

## **Use of semi empirical method for determination of the activation energy of thermal decomposition of vinyl ethers**

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Received April 2014; Accepted May 2014

### **ABSTRACT**

In this research, a semi empirical approach has been suggested for calculating the activation energy of unimolecular thermal decomposition of vinyl ethers yielding saturated products. The calculation procedure is based on the use of molecular mechanics (MM) methods. These methods which involve the construction of the transition state for a molecule mainly consider the formation of a "Hydrogen Bridge" between the alkyl and vinyl groups and also use the Lennard - Jones potential. The activation energy of the decay is calculated as the difference between bond energy of the Hydrogen atom jumping from the alkyl group to the vinyl group, and the strain energy of the molecule due to the formation of the transition state (TS). A new semi empirical method for computing the activation energy at spontaneous decay of vinyl ethyl ether (VEE), vinyl propyl ether (VPE) and vinyl butyl ether (VBE) molecules has been developed. It allows calculating the values of the activation energy by simple procedures. The obtained results for the decay of vinyl ethers are in good agreement with the known experimental data in the literature.

**Keywords:** Semi empirical; MM2; Vinyl ether; Transition state

### **INTRODUCTION**

Theoretical methods for determining the value of the rate constant, including the activation energy of chemical reactions, specially the spontaneous reactions of the thermal decomposition of molecules in most cases give good results [1].

In particular, the theory of transition state (TS) satisfactorily describes the process, if it is possible to calculate accurately the potential energy surface (PES) and localize TS on the surface. However, in the study of reactions of complex systems including Vinyl esters, calculation of PES, finding its

extremes and therefore, determination of the activation energy is not always possible with sufficient accuracy and the results are not always satisfactory.

In this regard, developing relevant semi empirical methods for determining the activation energy of complex processes is urgent. One can find several examples of using semi-empirical methods in the literature that allow estimating the activation energy of reactions. For example, the rule of Polanyi-Semenov [2,3] allows to find the activation energy of

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the exothermic reactions of  $\text{CF}_3 + \text{RH} = \text{CF}_3\text{H} + \text{R}$  type, in which the activation energy ( $E_a$ ) is decreasing with the increase in the heat of reaction ( $Q$ ). For this case, an empirical relation  $E_a = \beta - \alpha Q$  is found, where  $\beta$  is a constant for the given class of reactions,  $\alpha$  is a factor with values ranging from 0 to 1.

In the method of Sabo [4], similar to the previous one, the expression  $E_a = \sum D_i - \alpha \sum D_j$  is used, where  $\sum D_i$  is the sum of the bond energies in the initial molecules,  $\sum D_j$  is the same sum in the molecules of the reaction products,  $\alpha$  is a constant, which depends on the structure of the transition state. The methods of Moin [5] and Benson [6] also may be noted, as they are similar with the above methods, and in many cases provide good results. However, these methods are used for small numbers of reactions and are not applicable for wide classes of chemical transformations.

Specifically, in the case of the spontaneous decay of Vinyl Ethers, these methods cannot be applied due to the specificity of the problem, namely the mechanism of the decay of Vinyl Ethers, which according to [7] most likely occurs by the formation of the intermolecular Hydrogen bonds.

## COMPUTATIONAL METHODS

The main principles of the developed approach are as follow: Based on the mechanism of the reaction suggested in [7] (inside the thermally excited molecules of vinyl ethers intermolecular hydrogen bonds may appear that then lead to decay of molecules) by using computer programs MM2, the intermediate state of a vinyl ether molecule is constructed. Further, on the basis of the formatted state the most distorted bonds are determined and energy of deformation leading to transformation of the PES is calculated. Using this value

of the deformation the activation energy of thermal unimolecular decay of vinyl ethers is calculated as a difference between the bond energy of hydrogen atom in the alkyl group and the deformation energy of the molecule due to formation of the TS.

The concept of transformation energy is used to describe the isomerization of molecules and means changing internal energy of molecule in its modification (bond angles, intermolecular distances, tetrahedral angles and etc.).

The transformation of a molecule of vinyl ether due to the activation may be schematically presented by the sequence of stages shown in Fig.1 by the example of VEE molecule. When activated, the rotation around the C---O axis of the alkyl group takes place, leading eventually to the formation of the activated state. Here attention should be focused on possible sequential changes in the structure. That is, at the rotation firstly two carbon atoms are approached and an antibinding orbital appears between them (because they have filled electron shells), manifesting itself as excitation of electronic levels of the molecule. This leads to a decrease in the absolute value of the potential energy. Upon further rotation of the alkyl group, a hydrogen bond forms between  $\beta$ -hydrogen atom of this group and carbon atom of the vinyl group. If the excitation energy of the hydrogen atom is sufficient to overcome the energy barrier, the formatted state is a pre-decay one, so the hydrogen atom of the alkyl group skips to the vinyl group. Further redistribution of energy within the molecule results in its decomposition into fragments.

To calculate the energy of the antibinding link at interaction of atoms as a rule the Lennard - Jones [8] potential is used. This latter is usually applied for finding the interatomic potential of inert gas atoms at their crystallization, as well as

with some accuracy for calculating electron energy of the pair of atoms forming an antibinding link. Thus, for the Lennard - Jones [8] potential  $U(r)$  we can write:

$$U(r) = 4\varepsilon[(\sigma/R)^{12} - (\sigma/R)^6] \quad (1)$$

where  $\varepsilon$ ,  $\sigma$  are semi empiric parameters,  $R$  is the distance between atoms.

A calculation of Lennard - Jones potential parameters for carbon atom which is bound and the outer electrons are paired quite difficult task and therefore were considered the best-known literature data for that parameters values calculated multiple times for the noble gas atoms.

For noble gases the value of parameters  $\sigma$  and  $\varepsilon$  are calculated with a satisfactory accuracy. So by location in the periodic table the carbon atom with a filled electron level is closer to the neon atom, then to avoid unnecessary complexity of the calculating nature for the interaction of two carbon atoms (in the Ether molecule) we can use the values  $\varepsilon = 2.844$ ,  $\sigma = 0.04$  eV calculated for the neon atom [8]. This appears to be a satisfactory approximation for the qualitative picture of the transformations in the VEE molecule at the formation of TS.

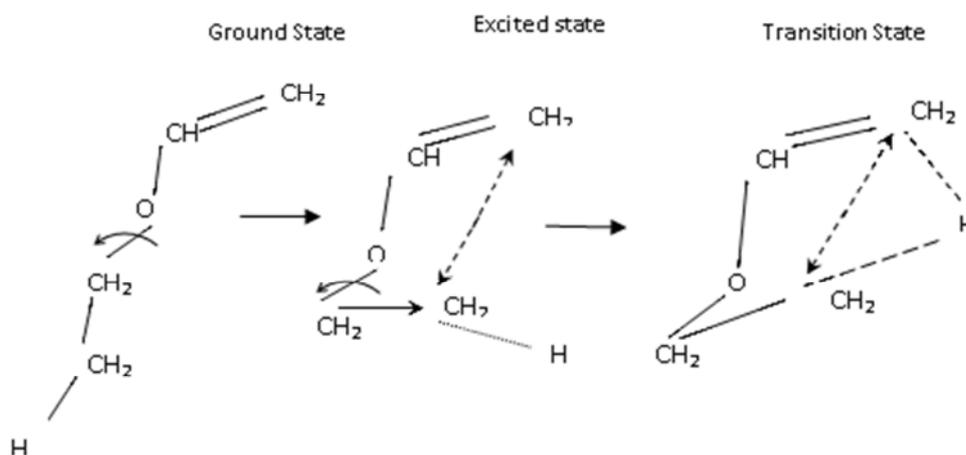
Using the computer programs MM2 and

program package Gaussian based functions 6-31G (energy minimization) ChemBio Office 2008 in the limits of the offered approach, ground state and transition states for the above mentioned molecules were constructed, enabling to determine which of them has the capability to decompose yielding molecular products.

## RESULTS AND DISCUSSION

Consider the application of the offered method in relation to the thermal decomposition of VEE Fig.2. The provides fundamental states at of decay of the thermally activated VEE molecule, obtained by the application of the MM2 program. According to Fig. 2., the formation of the TS is transformation of the molecule, resulting in approaching two carbon atoms: first from the alkyl group, and the second from the vinyl group). This yields a closed structure of the molecule involves all four carbon atoms of the molecule VEE.

In contrast to the standard approach, where it is assumed that the activation energy represent the difference between the energies of the ground state and the TS in this work it presents as the difference between the binding energy of hydrogen atom and the deformation energy of the molecule under the formation of the TS.



**Fig.1.** Schematic representation of states of the VEE molecule at activation.

As shown in [9,10], the formed TS lead to the disintegration of the molecule as a result of transfer of hydrogen atoms involved in hydrogen bonding. At the formation of a hydrogen bond in the activated molecule of VEE, as Fig. 2. shows, two carbon atoms are approaching significantly.

To calculate the deformation energy for VEE molecule at the formation of TS by formula (1) using the known values of  $\epsilon$  and  $\sigma$  parameters it is necessary to have the value of distance between two carbon atoms (Fig. 2.) . For the case of formation of TS1 this distance equal  $R_1 = 2,242 \text{ \AA}$ , and for the value of repulsive energy (energy of deformation of potential surface) obtained  $U(R_1) = 48.07 \text{ kcal/mol}$ . Hence, for the activation energy of thermal decay of VEE we can obtain:  $E_a (\text{TS1}) = 93 - 48.07 = 44.93 \text{ kcal/mol}$ , where the value of 93 kcal/mol was taken from the literature [1] as the energy of C – H bond in the alkyl group.

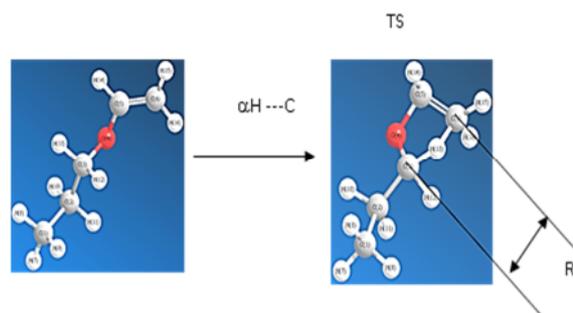
For the case of formation of TS2 (Fig. 2, cyclic structure formed by participation of  $\alpha$ - hydrogen atom of the alkyl group), calculation for the distance  $R_2$  by the program MM2 yields  $R_2 = 2.231 \text{ \AA}$ . Using this value in formula (1) for the deformation energy of potential surface  $U(R_2)$ , the value of 51.97 kcal/mol is obtained. Therefore, the activation energy of the VEE molecular decay by the second way is:  $E_a (\text{TS2}) = 93 - 51.97 = 41.03 \text{ kcal/mol}$ .

It should be noted that the values of activation energy obtained for thermal decomposition of VEE at two cases of TS formation (44.93 kcal/mol), are in good agreement with the experimentally determined value for unimolecular decomposition of VEE in [11] (43.28 kcal/mol). The maximum the maximum deviation of the calculated data from the

experimentally determined values was less than 7%.

### Calculation of activation energy for thermal decay of VPE

For vinyl propyl ether, the distance between carbon atoms ( $R_3$ ) after activation of VPE molecule was calculated by the program MM2 (Fig. 3.). For TS state, the magnitude of  $R_3 = 2.235 \text{ \AA}$  was obtained. And as a consequence for deformation energy is obtained:  $U(R_3) = 50.7 \text{ kcal/mol}$ . On this basis, for the activation energy the value of  $E_a = 93 - 50.7 = 42.32 \text{ kcal/mol}$  is received.



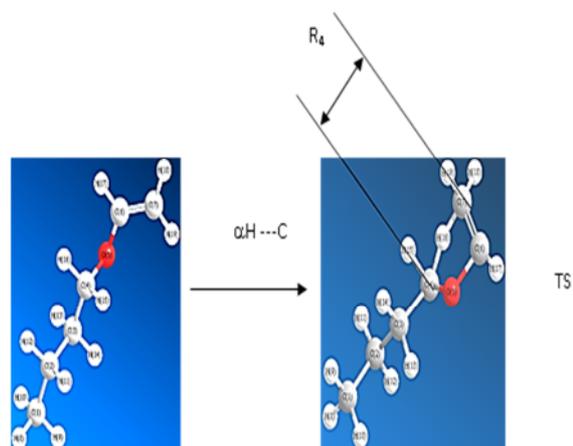
**Fig. 2.** Ground state of VPE molecule and intermediate state formed between  $\alpha$ -hydrogen atom of the alkyl group with the extreme carbon atom of vinyl group.

### Calculation of activation energy for thermal decay of VBE

The molecule of VBE has the most complex structure among all vinyl ethers studied in this work. However, it is established that in this molecule also rotation around C – O axis takes place with formation of a hydrogen bond. In this case, at thermal decomposition of VBE also only hydrogen bond formed between the  $\alpha$ -hydrogen atom of the alkyl group and extreme carbon atom of the vinyl group is responsible for the decay process. By using the MM2 program the distance ( $R_4$ ) between the carbon atoms within the formed cyclic structure (Fig. 4) was

calculated to be 2.25 Å. Just as in the case, of other ethers, using the values of  $\sigma$ ,  $\varepsilon$  parameters known in the literature for neon and Eq. (1), the value of deformation energy was calculated:  $U(R_4) = 46.2$  kcal/mol. Accordingly, the value of activation energy for VBE molecule decay is:  $E_a = 93 - 46.2 = 46.8$  kcal/mol.

It should be noted that in the literature there are no any data on the activation energy of thermal decay of VPE, and in this work, it has been determination the value of activation energy for decay of this substance for the first time. On the Table 1 shows, the energy values obtained for the thermal decomposition of vinyl ethers and the comparison with literature data.



**Fig. 3.** Ground state of VBE molecule and intermediate state formed between  $\alpha$ -hydrogen atom of the alkyl group with the extreme carbon atom of vinyl group.

**Table 1.** The activation energy for VEE, VPE, VBE obtained by simulation in this paper and the comparison with literature data

Ethers	Activation energy, Our data (kcal/mol)	Activation energy, literature data, (kcal/mol)
VVE	44.93 (TS1) 41.03 (TS2)	43.8 [11, 13]
VPE	42.32	-
VBE	46.8	42.4 [11, 13]

## CONCLUSION

Because the study of the reactions in complex systems such as decomposition of vinyl ethers and the calculation of potential energy surface and find its extremes values for determination of the activation energy is difficult task. In this regard, a relevant semi empirical method for determining the activation energy of complex processes becomes actuality.

The offered method demonstrates why the activation energy of process of transferring of hydrogen atom from the alkyl group to the vinyl group, is about two times smaller than binding energy of the hydrogen atom in the alkyl group. In the framework of this method, this effect is

appeared due to deformation of the molecule, at the formation of TS.

Thus in this work, we calculated values of activation energy for thermal decay of vinyl ethers and it is in good agreement with the empirical values known from literature. Therefore, it can confirm that proposed semi empirical method gives reasonable results. This method may be also applied in the case of thermal decomposition of other complex compounds, in which forming the intermolecular hydrogen bonds due to thermal activation is of high probability. The main advantage of this method is its simplicity. In addition, it requires easy procedures for calculating the values of the

activation energy.

#### ACKNOWLEDGMENT

The authors are heartily thankful to the researcher of the Institute of Chemical Physics of NAS of Armenia, Dr A. Davtyan, for his active assistance in exploiting of the applied computer programs.

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