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EFFICIENT METHOD OF STUDYING THE INTERMEDIATE REACTIONS IN THE HALOGENATION PROCESS OF 2-METHYL-BUTANE IN THE COURSE OF ORGANIC CHEMISTRY

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Abstract. The contemporary teaching methodology is in a dynamic development due to the multiple socio-economic changes, but mainly due to the rapid evolution of the technologies, which are implemented in the training process with the purpose of solving specific problems. The integration of the methods specific to the field of Chemistry with the information technologies creates new opportunities to make the teaching methodology more efficient in order to ensure the compatibility of the formed competences with the needs of the labour market. The use of quantum calculations allows the understanding of chemical processes in terms of energy efficiency. To delve into the intricacies of the radical substitution mechanism in Organic Chemistry, modern computing software in the field of Chemistry such as Gamess, Gaussian, ChemCraft, ChemBioDraw etc can be used. The use of theoretical calculations offers the possibility to study some complicated phenomena of organic nature, which arguably strengthens the pupils/students' knowledge about the probability of the chemical reaction taking place in different classes of organic compounds.

Keywords: Organic Chemistry, chemical modelling, chlorination, bromination, energy stability, performance in education.

METODĂ EFICIENTĂ DE STUDIU A REACȚIILOR INTERMEDIARE ÎN PROCESUL DE HALOGENARE A 2-METIL-BUTANULUI ÎN CADRUL CURSULUI DE CHIMIE ORGANICĂ

Rezumat. Metodologia didactică contemporană este într-o dezvoltare dinamică grație multiplelor schimbări socio-economice, dar în primul rând datorită evoluției rapide a tehnologiilor, care sunt implementate în procesul de instruire cu scopul soluționării unor probleme specifice. Integrarea metodelor specifice domeniului Chimie cu tehnologiile informaționale creează noi oportunități în eficientizarea metodologiei didactice cu scopul asigurării compatibilității competențelor formate cu necesitățile pieței muncii. Utilizarea calculelor cuantice permite înțelegerea proceselor chimice din punct de vedere a rentabilității energetice. Pentru a pătrunde în subtilitățile mecanismului de substituție radicalică în chimia organică pot fi utilizate softurile moderne de calcul în domeniul Chimiei cum ar fi: Gamess, Gaussian, ChemCraft, ChemBioDraw etc. Utilizarea calculelor teoretice oferă posibilitatea de a studia unele fenomene complicate de natură organică, fapt care consolidează argumentat cunoștințele elevilor/studenților despre probabilitatea desfășurării reacției chimice în cadrul diferitor clase de compuși organici.

Cuvinte-cheie: chimie organică, modelare chimică, clorurare, bromurare, stabilitate energetică, performanță în educație.

Introduction

One of the important goals of the actual educational system (especially in the fields of exact and natural sciences) is the development of motivating training technologies. This process of training the specific competences of the subject is facilitated by the complex combination of the technologies from different fields (informational, industrial etc.). Interdisciplinary studies create additional opportunities for understanding complex phenomena. In the field of Chemistry it is necessary to realize the connection between the assimilated matter and the daily activity to make the pupil to understand the advantages of a conscious and interested training. At the same time, it is important for the educational process to be interspersed with scientific research to ensure a functional theory-application-research-innovation connection [1-4]. Training by research creates favourable premises for the emergence of interdisciplinary educational contexts [5]. For the pupils and the students in the field of Chemistry, first of all, the connections with Physics and Biology are needed to create an integral picture of the material world [6], and in the last decades ICT creates multiple opportunities that allow studies at the border between different disciplines, generating new research directions and useful tools for the teaching methodology. At the same time, the elaboration of the methodology based on combining the digital applications with the technologies specific to the disciplines allows the development of a creative and self-taught training style [7]. The emergence of additional elements in the teaching methodology opens new possibilities for teachers who, manifesting creativity and personal vision, can generate new educational contexts in which the educates can reach more valuable performances and a higher degree of motivation. Adapting information technologies to various disciplines in the field of Education Sciences allows the study of some phenomena that cannot be traced under ordinary conditions. The study of the energetic states allows to determine the stability, as well as the geometrical configuration of the molecular systems [8], and the analysis of some processes of substitution, condensation etc. delivers valuable information to draw conclusions about the occurrence likelihood of some phenomena [9,10]. The use of methods of calculating the energy of molecular systems is necessary to determine the probability of the existence of some molecules in one of the possible geometric configurations. These computational modellings allow the teacher to argue by individual calculations the fairness of theoretical statements for both inorganic and organic molecules [8]. Even more valuable is the level at which the pupils themselves can carry out these studies in order to formulate personal conclusions regarding the possibility of the occurrence of certain phenomena, the molecular architecture of some substances etc.

Applied methods and materials

Calculation of the optimized geometries and imaginary frequencies for reactants, intermediates, products and transition states was performed using the modern software

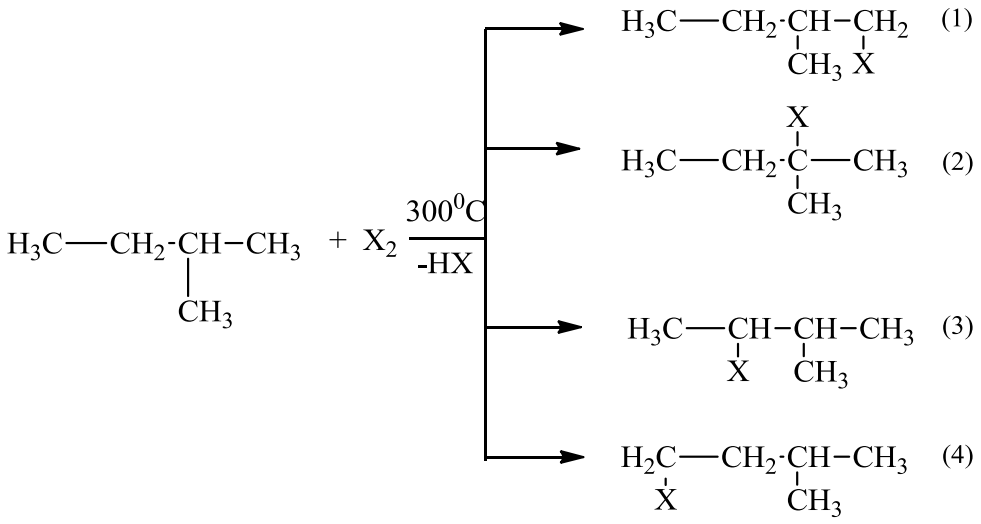
package GAUSSIAN 09 [11], using the standard base set 6-31G [12] for carbon and hydrogen atoms. The modelling results of the studied mechanisms (all possible substitution reactions) were obtained by applying ab initio quantum-chemical calculations. The quantum-chemical calculations performed for these systems allow a deep understanding of some aspects related to the energetic state, the spatial configuration and the molecular structure.

Results and discussions

Professional development based on the methodology focused on information technologies adapted to the specific of the discipline allows the formation of the research competence. As a result, personalities with their own style of training, self-taught, able to solve various problems through unique methods can be developed. The formation of the competence to use specialized software to solve the specific problems of Chemistry even at the pre-university level creates premises for the autonomous development of the pupil's personality in an interdisciplinary educational context.

As many processes could be carried out according to different scenarios depending on the energy of the reactions, external factors that can influence the direction of the flow etc, for the Chemistry teacher it is important to have, besides the theoretical material, practical arguments based on the calculations regarding the energy profitability for carrying out the chemical reaction. As an example we will examine the possible halogenation reactions of an organic compound containing different types of carbon atoms – 2-methyl-butane – to determine on the basis of calculations which of the examined species has a higher probability of formation. The free radicals, being particles with very high reactivity and a very short lifespan, in their stabilization tendency combine two by two or participate in reactions with other substances present in the system. Thus, the radicals are initiators of radical mechanism reactions.

As object of this study is proposed the radical substitution process for the 2-methyl-butane compound (substitution step of the first hydrogen atom):



The halogenation reaction of 2-methyl-butane is a chain and proceeds in a few steps: initiation, propagation and interruption of the reaction. In the first step, under the influence of light or temperature, it is obtained the halogen radical which in the second step reacts with the 2-methyl-butane molecule forming hydrogen bromide or chloride and free hydrocarbon radicals:

1. initiation of the reaction:

$$X\bullet \,|\, \bullet X \xrightarrow{h\nu} X^{\bullet} + X^{\bullet}$$

2. propagation of the reaction:

$$RH + X^{\bullet} \rightarrow R^{\bullet} + HX$$

$$R^{\bullet} + X_2 \rightarrow R\text{-}X + X^{\bullet}$$

3. interruption of the reaction:

$$X^{\bullet} + {}^{\bullet}X \rightarrow X_2$$

$$R^{\bullet} + X^{\bullet} \rightarrow R\text{-}X$$

$$R^{\bullet} + {}^{\bullet}R \rightarrow R\text{-}R$$

In the given case at the first halogenation step 4 different carbon atoms can be substituted and 4 radicals can be obtained. In turn, the free radicals can react with another halogen radical forming the halides: 1-X-3-methyl-butane, 2-X-3-methyl-butane, 2-X-2-methyl-butane, 1- X-2-methyl-butane.

Theoretical study of the species participating in the halogenation reaction.

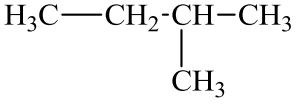
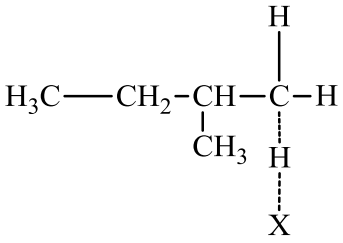
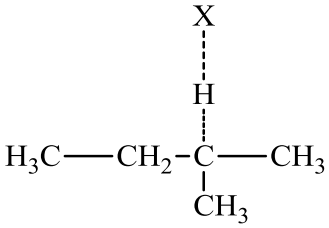
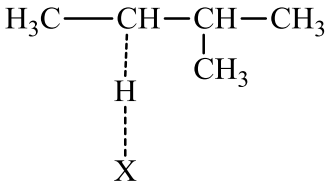
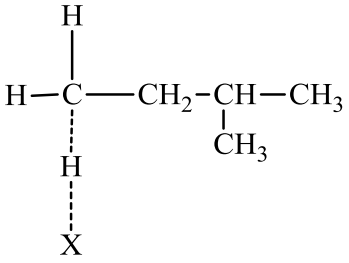
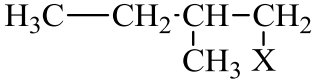
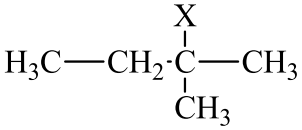
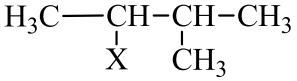
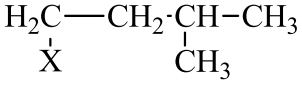
The geometric structure of the reactants (R), the transition states (TS) and the reaction products (P) were studied *ab initio* using the SCF method in the UHF approximation, using base 6-31n (UHF/6-31G) for atomic functions [12]. All calculations were performed using GAUSSIAN 09 [11], which is a modern software package used to investigate the structural properties, those determined by the electronic structure of molecules or complex molecular systems.

As models it has been studied the halogenation reactions of 2-methyl-butane that take place in the radical substitution process, which occur after the radical chain reaction mechanism. The energy status of the investigated chemical systems and the energy profile of the intermediate reactions were studied.

Using some theoretical calculation methods, a series of geometric and energetic parameters related to molecular structure, as well as the energy profile of some chemical processes, can be correlated and predicted. Using this model, calculations were performed for all species involved in this radical substitution reaction.

Initially, the values of total energies of the structures of the reactants and reaction products were calculated (Table 1).

Table 1. Total energy values of the studied species during halogenation reaction

No.	Species name	Geometric structure	E_{tot}	
			Cl	Br
1.	2- methyl-butane		-196.2522	
2.	TS1		-655.6561	-2765.9551
3.	TS 2		-655.6670	-2765.9658
4.	TS 3		-655.6623	-2765.9616
5.	TS 4		-655.6568	-2765.9553
6.	1-X-2- methyl-butane		-655.1346	-2765.9582
7.	2-X-2- methyl-butane		-655.1421	-2765.9672
8.	2-X-3- methyl-butane		-655.1384	-2765.9642
9.	1-X-3- methyl-butane		-655.1351	-2765.9594

For each particle from the mentioned reactions the optimum geometry was determined and the total energies were calculated.

Radical substitution mechanism

In the Chemistry discipline, it can be proposed several models that would allow for complex studies of molecular characteristics and chemical mechanisms. It is proposed the analysis of a model of training-research integrated application, in which the mechanism of substitution in the organic molecules is studied with the help of quantum-chemical calculations based on specialized software, which allow to determine the energetics of the investigated mechanism and the probability of the chemical reactions.

Based on this, we set out to calculate all the species involved in the reaction (reactants, reaction products, intermediates and transition states) and based on these calculations to obtain the energy profile of the radical reaction.

The transition states were localized and verified by vibrational analysis. For the intermediate species, an imaginary frequency was obtained, which demonstrates the presence of these activated states of the investigated systems. The values of the imaginary frequencies are described in the text and in the figures presented below. For all the studied molecules it was considered that the spatial nuclear configuration of the studied molecules corresponds to the C_1 symmetry group.

At the first halogenation step, which is also the initiation reaction that proceeds under the action of light or temperature, the homolytic cleavage of the halogen molecule takes place with the formation of two free radicals:

$$X_2 \overset{h\nu}{\rightarrow} 2\dot{X}, \quad X = Cl, Br$$

From an energy point of view this reaction is thermodynamically convenient (exothermic), because for the chlorine molecule ΔE=7.81 kcal/mol, and for the bromine molecule ΔE=7.72 kcal/mol.

In the case of the 2-methyl-butane chlorination reaction, which proceeds according to the general reaction: R-H + 2Cl$^{\bullet}$ = R-Cl + HCl, four substitution mechanisms were analyzed. Figure 1 shows the energy profiles of the reaction mechanisms of processes 1-4. The highest activation energy for the chlorination process of the studied reactions is owned by mechanism (1) with value 24.60 kcal/mol, while the lowest value being in reaction (2) with value 17.76 kcal/mol, a fact from which we can says that reaction (2) would proceed with a higher reaction rate. Studying the energy profile of mechanisms 1-4 as a whole, it was confirmed that these are exothermic reactions and the most energetically convenient one is reaction (2) with an energy gain equal to -25.79 kcal/mol. It can also be concluded that 2-chloro-2-methyl-butane compound is the most energetically stable, which is also known in the specialized literature.

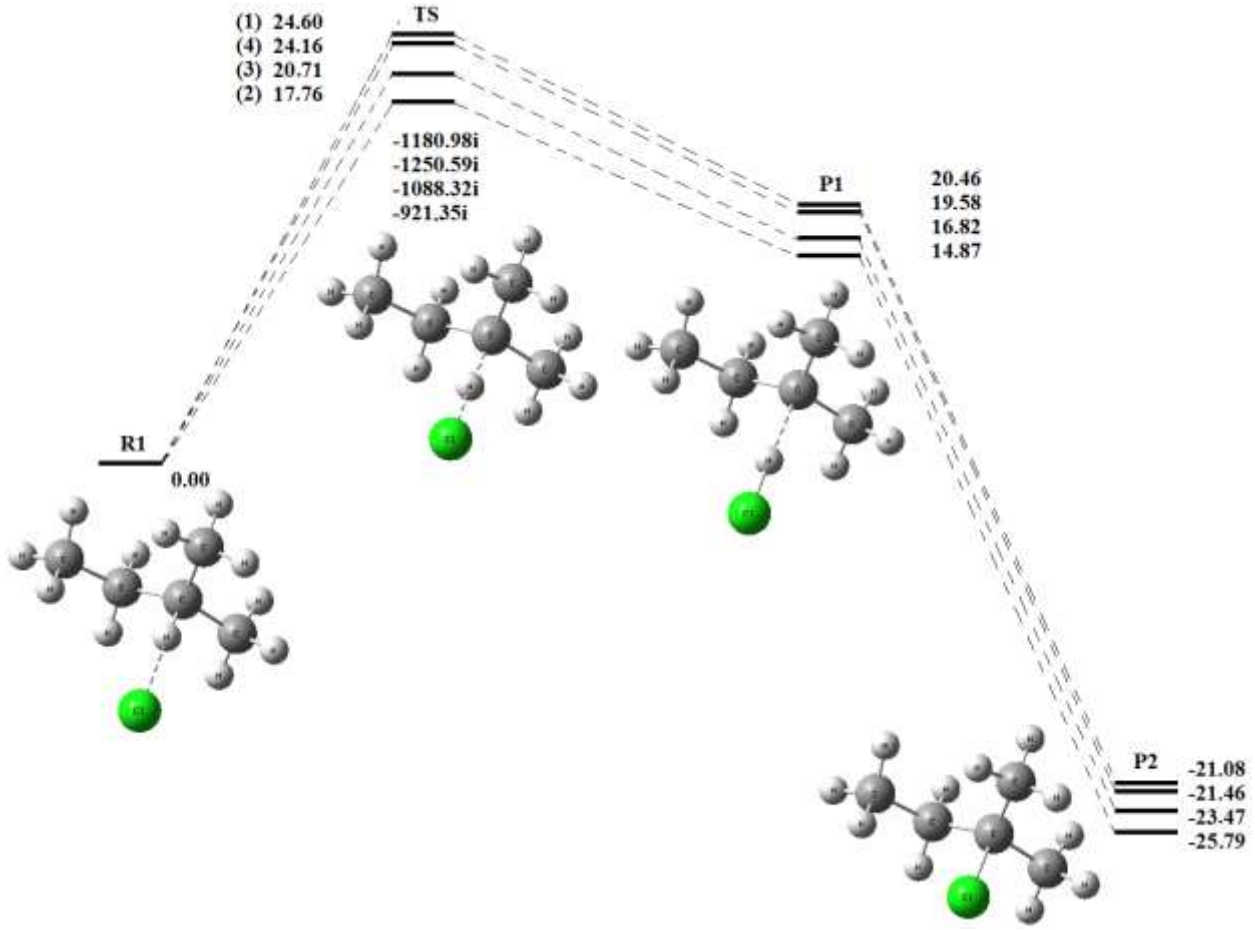


Figure 1. Energy profile of chlorination reactions 1-4 (kcal/mol)

The configuration of the transition states presented for reactions 1-4 in the figure above is characterized by the breakdown of the hydrogen atom from the respective carbon atom of the studied hydrocarbon and has a single imaginary frequency with value -1180.98i cm^{-1}, -921,35i cm^{-1}, -1088.32i cm^{-1}, -1250.59i cm^{-1}, corresponding to mechanisms 1-4 which show the movement of the hydrogen atom between the chlorine and carbon atoms. The intermolecular transfer of hydrogen in the studied mechanism takes place according to the reaction mechanism described above.

The own vector of the transition state, associated with the unique imaginary frequency, represents an adequate structure of the transition state with the migration of the hydrogen atom from the carbon atom to the chlorine one. Also, in this context we can say that the analyzed organic isomer is more energetically stable in form 2-chloro-2-methyl-butane.

In the case of bromination, which proceeds according to the general reaction: R- H +2Br$^{\bullet}$=R-Br+HBr, also based on the obtained energies, the graph of the energy profile of the reaction was elaborated according to Figure 2.

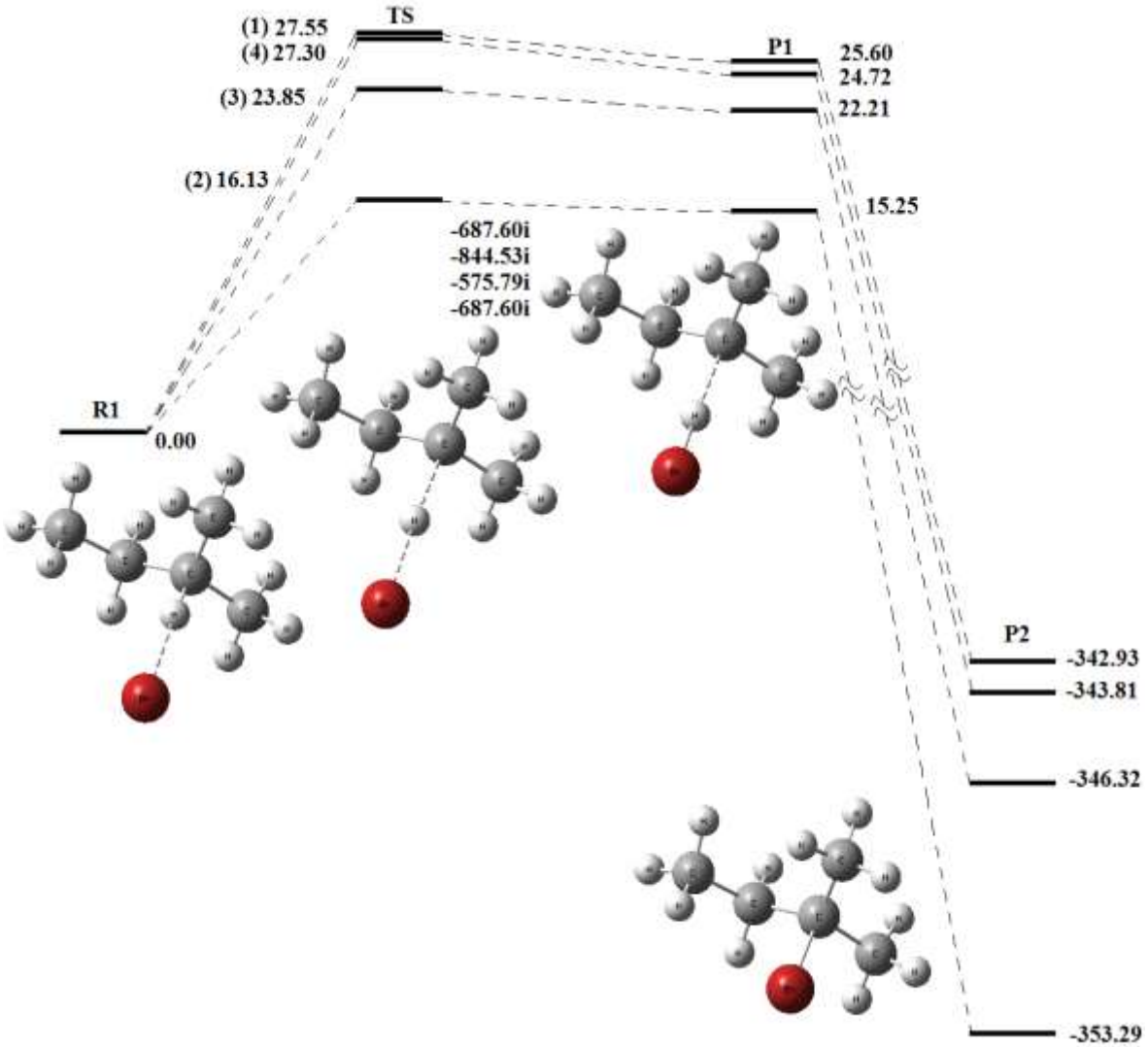


Figure 2. Energy profile of bromination reactions 1-4 (kcal/mol)

At first the first Br• radical forms with the saturated hydrocarbon a stable R-H-Br• complex (R1, Figure 2). There were located the transition states for this step which are characterized by a single imaginary frequency -687.60i cm^{-1}, -379.97i cm^{-1}, -575.79i cm^{-1}, -844.53i cm^{-1} corresponding to reactions 1-4 (TS complex in Figure 2). The transition vector indicates that the molecular motion of this frequency is dominated by the transfer of a hydrogen atom H from C to Br. It can be seen that the geometry of the transition state differs significantly from that of the reactants. The result of the first step is the formation of the free radical R• and the HBr molecule.

In the next step, that is considered to be the step of interrupting the bromination reaction, the combination of two hydrocarbon and bromine radicals takes place. It is interesting that this reaction takes place without any activation energy by obtaining stable and neutral halogenderivat.

In order to acquire the new applications that allow to perform quantum-chemical calculations in the study programmes Chemistry, Chemistry and Biology at cycle I, students are trained in the courses Information Technology in Chemistry and

Computational Modelling in Chemistry etc., and at cycle II in Computational Chemistry and Quantum Chemistry. As a result of the evolution of the competence of using information technologies in the field, the students begin to develop various graphic representations in Chemistry and related disciplines, PPT presentations, to solve tasks within the individual work, to process materials for conferences and articles in scientific journals. Some of the students are included in student research projects (eg: Quantum-Chemical Study of the Energy Stability of Some Molecules and the Energy Profile of the Mechanisms of Chemical Reactions). All students use these applications in the elaboration of their bachelor and master degree theses, and up to 20% of the graduates elaborate theses on scientific topics in the field of quantum-chemical calculations. These acquisitions are very useful in the professional activity.

Teachers in pre-university education can use these applications on different topics: the spatial structure of inorganic and organic molecules; determination of the geometrical parameters of the molecules (bond length, bond angle, etc.); probability of the existence of a molecule in a certain isomeric configuration; energy stability of some species and molecular systems; strength of the chemical bond; electrolytic dissociation etc. In university education these applications can be used for the topics: the determination of the activation energy and the transition state; study of the mechanisms of some chemical reactions; caloric effects of thermodynamic processes; charges on the atom; HOMO LUMO etc. During the continuous training courses and additional professional qualification the teachers are trained how to use these tools to carry out interdisciplinary activities in Chemistry.

These things allow us to state that the use of calculation methods based on modern information technologies ensures the creation of an interdisciplinary educational context, which allows the development of strong skills and the readiness for solving different problems of specific character in the field of Chemistry. These practical examples allow the motivation for a conscious and deep training, the development of some individual aspects of the specialist and the self-taught capacity of development, marking positively the trajectory of formation of the professional competence.

Conclusions

In the context of rapid evolution of information technologies it is necessary to develop digital competence and acquire specific applications in specific fields, which increase pupils' level of motivation for the educational process and broaden the spectrum of available tools for solving problems with different aspect and degree of difficulty. The use of theoretical calculations to determine the energy of some chemical processes allows to determine the probability of their occurrence. These computerized calculations allow pupils and students to individually identify the energy profile of some processes in Organic Chemistry. The proposed methodology aims to provide the school and university teachers

with real mechanisms for the substantiated demonstration of the occurrence direction of some reactions in Organic Chemistry. The method is recommended for use at the university level, while for the pre-university level it may be optional for the students who show interest or are preparing for various competitions in the field.

It has been established that students/students who use a large set of information technologies in the process of studying Chemistry achieve high performance in the following stages of study and employment in the field of work.

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