

An Approach to Developing Electronic Textbook for Chemical Experiment

Taking Walden's Inversion as an Example

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Abstract: We are developing electronic textbook for of basic chemistry-experiment for university students in which reaction mechanisms are shown by computer graphics (CG). The CGs of chemical reactions was made based on the empirical molecular orbital calculations. The CGs include following reactions as a model of Walden's inversion where drastic change in structure takes place, such as, formation of 2-butyl alcohol and 1-butyl bromide. The CGs could simultaneously demonstrates the nature of the reaction such as structural change by the space-filling model and by the ball-and-stick model in addition to providing image of energy change by the reaction profile. The electronic textbook also displays picture of apparatus and flow-chart of small-scale experiment. Result of preliminary study on effectiveness of the CG is included.

1 INTRODUCTION

Understanding the observation of the reaction, chemists try to explain observations by using molecular models. Observation and molecular models are then described by chemical equation. 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 molecule (Tuvi-Arad, 2006).

It is our aim to produce a CG teaching material based on quantum chemistry calculations, which provides realizable images of the nature of 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 is combined with textbook of chemical experiments of student's laboratory, students can observe the reaction from the three thinking levels (Gilbert, 2009 and Tasker, 2010), namely, phenomena in the observable level and the CG in the molecular level, and chemical equation in the symbolic level. Our ultimate goal is to produce an electronic textbook of chemical experiment, which integrates these three thinking levels.

Electronic textbook has several advantages over paper textbook. For example, realistic image can be shown by photograph or 3-dimensional CG, and movie. These images could be, photograph of experimental apparatus, CG of molecular structure and CG movie of reaction mechanism. In addition, programmable capability (for example, Singhose, 2013), hyper-link, and networking features provide inter-active operation. Many electronic textbooks of chemistry are found but most of them are very similar to the paper book, and very few are related to the chemical experiment (Morvant, 2013). Moreover, combination of the CG movie of reaction and experiment are not seen.

Walden's inversion is one of typical reactions in organic chemistry, and the reaction is often adopted in teaching material on the curriculum of the university, including some appropriate schemes, which are trying to show drastic change in structure (McMurry, 2001). The schemes should be developed for student to acquire more realizable images of the nature of the reaction. Reaction of hydroxide and chloromethane is a typical example of the Nucleophilic Substitution in the 2nd order reaction. Carbon atom at the centre to which halogen attaches is attacked by the nucleophile, hydroxide, from a position 180 degrees from chlorine and then methyl alcohol forms. We reported CG visualization of the

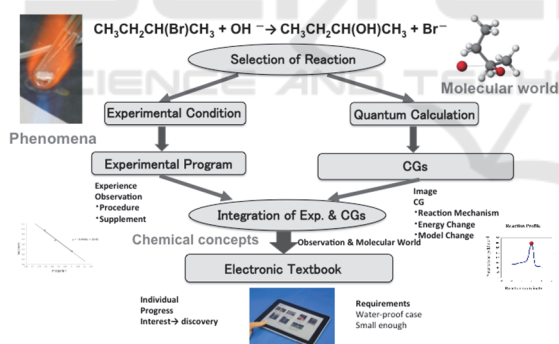
reaction as a simple model of Walden's inversion and the produced CG in the tablet PC effectively provide information about the nature of the reaction, such as drastic structural change (Ikuo, 2012).

This paper introduces our works of CG visualization of formation of 2-butyl alcohol and 1-butyl bromide for realizing certain images of the reaction mechanism of Walden's inversion, which is aiming at development of the electronic textbook for chemical experiment of student's laboratory at the university and trying to integrate the observable level experiment and the molecular world of the Walden's inversion.

2 METHOD

2.1 Developing Experimental Program and Textbook

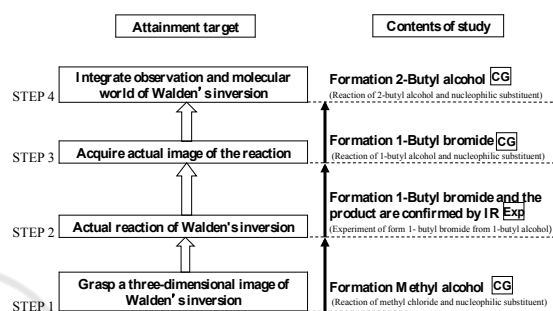
Flow chart adopting a policy (Ikuo, 2015) of developing an electronic textbook for chemical experiment is shown in the Scheme 1. Reaction was selected based on importance in fundamental chemistry. To exhibit phenomena (left side), experimental condition was optimized for college level small-scale chemistry-experiment.



Scheme 1: Flow chart of developing experimental program and textbook.

The experimental program is made based on the above-mentioned policy. The attainment targets and contents of an experimental program are shown in the Scheme 2. The reaction to which methyl alcohol is generated from methyl chloride is studied with CG teaching material as a typical example of the nucleophilic substitution in the 2nd order reaction. A learner is expected to grasp a three-dimensional image of Walden's inversion in STEP1. The experiment that forms 1-butyl bromide from 1-butyl alcohol with simple experiment apparatus is conducted and the reactant and the product are

confirmed by the infrared spectroscopy. A learner studies an actual reaction of Walden's inversion by this unit in STEP2. In addition, the reaction that forms 1-butyl bromide done by the experiment is studied with CG teaching material to obtain molecular image of the reaction. A learner is expected to acquire an actual image of the reaction in STEP3. The reaction to which 2-butyl alcohol is generated from 2-butyl bromide and the nucleophilic substitution is studied with CG and a learner is expected to integrate observation and molecular world of Walden's inversion in STEP4.



Scheme 2: The attainment target and contents of an experimental program.

2.2 Creating CG based on Quantum Chemistry Calculation

Structures of intermediates on reaction 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). A single absorption peak in the imaginary region was confirmed by -134.36 cm^{-1} in the reaction of 1-butyl bromide formation and -327.28 cm^{-1} in the reaction of 2-butyl alcohol formation. Structure changes of intermediate at the transition state were confirmed. The structures of the initial state, the transition state and the final state were obtained by the IRC calculation as shown in Figure 1 and 2.

The Gibbs energies and the inter-atomic distances obtained by the calculation were in good agreement with the literature values. Energy changes during reactions were confirmed. Therefore, it was concluded that the reaction path and the molecular

geometry obtained by the calculation were appropriate for making the CG teaching material.

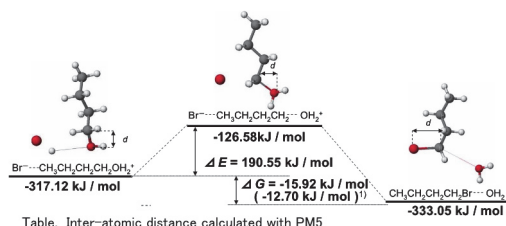


Table. Inter-atomic distance calculated with PM5

Sample	d / Å		
	Calculation	Experimental	Subtraction
Br ⁻ ...CH ₂ CH ₂ CH ₂ CH ₂ OH ₂ ⁺	1.40	1.43± 0.01 ²⁾	-0.03
Br ⁻ ...CH ₂ CH ₂ CH ₂ CH ₂ ...OH ₂ ⁺	2.57		
CH ₂ CH ₂ CH ₂ CH ₂ Br...H ₂ O	1.97	1.937± 0.003 ²⁾	0.03

1) Nihonkagakukai Ed., 1984. Handbook of chemistry Basic 3rd edition, Maruzen, 314. 2) Robert C. Weast Ph.D. Ed.1982. CRC Handbook of Chemistry and Physics 63rd edition, CRC Press, Inc., F180-181

Figure 1: Results of formation 1-butyl bromide.

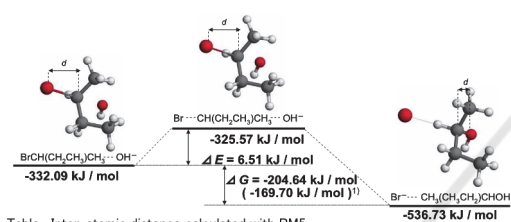


Table. Inter-atomic distance calculated with PM5

Sample	d / Å		
	Calculation	Experimental	Subtraction
BrCH(CH ₂ CH ₂)CH ₂ ...OH ⁻	2.09	1.937± 0.003 ²⁾	0.15
Br...CH(CH ₂ CH ₂)CH ₂ ...OH ⁻	2.30		
Br ⁻ ...CH ₂ (CH ₂ CH ₂)CHOH	1.42	1.43± 0.01 ²⁾	-0.01

1) Nihonkagakukai Ed., 1984. Handbook of chemistry Basic 3rd edition, Maruzen, 314. 2) Robert C. Weast Ph.D. Ed.1982. CRC Handbook of Chemistry and Physics 63rd edition, CRC Press, Inc., F180-181

Figure 2: Results of formation 2-butyl alcohol.

2.3 Creating CG Teaching Material 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 the ball-and-stick and space filling models were combined with reaction profile of the corresponding reaction stage. It was confirmed that the drawn CGs of the molecular models of reactants moves smoothly. The ball, which indicates progress of the reaction, was arranged on the reaction profile and simultaneous movements of the ball and the reactants were confirmed. Rotational models were made with PyMOL (ver. 1.7, Schrödinger). 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. 2.4, Apple, Inc.) and was saved to iPad (Apple, Inc.) by using the iTunes (ver. 12.3, Apple, Inc.).

3 RESULTS AND DISCUSSION

3.1 Feature of Electronic Textbook

CG teaching materials of the Walden's inversion were combined 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 of the flow chart (Figure 3) and slides of photographs (Figure 4), which can be enlarged by students touch.

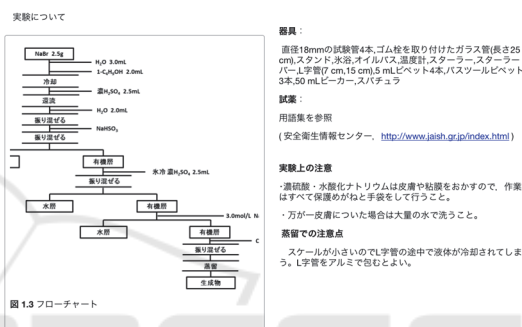


Figure 3: Enlargeable flow chart of experimental procedure.

CG teaching materials of reaction profiles in both models, the space filling and the ball-and-stick, were also inserted (Figure 5). The CG shows the reaction profile, which demonstrates the degree of the reaction progress by the ball indicating the potential energy vs. the reaction coordinate. 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. If student touches the material again, the Quick Time control bar appears and the red 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. A student is expected to obtain the image of an umbrella reverse like motion in Walden's inversion.

If student wants to watch the model from different angle, one could rotate the model (Figure 6) by touching the CG.



Figure 4: Slide Picture of apparatus.

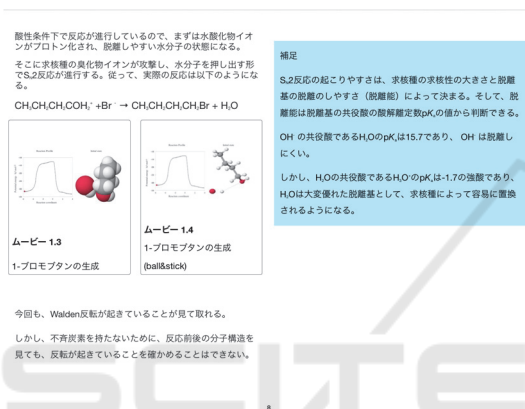


Figure 5: CG teaching materials.

② 1-プロモブタンの生成

次は、実験によって以下のようなS₂反応を実際に進めてみよう。また、得られた生成物はIRを用いて確認してみよう。

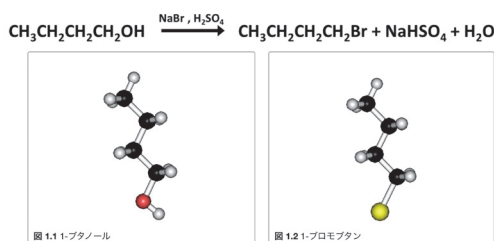


Figure 6: Rotational models.

3.2 Practice of Teaching Material

The CG Teaching material was practiced on 5 students, the second and third year students of teacher training course at Tokyo Gakugei University. Teaching material used for the trial was the CG movie shown by the tablet computer. Pre and Post survey about image of Walden's inversion reaction were conducted.

After watching CG teaching material, student image of the structure change was improved. Students described their comments in the free description section of the questionnaire, such as, "With image, it was easier for me to understand the way of inversion," and "I could see the reaction mechanism and progress by the movie." These comments suggested that the teaching material was able to provide image of the inversion. Another student commented "It was good because I could rotate the molecule." This comment suggested that the rotational model helped student to obtain structure of molecule.

Although more study need to be done on the effectiveness of the electronic textbook, students were able to obtain image of the Walden's inversion.

4 CONCLUSIONS

We developed computer graphics teaching material for university student, concerning reaction with drastic change of the structure of reactants in following reaction as example of Walden's inversion; formation of 2-butyl alcohol and 1-butyl bromide. The CGs could demonstrate the drastic change of the structure and the reaction profile can provide image of energy change during the reaction. The textbook could display picture of apparatus and flow-chart of experiment in addition to CGs. Preliminary study on effectiveness of the CG suggested that students were able to obtain image of the Walden's inversion. The developed electronic textbook in the tablet could be used to integrate the observable level experiment and the molecular world.

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