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An Approach to Electronic Textbook Linking Chemical Experiment - Esterification of Acetic Acid and Ethanol -

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Abstract: A computer graphics (CG) teaching material of the esterification of acetic acid and ethyl alcohol was made based on quantum chemical calculations. The teaching material could simultaneously display realistic shapes and electrostatic potentials of the intermediates of the reactants on the way of the reaction profile besides the ball-and-stick model of the intermediates. The material was tried to combine with chemical experiments of student's laboratory of the university for the purpose of making electronic textbook.

Keywords: CG, visualization, chemical reaction, electronic textbook, tablet computer.

1. Introduction

Understanding the observed phenomena, chemists use to imagine and explain observations in terms of molecules (Figure 1). Observed phenomena and molecular level models are then represented in terms of mathematics and chemical equation (Gilbert, 2009 and Tasker, 2010).

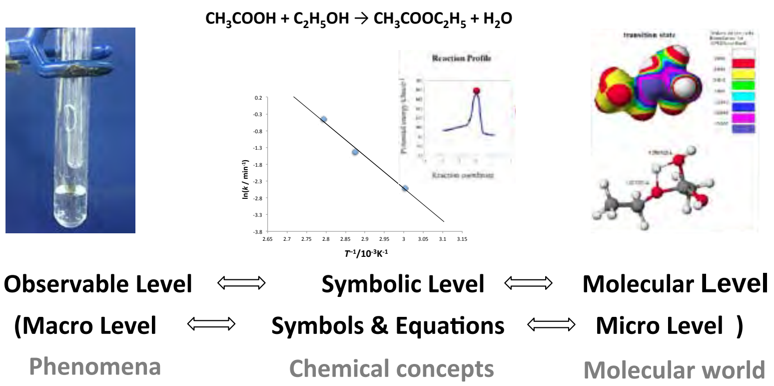


Figure 1 Dividing the image into the three thinking levels

Student's difficulties and misconceptions in chemistry are from inadequate or inaccurate models at the molecular level (Kleinman, 1987). A molecular structure visualized by the computer graphics (CG) provides a deeper understanding of molecular structure (Tuvi-Arad, 2006). It is our aim to produce a CG teaching material based on quantum chemical calculations, which provides realizable images of the nature of chemical reaction (Ikuo, 2006 and 2009). Molecular level animations combined with video clips of macroscopic phenomena enabled students to predict the outcome better (Velazquez-Marcano, 2004). If the CG teaching material is combined with chemical experiments of student's laboratory, students would observe the reaction from three thinking levels, namely, phenomena in the actual observable level and CG teaching material in the molecular level, and chemical equation in the symbolic level. The CG teaching material on the tablet computer was effective to provide image of "Energy" change and also effective to provide image of "Structure" change and “Migration of Electron” during chemical reaction (Ikuo, 2012). Our ultimate goal is to produce an electronic textbook linking chemical experiment, which integrates these three levels.

Chemical reaction is generally expressed by a chemical formula that provides information of the reaction about its stoichiometry; however, chemical formula does not provide information about its realistic shape and reactivity of molecule. This information is essential to realize images of chemical reaction. Molecular models such as wire, ball-and-stick, and space filling, are popularly used to realize images of molecule. They are used properly for the purpose of providing information of molecule about bond length and its angle, shape, and so on. Generally, the electron density iso-surface on CG is displayed with realistic shape of molecule, and electrostatic potential on CG provides information about electrical character of a certain part of molecule.

In this paper, we report here a CG teaching material adopting the CG with electrostatic potential on electron density that represents both realistic shape and electrostatic potential of molecule for the purpose of making electronic textbook for university student laboratory, which integrates the observable level experiment and the molecular world of the esterification.

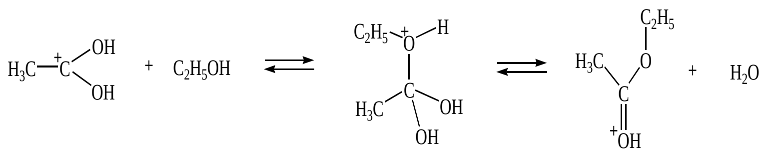
2. Procedure

2.1 Quantum Chemistry Calculation

Esterification of acetic acid and ethyl alcohol is described as shown in the equation (1).

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O \qquad (1)$$

The mechanism of the reaction is well known (For example Loudon, 1984), and generally, the esterification proceeds in the presence of proton catalyst. The rate-determining step includes the paths of an attack of the oxygen atom of hydroxyl group of ethyl alcohol to the central carbon of the formed carbonium ion and release of water as shown in the Scheme 1. This step dominates all over the reaction, and then the calculation based on quantum chemistry on the rate-determining step was carried out. Although another mechanism that involves more than a pair of reactants is possible as reported in the case of carbonic acid formation (Nguyen, 1984), it was not considered in this paper for simplicity of program.



Scheme 1 Mechanism of the esterification on the rate-determining step

Structures of intermediates on the esterification of acetic acid and ethyl alcohol and their electrostatic potentials on electron density were calculated as follows: the semi-empirical molecular orbital calculation software MOPAC (Stewart, 1989) with PM5 Hamiltonian in the CAChe Work System for Windows (Former name of SCIGRESS, ver. 6.01, FUJITSU, Inc.) was used in all of calculations for optimization of geometry by the Eigenvector Following method, for search of transition state by use of the program with Saddle point Search, and for search of the reaction path from the reactants to the products via the transition state by the intrinsic reaction coordinate (IRC) calculation (Fukui, 1970). Details of procedure of the quantum chemical calculations were described in the previous paper (Ikuo et al., 2006). The electrostatic potential on electron density (EPED) (Kahn, 1986) was calculated based on structures from the results of the IRC calculation (Ikuo et al., 2014).

2.2 Production of Teaching material of CG and Electronic Textbook

A movie of the reaction path was produced by the software DIRECTOR (ver. 8.5.1J, Macromedia, Inc.) following the display of the bond order of the structure of the reactants in each reaction stage, which was drawn by the CAChe. The obtained CG of EPED model was combined with those of ball-and-stick model and reaction profile in the same reaction stage. It was confirmed that the drawn CGs of the molecular models of reactants moves smoothly. The green ball, which indicates progress of the reaction, was arranged on the reaction profile and simultaneous movements of the ball and the reactants were confirmed. Created movie file was converted to the Quick Time movie for iPad by the Quick Time PRO (ver. 7.66, Apple, Inc.). Electric textbook was produced with iBooks Author (ver. 2.1.1, Apple, Inc.) and was saved to iPad (Apple, Inc.) by using the iTunes (ver. 11.2.1, Apple, Inc.).

3. Results and Discussion

3.1 CG Teaching Material

The Quick Time movie file was created as teaching material by use of 100 frames of combination CGs.

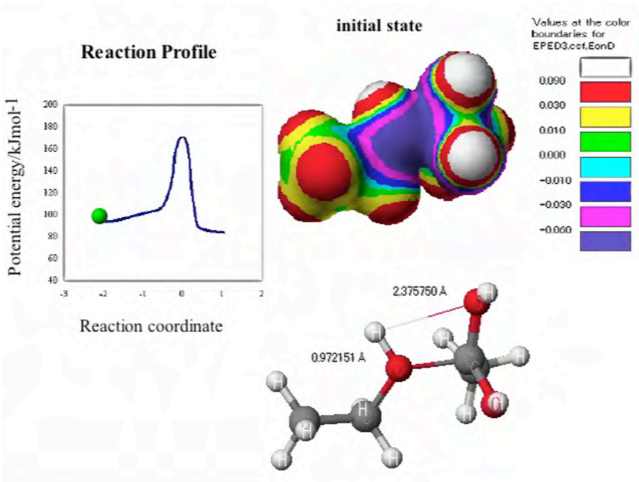


Figure 2 CG teaching material

The Figure 2 shows the combination CGs on the way from the state of reactants to that of products via the transition state. The teaching material demonstrates the changes of electrostatic potential and realistic shape of the intermediate of the reaction on the reaction profile in all stages at the same time.

The values of electrostatic potentials were represented in different colour on the model of intermediate, and figure legend of colour boundaries for electrostatic potential was also listed. Distribution of the electrostatic potential among the intermediate can be seen by the colours. For example, oxygen of ethanol is negatively charged with relative value of -0.06 based on evaluation of energy of interactions of prove proton to the charge of iso-surface, and hydrogen of carbonium ion is positively charged with the relative value of +0.09. The model by electrostatic potential provides information about electrostatic distribution of the intermediate on the way of the reaction.

The green ball on the reaction profile can move by users' choice of the way of automatic movement or manual movement along the reaction coordinate, which indicates the most probable pathway of chemical reaction according to the IRC theory (Fukui, 1970), by use of the Quick Time control bar. Other CGs such as EPED and ball-and stick modes are also synchronized with the movement of the ball so that the degree of the reaction progress and structural change of the molecules of all stages could be demonstrated simultaneously. The CG teaching material provides details of the chemical reaction mechanism dynamically.

3.2 Electronic Textbook

The teaching material was tried to combine with chemical experiments of student's laboratory for the purpose of making electronic textbook of basic chemistry to provide experiment at the observable-level, CG visualization at the molecular-level, and chemical equation at the symbolic-level.

The electronic textbook was inserted with images of experimental procedure in the flow charts and pictures, which can be enlarged by students touch (Figure 3). CG teaching materials of reaction profiles were also inserted (Figure 4). When student touches the CG teaching material in the tablet computer, the teaching material appears to show image of the structural change during the reaction. When student touches the material again, the Quick Time control bar appears and the green ball on the profile can move by student's choice. Student can manipulate the reaction back and forth until they obtain the image of the reaction.

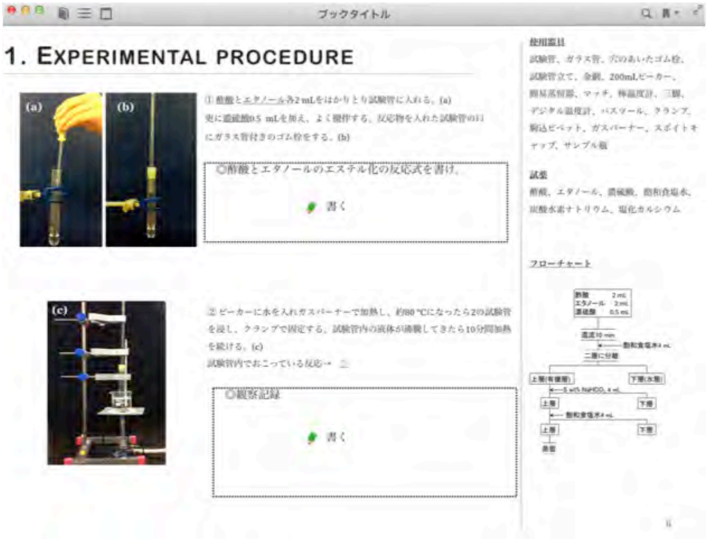


Figure 3 Experimental procedure from the electronic textbook

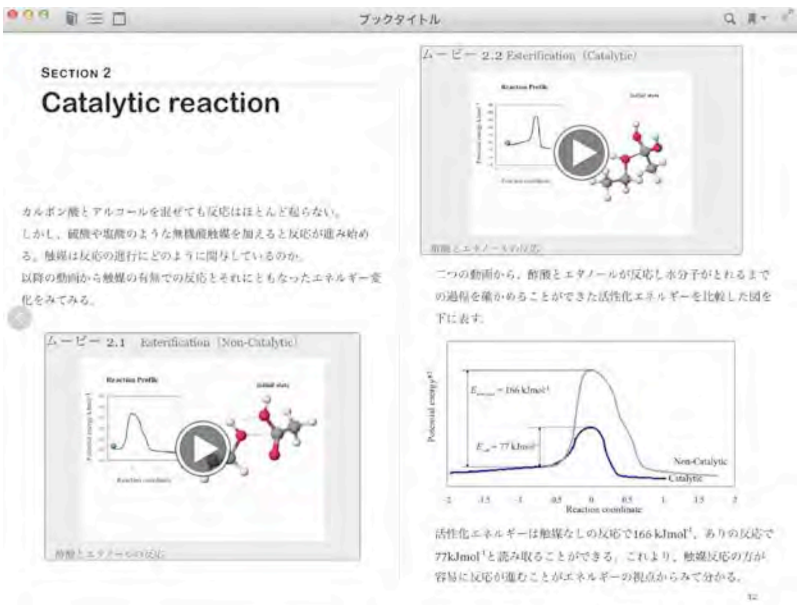


Figure 4 CG teaching material in the electronic textbook

4. Conclusions

A CG teaching material of the esterification of acetic acid and ethyl alcohol was made based on quantum chemical calculations. The teaching material could simultaneously display realistic shapes and electrostatic potentials of the intermediates of the reactants on the way of the reaction profile besides the ball-and-stick model of the intermediates. The material could demonstrate these images of dynamical reaction mechanism for the esterification. The material was tried to combine with chemical experiments of student's laboratory of the university for the purpose of making electronic textbook. The textbook could display picture of apparatus and flow-chart of experiment in addition to the CG teaching material. The electronic textbook could integrate the observable level experiment and the molecular world of the esterification.

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