CG Teaching Material for the Electronic Laboratory Textbook
Esterification of Acetic Acid and Ethanol

Akira Ikuo, Yusuke Yoshinaga and Haruo Ogawa
Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan

Keywords: Teaching Material, Visualization, Electrostatic Potential, Quantum Chemical Calculation.

Abstract: CG animation of the esterification of acetic acid and ethyl alcohol was made based on quantum chemical calculations by use of MOPAC with PM5 Hamiltonian. The CG animation 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. A survey of five chemistry textbooks used in Japanese high school revealed that molecular models in chemistry were illustrated by popular molecular models such as ball-and-stick, space filling, and free-hand. There were only a few examples illustrated by the models with characteristics of molecules for chemical reaction mechanism. The CG animation could demonstrate these images of dynamical reaction mechanism for the esterification and can be loaded with tablet PC and smart phone. We are trying to produce an electronic laboratory textbook of the esterification in which the CG teaching material is combined with chemical experiments of student's laboratory.

1 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 (Gilbert, 2009 and Tasker, 2010). Student's difficulties and misconceptions in chemistry are from inadequate or inaccurate models at the molecular level (Kleinman, 1987). 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 (Ikuo, 2006 and 2009). 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 an electronic laboratory textbook, 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 getting information of molecule about bond length and its angle, shape, and so on. Generally, 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 of realistic shape and electrostatic potential of molecule for the purpose of making electronic laboratory textbook of the esterification, which integrates the observable level experiment and the molecular world, along with a survey of five chemistry textbooks used in Japanese high school about molecular models in chemistry.

Ikuo A., Yoshinaga Y. and Ogawa H..
CG Teaching Material for the Electronic Laboratory Textbook - Esterification of Acetic Acid and Ethanol.
DOI: 10.5220/0004961702260231
In *Proceedings of the 6th International Conference on Computer Supported Education* (CSEDU-2014), pages 226-231
ISBN: 978-989-758-022-2

2 PROCEDURE

2.1 Quantum Chemical Calculation

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 s MOPAC (Stewart, 1989) with PM5 Hamiltonian in 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, 2006). The electrostatic potential on electron density (EPED) (Kahn, 1986) was calculated based on structures from the results of the IRC calculation.

2.2 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 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 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. 10.7, Apple, Inc.).

2.3 Survey of High School Textbooks

Survey of five chemistry textbooks of "Chemistry I, II" used in Japanese high school (Textbooks of "Chemistry I" and "Chemistry II" in Japanese high school, 2003 and 2004) was conducted to investigate how the molecular models were used in chemistry in the actual circumstances.

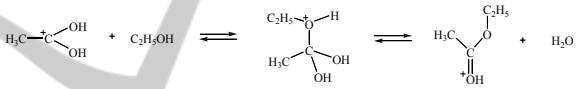
3 RESULTS AND DISCUSSION

3.1 Reaction Mechanism

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

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

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.

3.2 Optimization of the States of Reactants and Products on the Rate-determining Step

Appropriate geometry of reactants was calculated by the Eigenvector Following method in MOPAC. The calculation was carried out until the cut off value of less than 1 in root mean square (RMS) gradient. The calculation of optimization of the reactants was started from a certain state where reactants of acetic acid and ethyl alcohol with specific interactions. Tentative heat of formation, ΔH_f, was obtained by MOPAC calculation. ΔH_f s of the states of reactants and products are shown in the Table 1.

The ΔH_f value of the state of reactants was decreased from 262.6089 to 84.23436 kJ mol^{-1} after 40 cycles of geometry optimization with value of 0.96023 in RMS gradient. The value of RMS indicates that the calculation was converged. Therefore, calculated geometry of the reactants can be considered as the lowest in energy in the present calculation condition. Similarly, the calculation of the state of products was started from a certain state

where the carbonium ion and water with specific interactions. The ΔH_f value of the state was decreased from 891.7311 to 311.7951 kJ mol^{-1} after 87 cycles of geometry optimization with value of 0.67331 in RMS gradient. The value of RMS indicates that the calculation was also converged. Geometries of both the reactants and the products in the lowest energy were determined by these optimizations.

Table 1: Optimization of the states of reactants and products on the rate-determining step.

State	ΔH_f^a / kJ mol^{-1}		RMS gradient	Number of cycles
	Before optimization	After optimization		
Reactants[b]	262.6089	84.23436	0.96023	40
Products[c]	891.7311	311.7951	0.67331	87

[a] Tentative heat of formation by, was defined by MOPAC. Calculation was started from a certain state.
[b] Acetic acid and ethyl alcohol with specific interactions.
[c] The carbonium ion and water with specific interactions.

3.3 Determination of Transition State on Reaction Path of Rate-determining Step

Geometry of the intermediate in the transition state was searched by use of the program with the saddle point search in MOPAC. The optimized geometries of the reactants and the products mentioned in the above section were used with the data of starting files for the saddle point search. Through the calculation, reasonable structure of intermediate in the transition state was obtained. The structure was further refined by program refine transition state in MOPAC.

The vibrational analysis of the intermediate was performed by use of the program FORCE in MOPAC. A single absorption peak in the negative region was found at *ca.* -1200 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. The structure of intermediate obtained by MOPAC was almost identical to that calculated by Gaussian 03W at 6-31G(d) level. These mean a positive verification of optimized structure of the intermediate in the transition state.

The reaction path from the reactants to the products *via* the transition state was searched by the IRC calculation in MOPAC with the data files of the obtained intermediate of the transition state, and the files of the reactants and products as obtained in section 3.2. After the calculation, each reaction path from the transition state to the state of the reactants or reaction path from the transition state to the state of the products was searched individually where 1963 steps or 1046 steps were contained. Total number of 3010 steps means the same number of geometries of intermediates on all over the reaction path.

3.4 Atom Coordinates of the Intermediate

The atom-coordinates of the intermediate in transition state were extracted from the results of the IRC calculation in the above section. The Figure 1 shows them on three-dimensional coordinates, in which sphere size of atoms is proportional to atomic radius. The best angle of bird's-eye view on CG was selected to show all atoms composed in the intermediate.

Figure 1: Geometry of atoms in the transition state.
: oxygen, : carbon, : hydrogen

3.5 Iso-surface of Electron Density in the Transition State

An iso-surface of the electron density of the intermediate was calculated based on the coordinates of atoms mentioned in the above section and were shown in the Figure 2. The coordinates of atoms were converted to the iso-surface by this procedure. The iso-surface of the electron density at the value of 0.01 eÅ^{-3} was illustrated with the mesh pattern. The iso-surface demonstrates realistic shape of the intermediate.

3.6 Electrostatic Potential in the Transition State

The electrostatic potential (Kahn, 1986) was calculated based on the coordinates of atoms mentioned in section 3.4 and superimposed on to the iso-surface as shown in the Figure 3. The values of electrostatic potentials were represented in different colour on the model of intermediate in the transition state, 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 relative value of +0.09. The model by electrostatic potential provides information about electrostatic distribution of the intermediate on the way of the reaction.

3.7 Combination of the Electrostatic Potential Map, the Ball-and-stick Model, and the Reaction Profile on CG

The CGs of the EPED model mentioned in the above section, ball-and-stick model, which have been reported previously (Ikuo, 2006), and reaction profile on the same state were combined, and the obtained combination CG is shown in the Figure 4. The EPED model displays distribution of electrostatic potential on the surface of the intermediate with realistic shape, and the ball-and-stick model shows skeletal structure of the intermediate. The reaction profile demonstrates the degree of the reaction progress by the ball illustrated in the figure. The combination CG is able to provide information about electrostatic potential and structure of intermediate of molecule in a certain state simultaneously.

3.8 CG Teaching Material

The Quick Time movie file was created as teaching material by use of 100 frames of combination CGs. The Figure 5 shows five frames of representatives of 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 ball on the reaction

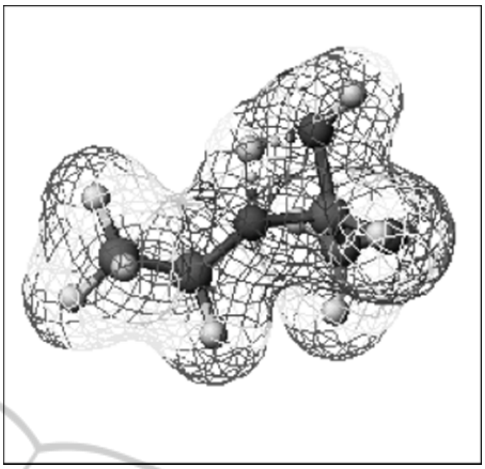


Figure 2: Iso-surface of electron density besides the ball-and-stick model in the transition state. Net represents iso-surface of electron density with 0.01 eÅ^{-3}

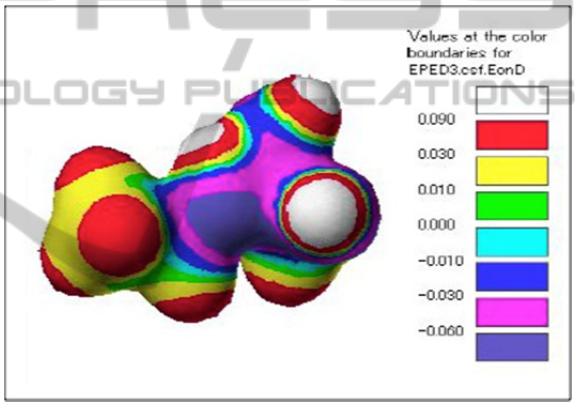


Figure 3: Electrostatic potential on electron density in the transition state.

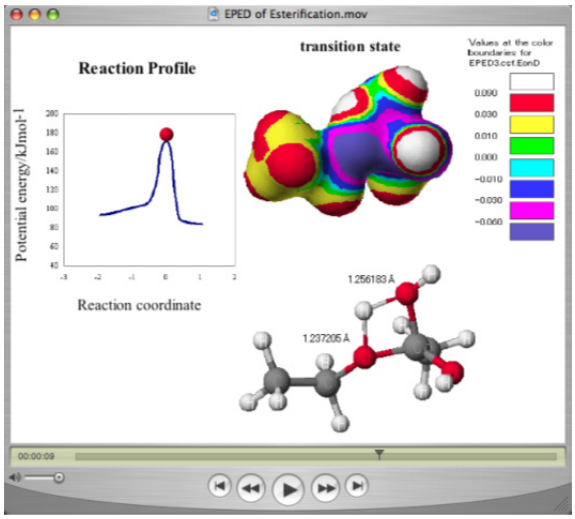


Figure 4: Combination CG of electrostatic potential map, ball-and-stick model, and reaction profile.

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). Other CGs such as EPED and ball-and stick modes are synchronized with the movement of the ball on the reaction profile by use of the Quick Time control bar so that the degree of the reaction progress and structural change of the molecules of all stages could be demonstrated simultaneously. The animation provides details of the chemical reaction mechanism dynamically. The CG teaching material can be loaded with tablet PC, and smart phone such as iPad and iPhone.

3.9 Survey of Textbooks

Since, it is usually the last chance for most of citizen to deal with molecular models, survey of five different textbooks each from "Chemistry I" and "Chemistry II" used in Japanese high school (Textbooks of "Chemistry I" and "Chemistry II" in Japanese high school, 2003 and 2004) was conducted to investigate how the molecular models were used in chemistry in the actual circumstances. Frequency of the use for representation of molecules by general molecular models is summarized in the Table 2.

Molecular models were illustrated by popular molecular models such as ball-and-stick, space filling, and free hand. A small number of molecular models were adopted to express polarity of molecule with a notation of δ^- or δ^+. Models expressing interactions of molecules such as hydrogen bond were found in some books. Models giving information about pseudo-reaction mechanism were found in two textbooks. These results reveal that there were only a few examples illustrated by the models with realistic shapes and characteristics of molecules for chemical reaction mechanism.

The survey implies that the proposed CG animation is significantly effective to realize images of the reaction mechanism for chemical reaction, *i.e.* the CG animation adopting the CG with electrostatic potential on electron density that can represent both of realistic shape and electrostatic potential of molecule. The CG animation would lead student to realize images of dynamical reaction mechanism for the reaction.

Integration of the present CG teaching material and laboratory textbook would serve as bridge between the observable level experiment and the molecular world.

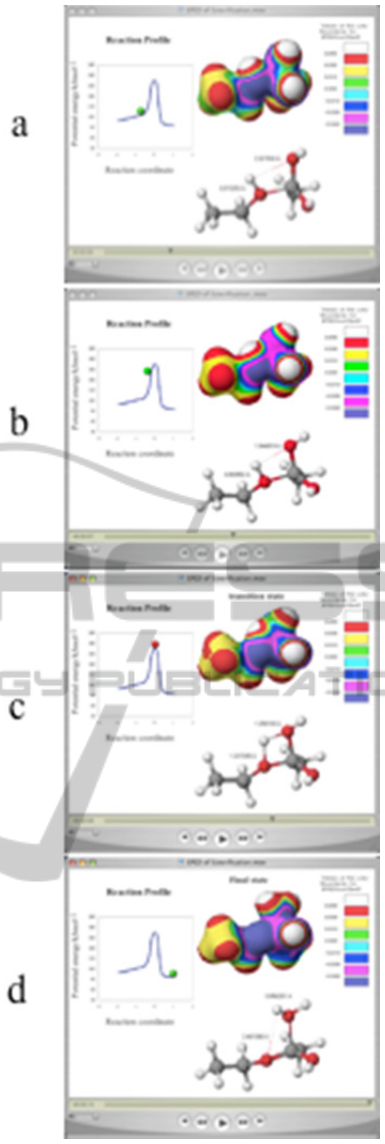


Figure 5: CG Teaching Material.

Table 2: Frequency of the use for representation of molecules by popular molecular models in high school chemistry textbooks.

Representation of molecules	Types of molecular models			
	Wire <Dreiding-like>	Ball-and-stick <HGS-like>	Space filling <Stuart-like>	Free-hand illustration
Structure	◎	◎	◎	◎
Polarity of molecule	–	○	○	○
Interactions of molecules	–	○	○	○
Reaction mechanism	–	–	△	△
Electrostatic potential	–	–	–	–

[a] Five Chemistry textbooks of "Chemistry I, II" in Japanese high school [7].
◎: used frequently in all textbooks; ○: used sometimes in all textbooks;
△: used once in two textbooks; –: not used in any textbooks.

4 CONCLUSIONS

The CG animation of esterification of acetic acid and ethyl alcohol could simultaneously display realistic shapes and electrostatic potentials of the intermediates on the way of the reaction profile besides the ball-and-stick model of the intermediates. A survey of five chemistry textbooks used in Japanese high school revealed that molecular models were illustrated by ball-and-stick, space filling, and free-hand, and there were only a few examples illustrated by the models with characteristics of molecules for chemical reaction mechanism. The proposed CG animation could demonstrate these realistic shapes and characteristics of molecules. The CG teaching material can be loaded with tablet PC, and smart phone such as iPad and iPhone. Now we are trying to produce an electronic laboratory textbook of the esterification in which the CG teaching material is combined with chemical experiments of student's laboratory.

ACKNOWLEDGEMENTS

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

REFERENCES

Fukui, K., 1970. A Formulation of the Reaction Coordinate, *J. Phys. Chem*., 74, 4161-4163.

Gilbert, J. K., Treagust, D. F., 2009. in Gilbert, J. K., Treagust, D. (eds.), "Models and Modelling in Science Education Vol. 4 Multiple Representations in Chemical Education", Springer, 333-350.

Ikuo, A., Ichikawa, T., Yoshimura, A. and Teratani, S., 1999. Computer Microscope ? Dynamics of Chemical Reactions, *Proc. Int. Conf. on Computers in Education*, 916-917.

Ikuo, A., Ichikawa, T. and Teratani, S., 2000. Chemical Reaction Observed with Computer Microscope, *J. Chemical software*, 6, 45-54 (In Japanese).

Ikuo, A., Tamura, S., Kojima, Y., Buqueron, S. S., Rahmat S. and Teratani, S., 2002. Interactive Animation of Chemical Reaction Based on Quantum Chemical Calculations - Computer Microscope 2002 -, *Proc. Int. Conf. on Computers in Education*, 1453-1452(30_73.PDF).

Ikuo, A., Ikarashi, Y., Shishido, T. and Ogawa, H., 2006. User-friendly CG visualization with animation of chemical reaction: esterification of acetic acid and ethyl alcohol and survey of textbooks of high school chemistry, *Journal of Science Education in Japan*, 30 (4), 210-215.

Ikuo A., Nagashima H., Yoshinaga Y., and Ogawa H., 2009. Calculation of potential energy in the. reaction of "I + H_2 → HI + H", and its visualization, *The Chemical Education Journal (CEJ)*, Registration #13-2.

Kahn, S. D., Pau, C. F., Overman, L. E. and Hehre, W. J., 1986. Modeling Chemical Reactivity. 1. Regioselectivity of Diels-Alder Cycloadditions of Electron-Rich Dienes with Electron-Deficient Dienophiles, *J. Am. Chem. Soc*., 108, 7381-7396.

Kleinman, R. W., Griffin, H. C., Kerner, N. K., 1987. *J. Chem. Edu.*, 64, 766-770.

Loudon, G. M., 1984. *Organic Chemistry*, Addison-Wesley Publishing Co., Inc., p.1010.

Nguyen, M. T., Ha, T. K., 1984. A theoretical study of the formation of carbonic acid from the hydration of carbon dioxide: a case of active solvent catalysis, *J. Am. Chem. Soc*., 106(3), 599-602.

Stewart, J. J. P., 1989a. Optimization of parameters for semi empirical methods I. Method*, J Comp. Chem*., 10 (2), 209–220.

Tasker, R., Dalton, R., 2010. in Gilbert, J. K., Reiner, M., Nakhleh, M. (Eds.), "Models and Modelling in Science Education Vol. 3 Visualization: Theory and Practice in Science Education", Springer, 103-131.

Textbooks of "Chemistry I" and "Chemistry II" in Japanese high school: Daiichigakusyusya, 2003 and 2004; Jikkyosyuppan, 2003 and 2004; Keirinkan, 2002 and 2003; Sanseido, 2003 and 2004; Tokyosyoseki, 2003 and 2004. (In Japanese) Textbooks were listed in alphabetical order.