract*—**Investigations of the unimolecular decomposition of vinyl ethyl ether (VEE), vinyl propyl ether (VPE) and vinyl butyl ether (VBE) have shown that activation of the molecule of a ether results in formation of a cyclic construction - the transition state (TS), which may lead to the displacement of the thermodynamic equilibrium towards the reaction products. The TS is obtained by applying energy minimization relative to the ground state of an ether under the program MM2 when taking into account the hydrogen bond formation between a hydrogen atom of alkyl residue and the extreme atom of carbon of the vinyl group. The dissociation of TS up to the products is studied by energy minimization procedure using the mathematical program Gaussian. The obtained calculation data for VEE testify that the decomposition of this ether may be conditioned by hydrogen bond formation for two possible versions: when α- or β-hydrogen atoms of the ethyl group are bound to carbon atom of the vinyl group. Applying the same calculation methods to other ethers (VPE and VBE) it is shown that only in the case of hydrogen bonding between α-hydrogen atom of the alkyl residue and the extreme atom of carbon of the vinyl group (αH---C) results in decay of theses ethers.

***Keywords*—**Gaussian, MM2, ethers, TS, decomposition

## I. Introduction

UNDER thermal activation of complex organic compounds (polyatomic molecules) and their decay, as a rule, atoms and radicals are formed. However, due to intermolecular rearrangement of the atoms at the same time the processes can occur, resulting in decomposition products in the form of various isomers, and often saturated molecules [1].A great many of experimental and theoretical investigations are known [2]-[12],[16],[17], in which the decay of vinyl and other esters were considered and on the basis of experimental data decomposition rate constant are determined.

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## II. Computational Methods

Description of monomolecular decomposition of organic compounds and the establishment of mechanisms that lead to their spontaneous decay only by experimental methods is complicated as these systems are multi-component. This research is devoted to studying the mechanism of thermal unimolecular decomposition of VEE, VPE, VBE applying the methods of molecular mechanics (MM) and quantum-chemical theories, as well as to calculate the dependence of the rate constant of decomposition on the pressure. To calculate energy and geometrical parameters of the systems considered the software systems MM2 and Gaussian were used. These methods are widely used in solving the problems of molecular isomerization or decay, also are effective tools in the study of the thermal decomposition of complex compounds. In this case MM2 is used to determine the transition state (TS) at activation of vinyl ethers, and Gaussian is used to determine the frequency factor of the most probable decay channel of the TS.

At present we can say with reasonable confidence that intermolecular rearrangements in many organic compounds, leading to their degradation, are realized via the formation of hydrogen bond [1] between the hydrogen and oxygen (in ketones) or carbon atoms (in ethers), which is a consequence of the difference between the electronegativities of these atoms and the small size of the hydrogen atom.

This phenomenon can be represented as the decay of a hypothetical diatomic molecule under the influence of external forces. Its explanation in the framework of quantum theory can be found in perturbation theory as the transition of a quantum system in the continuum under the influence of time-dependent external forces [14],[15]. From the perturbation theory of quantum mechanics it is known that if a quantum system is under the effect of an external electric force of the oscillating nature, then the solution of the Schrödinger equation permits for transitions to the continuous spectrum, i.e. the system can decay. The decay probability (W) of the system is described by the formula:

$$W = \frac{\left|F_{E,n}\right|^2}{h} \quad (1)$$

Where $h$ is the Planck's constant, $F_{E,n}$ is matrix element of

transition from the discrete spectrum (bound state) to the continuous spectrum.

If a C – H bond in the ethyl group is highly excited and hydrogen atom forms a hydrogen bond with the extreme atom of carbon of the vinyl group, and if the double bond C= C is also vibrationally excited, one can imagine that an external oscillating field acts on this C – H bond. Within the quantum perturbation theory this may yield a broadening of line (uncertainty in the energy of state), hence decay of the state becomes possible:

$$\Gamma = \left|F_{E,n}\right|^2 \quad (2)$$

Where Γ is the width of the line in the excited hypothetical "diatomic" molecule H–(ROCHCH$_2$). Here R denotes CH$_2$CH$_2$ for the molecule of VEE, CH$_2$CH$_2$CH$_2$ for VPE, and CH$_2$CH$_2$CH$_2$CH$_2$ for VBE.

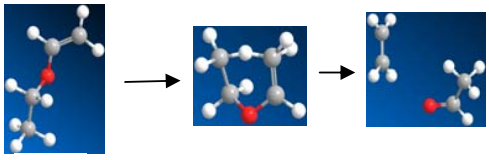
*The proposed approach developing in this research involves the following stages:*

- construction of the molecular structure of a ether with the use of the program Chem. Bio Ultra 11.0;
- introduction of a new polar connection (hydrogen bond) between a hydrogen atom of an alkyl group and the extreme carbon atom of the vinyl group into the obtained structure;
- minimization of the energy of this new structure by the program MM2;
- minimization of the energy of the formed intermediate state under the program Gaussian with consideration for quantum effects that enables to establish what fragments are formed after decay of the intermediate state, as well as to calculate the frequency factor.

## III. Calculation

It is necessary to note that computer modeling and calculation of the molecule structure for VEE under the program MM2 (obtaining of transition state) are carried out for the first time, and the results obtained, as will be shown below, are in good agreement with the available literary data.

Stages of thermal decay of the VEE molecule are presented in Figs. 1and 2.



a b c

Fig. 1 Transformation stages of the VEE molecule from the basic state (a) to the formation of βH---C hydrogen bond (b), and decay (c).

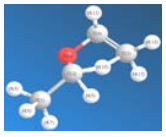


Fig. 2 Formation of αH---C hydrogen bond and energy minimization under the program MM2

As a result of calculations carried out the values of frequencies (ν) for two versions of the VEE molecule decay have been obtained within the limits of the Hartree-Fock method (*one of methods of the self-coordinated field*) in the 6-31G basis:

a) in case of decay by hydrogen bonding between the β hydrogen atom of the ethyl group with carbon atom of the vinyl group ν = 344.1315 cm$^{-1}$ .

b) in case of decay by hydrogen bonding between the α hydrogen atom of the ethyl group with carbon atom of the vinyl group ν = 278.1486 cm$^{-1}$.

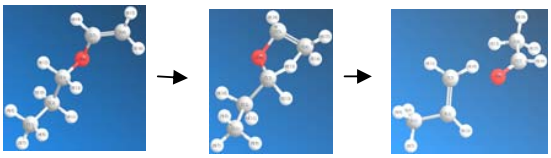
As a frequency factor we have selected the least from the negative frequencies, as it corresponds to the least value of excitation energy.

Thus, application of the approach suggested in the present research in relation to spontaneous decay of VEE shows that, really, highly excited β- and α-hydrogen atoms of the ethyl group under activation of the VEE molecule can be the reason of thermal dissociation of this molecule (Figs. 1 and 2).

Application of the same approach to describe thermal decay of a more complex molecule such as VPE did not give positive results in cases when hydrogen bond formation between β- and γ-hydrogen atoms of the propyl group were considered. That is, the formed intermediate state, after the procedure of energy minimization for TS under the program Gaussian state have led to the initial state of VPE molecule.

Absolutely other situation was observed, if hydrogen bond is formed between α-hydrogen atom of the propyl group and carbon atom of the vinyl group. The formed the intermediate state is TS with the displacement of thermodynamic equilibrium towards the reaction products, namely acetaldehyde and propylene. So, application of energy minimization procedure under the program Gaussian to the TS results in the products of decomposition.

Fig.3 shows the stages of development of thermal decay of the VPE molecule.



a b c

Fig. 3 Transformation stages of the VPE molecule from the basic state (a) to the transition state (b) with formation of αH---C hydrogen bond, and decay (c)

The smallest calculated magnitude of the frequency (ν) with negative sign is 192.1585 cm$^{-1}$ (5.76·1012 s$^{-1}$), which corresponds to the minimum energy for decay of VPE.

Rate constant is calculated under the formula [13]:

$$k = \nu \cdot \exp(-E_a/RT) \quad (3)$$

Where ν is the magnitude of frequency resulting in decomposition of a molecule (frequency factor); $E_a$ is the

activation energy; T is absolute temperature, and R is the universal gas constant. The value of activation energy for decay of VPE was determined experimentally in [16] to be: $E_a \approx 44.0$ kcal/mol. Having this value of $E_a$ it is possible to calculate the rate constant for VPE decay according to formula (3). At temperature value T = 700K: k=0.129 $s^{-1}$. Note that in [16] this constant at temperature T = 721.3K was determined to be k = 0.189 $s^{-1}$. This may be considered as a good agreement because usually the accuracy of experimental determination of activation energy is in the limits 10-30 %.

The molecule of vinyl butyl ether (VBE) has more complex structure in comparison with above considered vinyl ethers. In this context more possible configurations are possible and the molecule may accumulate more internal energy.

In the literature only a few works are known devoted to thermal decay of VBE [16],[17] owing to difficulties of the problem.

It is known [16] that at thermal decay of VBE as a rule acetaldehyde, butane and small amounts of propylene are formed. It is also known [16] that if toluene is used as a carrier gas in products other substances were observed: 25% of CO, 2 – 5% of hydrogen and also methane.

Application of the method suggested in this research in relation to VBE aimed at finding transition state and investigation of thermal decomposition process in this case is more difficult.

In this relation all possible variants of hydrogen bonding formation in the excited molecule of VBE have been carefully explored. Performing the procedure of energy minimization for TS by means of the program Gaussian has shown that only hydrogen bonding between the α-hydrogen atom of the butyl group (with respect to the oxygen atom) and the extreme atom of carbon of the vinyl group has led to decomposition of the VBE molecule.

Development stages of the VBE molecule thermal decay are presented in fig. 4.

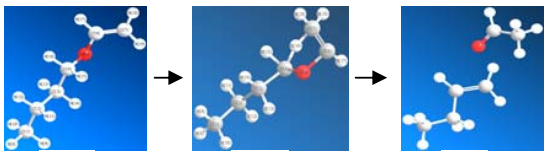



Fig. 4 Transformation stages of the VBE molecule from the basic state (a) to the transition state ((b) with formation of αH---C hydrogen bond, and decay (c)

Calculations of the frequency factor for the VBE molecule by Gaussian Job: # RHF/6-31G Freq Test, resulted in ν = 174.7585 $cm^{-1}$.

Taking into account the experimentally determined value for activation energy of monomolecular decay of VBE to be Ea ≈ 42.4 kcal/mol [16] the rate constant for VBE decay at temperature T=700 K was calculated: k = 0.405 $s^{-1}$. This value matches well with the literary data.

## IV. Conclusion

The investigations of decay processes of vinyl ethers by the approach developed in this research resulted in some interesting singularities.

The obtained theoretical data testify that suggestion about the thermal decay of vinyl ethers through the formation of hydrogen bonding between β- and α-hydrogen atoms of alkyl groups (in relation to the oxygen atom) with the carbon atom of the vinyl group explain correctly the mechanism of the process considered.

Another situation is observed in cases of more complex ethers, VPE and VBE. Detailed calculations by the use of MM2 and Gaussian programs have established that only hydrogen bonds formed by α-hydrogen atoms of alkyl groups are responsible for thermal decay of these ethers.

In summary it is necessary to note, that the approach suggested in this work also enables to reveal the more effective channel of thermal decay of vinyl ethers and to calculate the frequency factor by visual manner.

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