VISUALIZATION OF REACTION MECHANISM BY CG BASED ON QUANTUM CHEMICAL CALCULATION
- AN APPROACH TO ELECTRONIC LABORATORY TEXTBOOK -

Akira Ikuo and Haruo Ogawa
Department of Chemistry, Tokyo Gakugei University, Japan
Corresponding Email: ikuo@u-gakugei.ac.jp

ABSTRACT

Visualization by computer graphics is great help for students to have images in the molecular level. In this work, the change in the molecular configuration in fundamental chemical reactions such as, $F + HCl \rightarrow HF + Cl$, $I + H_2 \rightarrow HI + H$, $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$, and esterification of acetic acid and ethyl alcohol were visualized by the quantum chemical calculation MOPAC with PM5 Hamiltonian. The CG teaching material could simultaneously display realistic shapes and electrostatic potentials of reactants on the way of the reaction profile besides the ball-and-stick model. The CG teaching material could be an effective tool to provide information about the nature of the reaction. The teaching material was tried to combine with chemical experiments of student's lab used tablet PC for the purpose of making electronic textbook of chemical experiments, which integrates observable level, molecular level, and symbolic level. *[AJCE 4(3), Special Issue, May 2014]*

INTRODUCTION

Chemical education has the circumstances performed through an experiment. Understanding the observed phenomena, chemists use to imagine and explain observations in terms of molecules. Observed phenomena and molecular level models are then represented in terms of mathematics and chemical equation [1, 2]. Student's difficulties and misconceptions in chemistry are from inadequate or inaccurate models at the molecular level [3].

Visualization is great help for students to have images in the molecular level. It is our aim to produce computer graphics (CG) teaching material based on quantum chemical calculations, which provides realizable images of the nature of chemical reaction [4, 5]. 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 observable level and CG teaching material in the molecular level, and chemical equation in the symbolic level. Our ultimate goal is to produce such an electronic textbook that can be used in the experimental laboratory. This paper describes our approach to the electronic laboratory textbook of chemical experiments, which integrates the three thinking levels.

PROCEDURES

Quantum Chemical Calculation

The semi-empirical molecular orbital calculation software MOPAC [6] with PM5 Hamiltonian in SCIGRESS for Windows (FUJITSU, Inc.) was used in all of calculations for optimization of geometry, for search of potential energies of various geometries of intermediates, for search of transition state, and search of the reaction path from the reactants to the products *via* the transition state. The optimized structure of the transition state was verified by the observation of a single absorption peak in the imaginary number by the use of the program Force in MOPAC for vibration analysis. If the peak was observed, Intrinsic Reaction Coordinate (IRC) [7] calculation was done and the reaction path was confirmed.

CG teaching material

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 SCIGRESS. It was confirmed that the drawn CGs of the molecular models of reactants moves smoothly. The red ball, which indicates progress of the reaction, was arranged on the reaction profile and simultaneous movements of the ball and the reactants were confirmed. The movie file was converted to the Quick Time movie by the Quick Time PRO (ver. 7.66, Apple, Inc.) and was saved to iPad (Apple, Inc.) by using the iTunes (ver. 11.1.5, Apple, Inc.).

RESULTS AND DISCUSSION

Reaction of $F + HCl \rightarrow HF + Cl$

The study of simple reaction of two atoms molecule on the reaction of equation (Eq.1) was conducted by the calculation of potential energy (PE).

$$F + HCl \rightarrow HF + Cl \qquad \text{(Eq. 1)}$$

Changes of PE in the reaction have been reported experimentally [8] and theoretically [9]. However, the reaction has not been clarified enough in details such as PE surface in three-dimension (3-D). PE of 2-D and 3-D are shown in the Figure 1 along with structure of reactants in the ball-and-stick model and the reaction profile, which demonstrates the degree of the reaction progress by the ball.

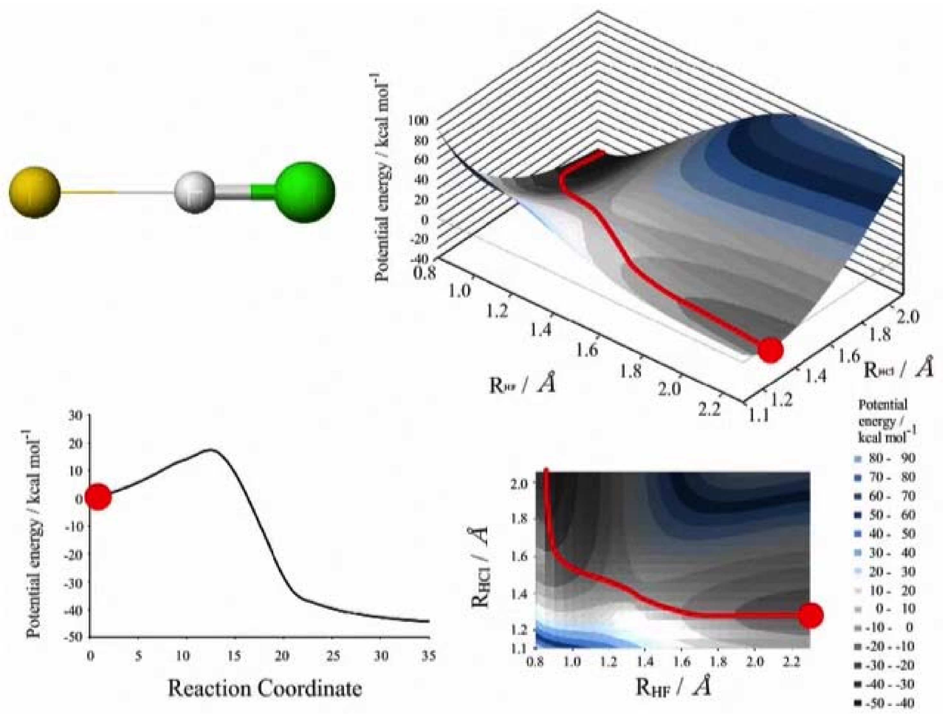

Figure 1 CG teaching material of F + HCl → HF + Cl

The transition state is located near the point of H-F distance of 1.376Å and H-Cl distance of 1.354 Å. The IRC method [7] supported the transition state. A single absorption peak in the negative region was found at -2858 cm^{-1}. The result indicates vibrational mode due to the decrease of potential energy for the direction of only one path *via* a true transition state at the saddle point. Energy between the initial state of reactants and the final state of products was 38.96 kcal mol^{-1}[10]. The value was in fairly good agreement with an experimental [8] value of 33.06 kcal mol^{-1}.

The Figure 1 clearly shows these changes of PEs with display on PE surface in 3-D, which offers a bird-eye view of the reaction profile. Two Valleys of lower energies and hilltop on the transition state at the saddle point can be recognized boldly. Possible pathways of the reaction from the reactants of F and HCl to the products of HF and Cl *via* the transition state at saddle point can be readily traced. CG teaching material is able to provide information about change of the PE and structure of reactants in a certain state simultaneously.

Reaction of $I + H_2 \rightarrow HI + H$

We developed a CG teaching material of rearrangement by collision of diatomic molecule and one atom. The transition state of the reaction is located nearby the point of 1.6 Å of I-H distance and 1.8 Å of H-H distance [5]. The electrostatic potential on electron density (EPED) model and the ball-and-stick model of the intermediate, I-H-H, and the reaction profile were combined in the left side of the Figure 2 for easier recognition of those three.

The electrostatic potential [11] was calculated based on the coordinates of atoms from the IRC calculation[7] and superimposed on to the iso-surface of the electron density at the value of 0.01 e $Å^{-3}$ as shown in the upper left part of the CG. The values of electrostatic potentials were represented in different color on the model of intermediate on the way of the reaction, and figure legend of color boundaries for electrostatic potential was also listed. Distribution of the electrostatic potential among the intermediate can be seen by the colors. For example, right side of H_2 molecule is positively charged with relative value of +0.09 based on evaluation of energy of interactions of prove proton to the charge of iso-surface. The model by EPED provides information about electrostatic distribution in intermediate with realistic shape on the way of the reaction.

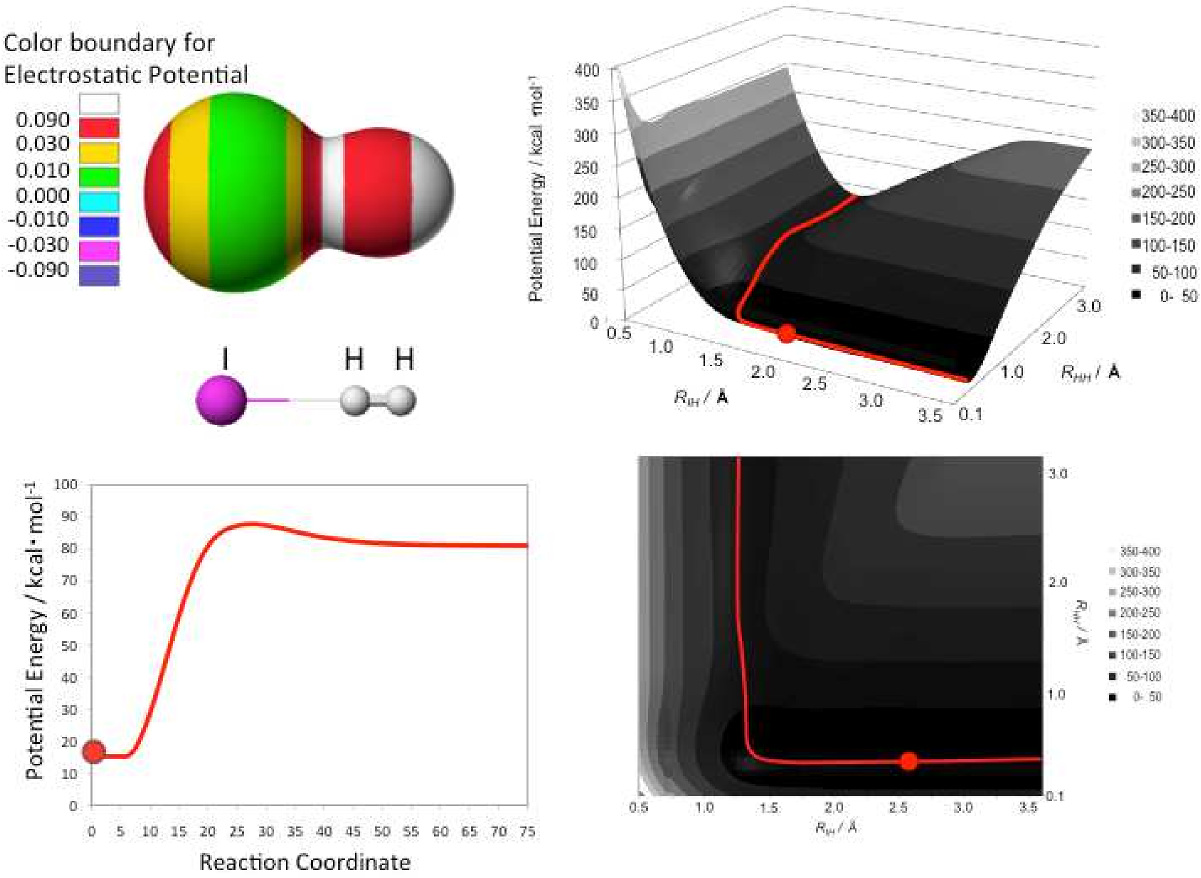

Figure 2 CG teaching material of I + H2 → HI + H

In the middle of CG, skeletal structure in the ball-and-stick model in which diameter of the stick reflects calculated bond order is shown. Lower left part of the CG shows PE *vs*. reaction coordinate, the reaction profile, which demonstrates the degree of the reaction progress by the ball. Student could correlate this reaction profile with the reaction path in the right side of CG. The left side of the CG is able to provide information about characteristics of intermediate of molecule in a certain state on the progress of reaction.

Form the survey conducted to the university student [12], the CG teaching material on the tablet computer (iPad) may creates positive attitude among the students toward the subject and it was effective to provide images of “Energy” change, “Structure” change, and “Migration of

Electron" during chemical reaction. Results of surveys suggested that the teaching material in the tablet computer could be an effective tool in laboratory class.

Reaction of $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$

Walden's inversion is one of important example of the bimolecular nucleophilic substitution reaction (S_N2 reaction), which inverse configuration of reactant. Therefore, the reaction is often adopted in teaching material on the curriculum of the university, including some appropriate schemes [13]. The schemes should be developed for student to acquire more realizable images of the nature of the reaction.

We developed CG teaching material for university student, concerned about reaction with drastic change of the structure of reactants in the reaction (Eq. 2) as a model of Walden's inversion. CG teaching material could demonstrate dynamism of structural change.

$OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$ (Eq. 2)

The inter-atomic distances of C-Cl in CH_3Cl was calculated as 1.87 Å (1.87 Å) [14], and C-O in CH_3OH was 1.41 Å (1.43 Å) [15]. These values were in good agreement with the literature values in the parentheses. Energy between the initial state of reactants and the final state of products was 165.01 kJ mol^{-1}. The value was in fairly good agreement with literature [16] value of 162.90 kJ mol^{-1}.

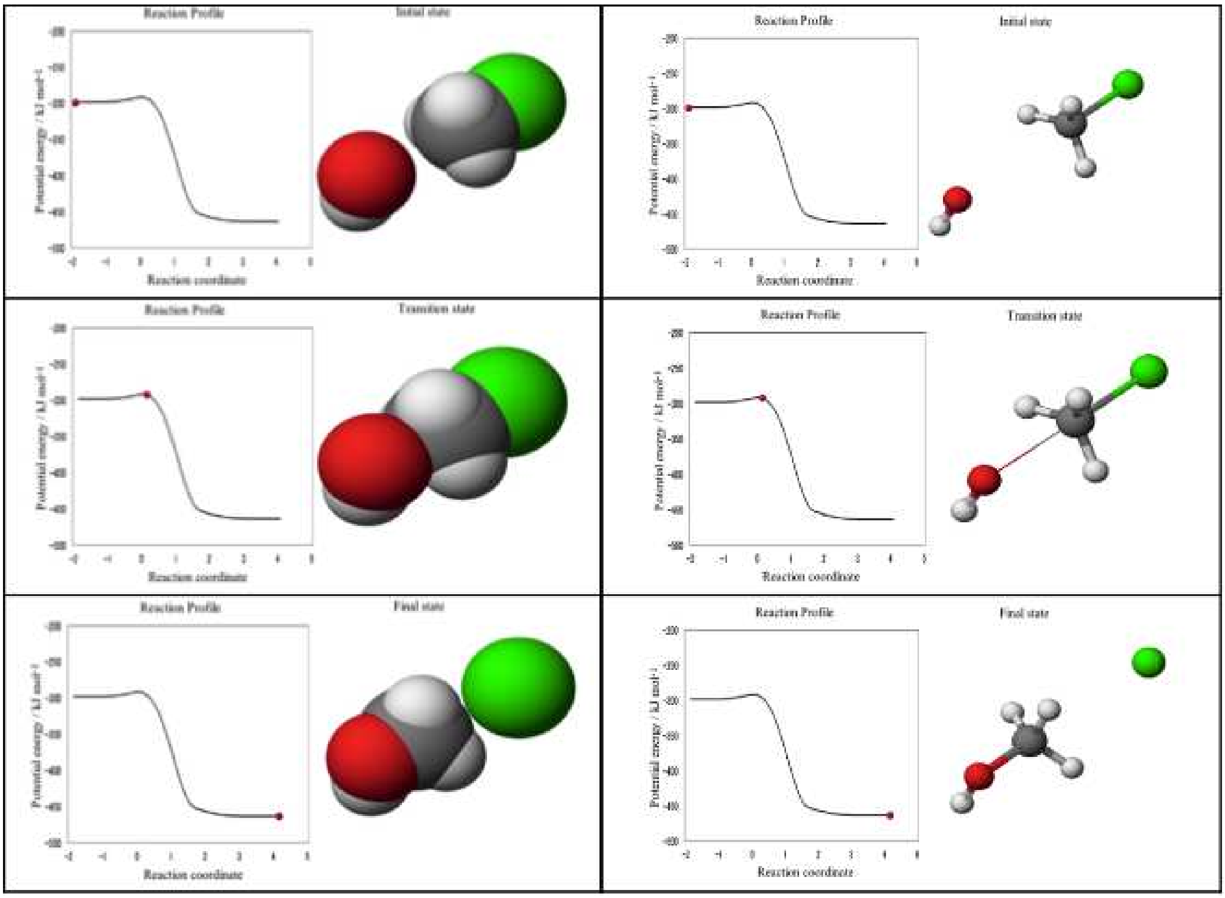

Figure 3 Selected picture from the CG teaching material

Selected picture of CG movies are shown in the Figure 3. The CG shows the reaction profile, potential energy vs. reaction coordinate, which demonstrates the degree of the reaction progress by the ball. Movies were made by using not only by the space filling model, which shows realistic shape, but also the ball-and-stick model, which shows change in molecular configuration easily.

A student is expected to obtain the image of an umbrella reversal like motion in Walden's inversion. In the space filling, the existence probability of the electron is 90 %. In the ball-and-stick, the thickness of stick changes by bond order. When the CG teaching material in the tablet PC is touched by student, the Quick Time control bar appears and the red ball can move by student's choice. This manual control feature provides "Hands-on" feeling to student. This CG teaching material could provide not only images of energy change during reaction but also images of dynamical structure change during chemical reaction.

The CG teaching material could demonstrate the structural change of reactants with both the space filling and the ball-and-stick models along with the reaction profile, which can provide image of energy change during the reaction.

Esterification of acetic acid and ethyl alcohol

CG teaching material of the esterification of acetic acid and ethyl alcohol is shown in the Figure 4. The electrostatic potential [11] was calculated based on the coordinates of atoms obtained previously [4] and superimposed on to the iso-surface as shown in the Figure 4.

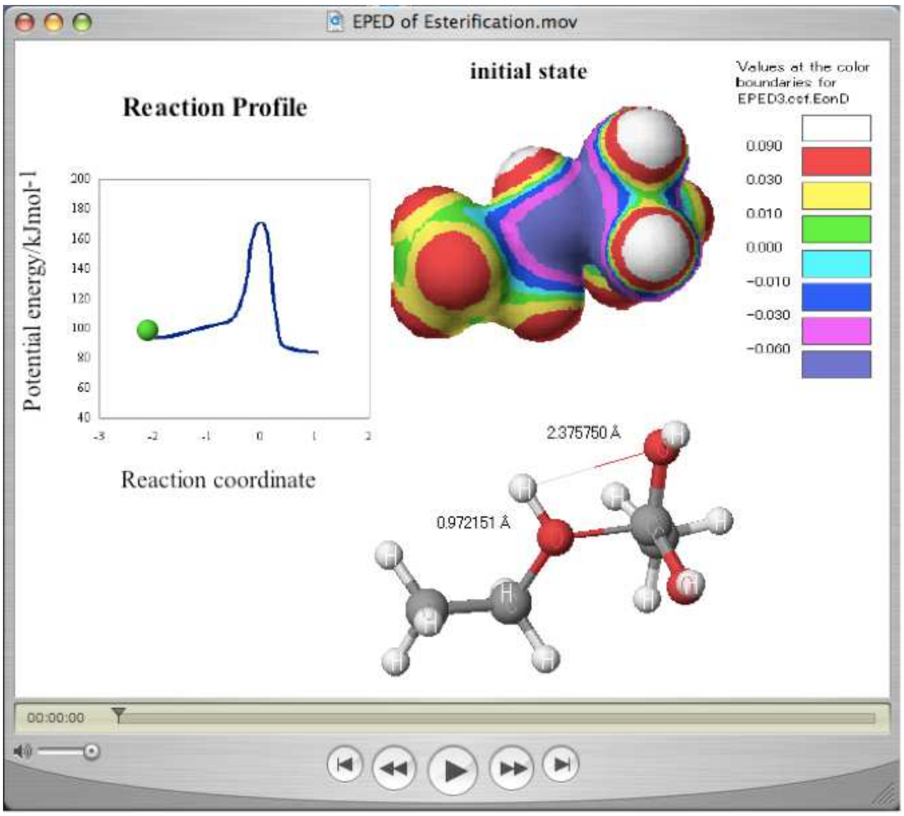

Figure 4 CG teaching material of the esterification

The values of electrostatic potentials were represented in different color on the model of intermediate in the transition state, and figure legend of color boundaries for electrostatic potential was also listed. Distribution of the electrostatic potential among the intermediate can be seen by the colors. 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 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 CG teaching material could simultaneously display realistic shapes and electrostatic potentials of reactants on the way of the reaction profile besides the ball-and-stick model as shown in the Figure 5.

The teaching material can play by student's choice of the way of automatic movement or manual movement. The CG teaching material can be loaded with note PC, tablet PC, and smart phone.

Prototype Electronic Laboratory Textbook

Produced CG teaching material could demonstrate the structural change of reactants in both the space filling with electrostatic potential and the ball-and-stick models along with the reaction profile, which could provide image of energy change during the reaction. The CG teaching material was integrated with electronic laboratory textbook for university student by means of iBooks Author (ver. 2.1.1, Apple, Inc.). The laboratory textbook could display picture of apparatus and

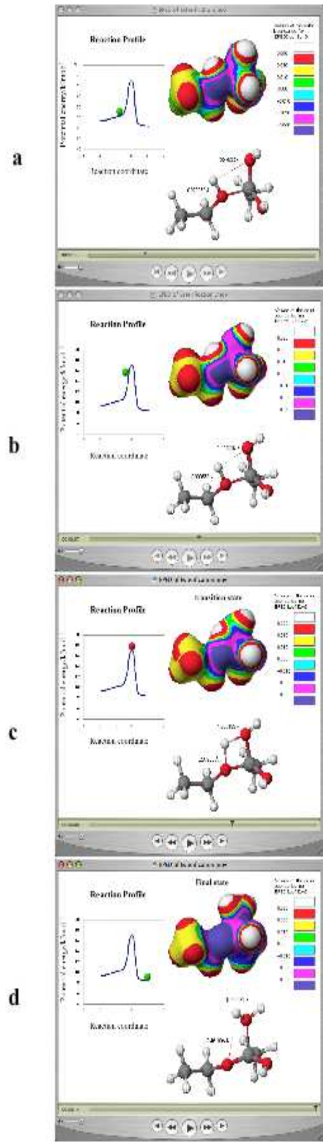

Figure 5 Selected picture of CG teaching material of the

flow-chart of small-scale experiment in addition to the CG teaching material of reaction mechanism.

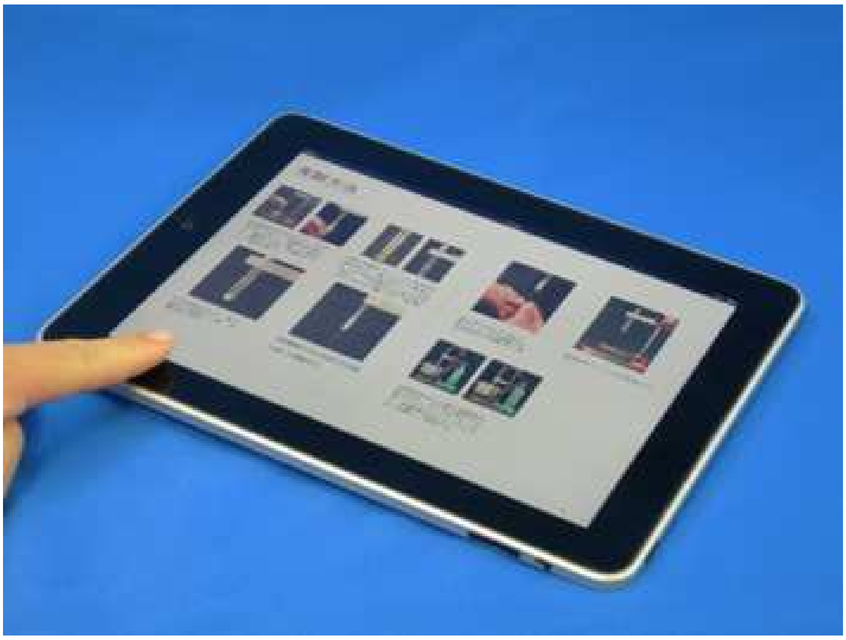

Figure 6 Prototype electronic textbook

The CG teaching material was tried to combine with chemical experiments of student's lab used tablet PC for the purpose of making electronic textbook of chemistry laboratory. Prototype electronic textbook is shown in the Figure 6. The textbook provides images of experimental procedure in the form of flow chart and picture of apparatus, which can be enlarged by students touch.

CONCLUSIONS

In this work, the change in the molecular configuration in basic chemical reaction such as, $F + HCl \rightarrow HF + Cl$, $I + H_2 \rightarrow HI + H$, $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$, and esterification of acetic acid and ethyl alcohol were visualized by the quantum chemical calculation. The CG teaching material could simultaneously display realistic shapes and electrostatic potentials of reactants on the way of the reaction profile besides the ball-and-stick model. The CG teaching material could be an effective tool to provide information about the nature of the reaction. The teaching material was tried to combine with chemical experiments of student's lab used tablet PC for the purpose of making electronic textbook of chemical experiments, which integrates observable level, molecular level, and symbolic level.

REFERENCES

1. Gilbert, J. K., Treagust, D. F., in Gilbert, J. K., Treagust, D. (Eds.), "Models and Modeling in Science Education **4** Multiple Representations in Chemical Education", Springer, (2009), 333-350.
2. Tasker, R., Dalton, R., in Gilbert, J. K., Reiner, M., Nakhleh, M. (Eds.), "Models and Modeling in Science Education **3** Visualization: Theory and Practice in Science Education", Springer, (2010), 103-131.
3. Kleinman, R. W., Griffin, H. C., Kerner, N. K., *J. Chem. Edu*., **64**, 766-770 (1987).
4. Ikuo, A., Ikarashi, Y., Shishido, T., Ogawa, H., *J. Sci. Educ. Jpn*., **30** (4), 210-215 (2006).
5. Ikuo A., Nagashima H., Yoshinaga Y., Ogawa H., *Chem. Educ. J*., **13**, Registration #13-2 (2009).
6. Stewart, J. J. P., *J. Comp. Chem*., **10 (2)**, 209-220 (1989).
7. Fukui, K., *J. Phys. Chem*., **74**, 4161-4163 (1970).
8. Martin, J. D. D., Hepburn, J. W., *J. Chem. Phys*., **109**, 8139-8142(1998).
9. Deskevich, M. P., Hayes, M. Y., Takahashi, K., Skodje, R. T., Nesbitt, D. J., *J. Chem. Phys*., **124**, 224303-1-224303-12(2006).
10. Ikuo, A., Nagashima, H., Yoshinaga, Y., Ogawa, H., in Guputa-Bhowon, M., Jhaumeer-Laulloo, S., Wah, H. L. K., Ramasami, P. (Eds.), "Chemistry Education in the ICT Age", Springer, (2009), 301-309.
11. Kahn, S. D., Pau, C. F., Overman, L. E., Hehre, W. J., *J. Am. Chem. Soc*., **108**, 7381-7396(1986).
12. Ikuo, A., Nagashima, H., Yoshinaga, Y., Ogawa, H., in Werner, B (Ed.), "Proceedings 2012 7th IEEE International Conference on Wireless, Mobile and Ubiquitous Technology in Education.", IEEE Computer Soc. CPS, (2012), 82-86.
13. For example: McMurry, J., "McMurry Organic chemistry" Tokyo Kagaku Dojin, Tokyo (2001), 272.
14. Weast, R. C., "CRC Handbookof Chemistry and Physics" 63rd ed., CRC Press, Inc, Boca Raton, Florida (1982), F180-181.
15. Shida, S., "Kagakujiten", Morikitasyuppan,Tokyo (1981), 1251.
16. Nihonkagakukai-hen, "Kagakubinran Kisohen" 3rd. ed., Maruzen, Tokyo(1984), II-314 and 319.

ACKNOWLEDGEMENT

This work was supported by JSPS Grant-in-Aid for Scientific Research (C) (25350188).