Chapter 19
An Approach to Developing Electronic Laboratory Textbook—Experimental Program of Esterification of Acetic Acid and Ethanol

A. Ikuo, Y. Yoshinaga and H. Ogawa

Abstract A computer graphics (CG) teaching material of the esterification of acetic acid and ethyl alcohol was made based on the quantum chemistry calculation. The CG teaching material could simultaneously display realistic shapes and electrostatic potentials of the molecules on the way from the state of reactants to that of products. The teaching material could demonstrate images of dynamical reaction mechanism of the esterification. We have integrated the teaching material with the laboratory manual of chemical experiments for University students to develop an electronic textbook. The textbook in the tablet PC could display not only experimental procedure but also the reaction mechanism by the CG teaching material.

Keywords CG · Visualization · Electronic textbook

19.1 Introduction

To understand the observed phenomena, chemists have been used to imagine and explain observation in terms of molecules (Fig. 19.1).

Observed phenomena and molecular level models are then represented in terms of mathematics and chemical equation [1, 2]. Students' difficulties and misconceptions in chemistry are from inadequate or inaccurate models at the molecular level [3]. Visualization is of great help for students to have images at the molecular level. It is our aim to produce computer graphics (CG) teaching material based on

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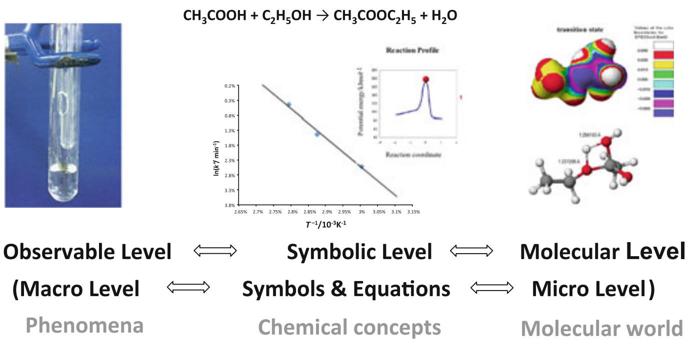


Fig. 19.1 Dividing the image into the three thinking levels

the quantum chemistry calculation, which provides students with clear images of the nature of chemical reaction [4]. If the CG teaching material is integrated with the laboratory manual of chemical experiments for University students, students would observe the reaction from three thinking levels, namely, phenomena in the observable level, the CG teaching material in the molecular level, and chemical equation in the symbolic level. Our ultimate goal is to produce an electronic textbook for chemistry experiments, which integrates these three thinking levels.

Electronic textbook has several advantages, such as attaching movie and programmable capability, over paper textbook. Interactive web-based electronic textbook was reported [5]. By using the tablet PC, interactive electronic textbook was produced for the mechanical engineering [6]. In the field of chemistry, inclusion of lecture movie to the electronic textbooks is common [7, 8]; however, limited number of electronic textbook deals with the laboratory manual [9]. Moreover, combination of CG movie of reaction mechanism and experiment has not been reported.

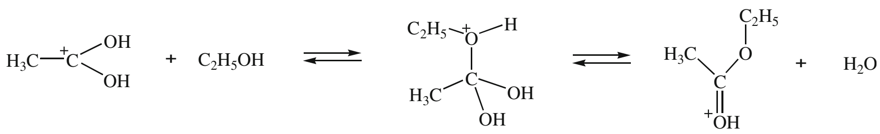
We report here a CG teaching material adopting the CG with the electrostatic potential on electron density (EPED) model that represents both the realistic shape and electrostatic potential of molecule, and an approach to developing electronic textbook for University students which could encourage students to integrate the observable level experiment and the molecular world of the esterification reaction.

19.2 Procedure

19.2.1 Calculation

Esterification of acetic acid and ethyl alcohol is described as shown in the Eq. 19.1.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O \quad (19.1)$$



Scheme 19.1 Mechanism of the esterification in the rate-determining step

The mechanism of the reaction is well known [10], and generally, the esterification proceeds in the presence of a proton catalyst. The rate-determining step includes the 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 19.1. As this step dominates all over the reaction, therefore, 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 [11], it was not considered in this paper for simplicity of the program.

The structures of intermediates of the esterification of acetic acid and ethyl alcohol and their electrostatic potentials on electron density were calculated as follows: the semi-empirical molecular orbital calculations MOPAC [12] with PM5 Hamiltonian in CAChe Work System for Windows (Former name of Scigress, ver. 6.01, FUJITSU, Inc.) was used in all the 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 [13]. Details of procedure of the quantum chemistry calculations were described in a previous paper [4]. The electrostatic potential on electron density (EPED) model [14] was calculated [15] based on structures from the results of the IRC calculation.

19.2.2 Production of Electronic Textbook

A movie of the reaction path was produced by the DIRECTOR (ver. 8.5.1J, Macromedia, Inc.) software, after displaying the bond order of structure of reactants in each reaction stage, which was drawn by the CAChe software. The obtained CGs of the EPED model, the ball-and-stick model, and reaction profile were combined. The Quick Time movie file was created by use of 100 frames of combination CGs. It was confirmed that the drawn CGs of the molecular models of reactants move smoothly in the produced movie. The green ball, which indicates progress of the reaction, was arranged on the reaction profile and simultaneous movements of the ball and the models of reactants were confirmed. The produced movie file was converted to the Quick Time movie for iPad by the Quick Time PRO (ver. 7.66, Apple, Inc.) software. Electronic textbook was produced with iBooks Author software (ver. 2.1.3, Apple, Inc.).

19.3 Results and Discussion

19.3.1 CG Teaching Material in Tablet PC

Figure 19.2 shows the combination CGs of molecules on the way from the state of reactants to that of products via the transition state. The CG teaching material demonstrates changes of the electrostatic potential and realistic shape of the reactants on the reaction profile in all stages at the same time.

The values of electrostatic potentials were represented in different color on the model of reactants in the transition state, and the figure legend of color boundaries for electrostatic potential was also listed. Distribution of the electrostatic potential among the reactant 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 the iso-surface, and hydrogen of carbonium ion is positively charged with relative value of +0.09. The model by the electrostatic potential provides information about change of electrostatic distribution of molecules on the way from the state of reactants to that of products.

The green ball on the reaction profile indicates the most probable pathway of chemical reaction according to the IRC theory [13]. Other CGs such as the EPED model and the ball-and-stick model are synchronized with the movement of the ball

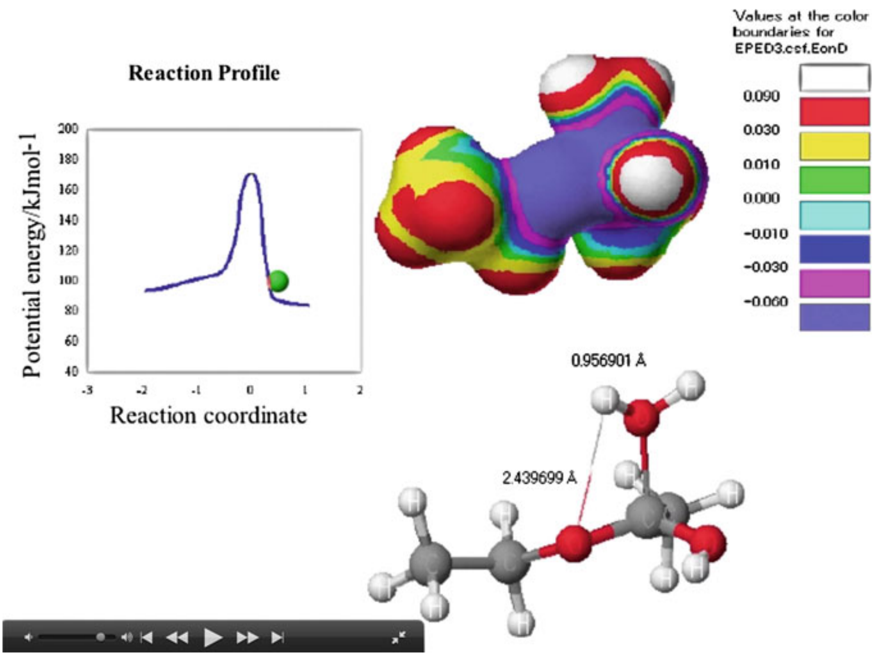


Fig. 19.2 CG teaching material

on the reaction profile. By using the Quick Time control bar, the degree of the reaction progress can be changed which simultaneously changes the structure of the reactant. When a student touches the teaching material in the tablet computer, the Quick Time control bar appears and the green ball on the profile can be moved by student's choice. The students can manipulate the reaction back and forth until they obtain the image of the reaction. The CG teaching material provides details of the chemical reaction mechanism dynamically.

19.3.2 Electronic Textbook in Tablet PC

In order to integrate the observable level and the molecular level, the small-scale chemical experiments of students' laboratory, and the CG teaching material were integrated in the electronic textbook. The experimental section of the electronic textbook was inserted with images of experimental procedure in the forms of flowcharts and pictures, which can be enlarged by students' touch (Fig. 19.3). The CG teaching materials of reaction profiles were inserted in the textbook (Fig. 19.4). When a student touches the icon on the profile, the teaching material appears to show the image of the structural change during the reaction. After studying the concept of activation energy with the text and the CG teaching

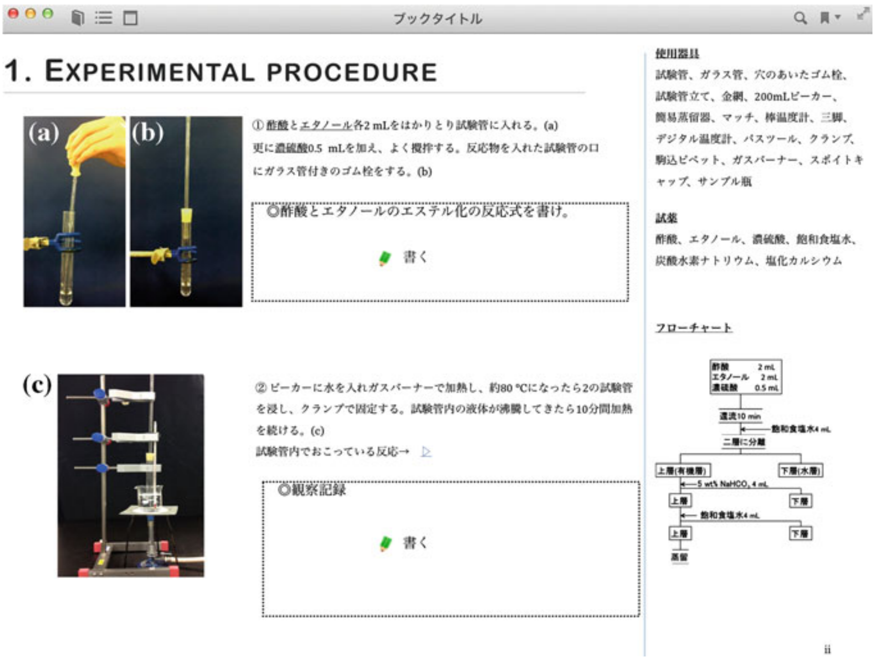
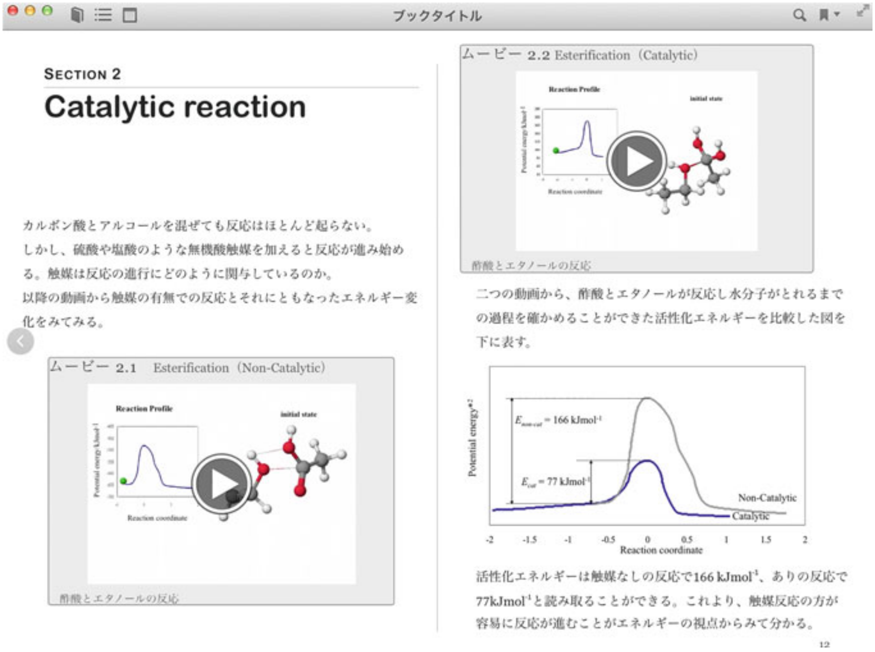


Fig. 19.3 Experimental procedure from the electronic textbook



ブックタイトル

SECTION 2

Catalytic reaction

カルボン酸とアルコールを混ぜても反応はほとんど起らない。
しかし、硫酸や塩酸のような無機酸触媒を加えると反応が進み始める。触媒は反応の進行にどのように関与しているのか。
以降の動画から触媒の有無での反応とそれにともなったエネルギー変化をみてみる。

ムービー 2.1 Esterification（Non-Catalytic）

酢酸とエタノールの反応

ムービー 2.2 Esterification（Catalytic）

酢酸とエタノールの反応

二つの動画から、酢酸とエタノールが反応し水分子がとれるまでの過程を確かめることができた活性化エネルギーを比較した図を下に表す。

活性化エネルギーは触媒なしの反応で166 kJmol^{-1}、ありの反応で77kJmol^{-1}と読み取ることができる。これより、触媒反応の方が容易に反応が進むことがエネルギーの視点からみて分かる。

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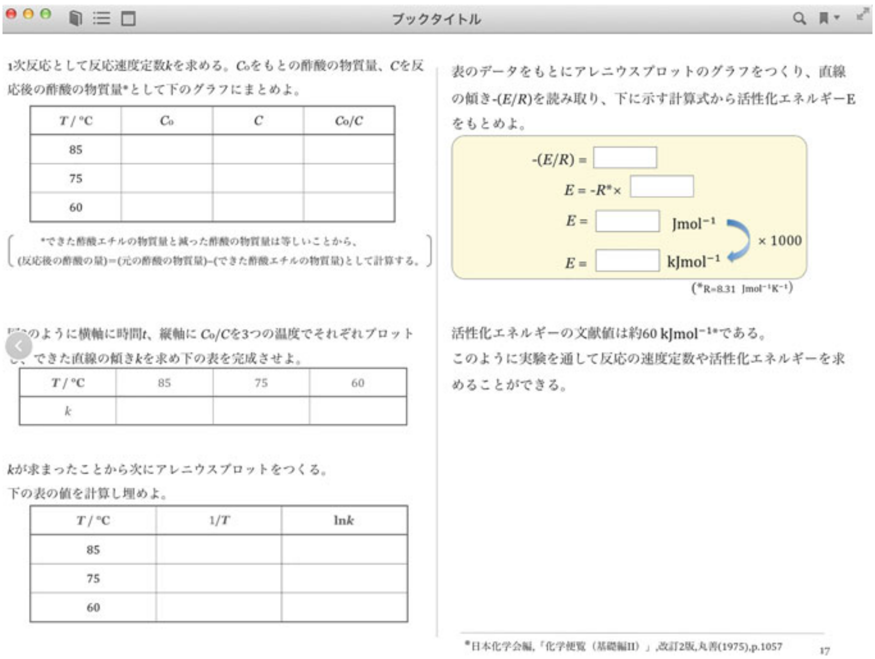
Fig. 19.4 CG teaching material in the electronic textbook



ブックタイトル

1次反応として反応速度定数kを求める。C_0をもとの酢酸の物質量、Cを反応後の酢酸の物質量*として下のグラフにまとめよ。

T / °C	C_0	C	C_0/C
85			
75			
60			

*できた酢酸エチルの物質量と減った酢酸の物質量は等しいことから、
(反応後の酢酸の量)=(元の酢酸の物質量)−(できた酢酸エチルの物質量)として計算する。

[illegible]のように横軸に時間t、縦軸にC_0/Cを3つの温度でそれぞれプロットし、できた直線の傾きkを求め下の表を完成させよ。

T / °C	85	75	60
k			

kが求まったことから次にアレニウスプロットをつくる。
下の表の値を計算し埋めよ。

T / °C	$1/T$	ln$k$
85		
75		
60		

表のデータをもとにアレニウスプロットのグラフをつくり、直線の傾き-(E/R)を読み取り、下に示す計算式から活性化エネルギーEをもとめよ。

$-(E/R) =$ □
$E = -R^{*} \times$ □
$E =$ □ Jmol^{-1}
$E =$ □ kJmol^{-1}
× 1000
(*R=8.31 Jmol^{-1}K^{-1})

活性化エネルギーの文献値は約60 kJmol^{-1}*である。
このように実験を通して反応の速度定数や活性化エネルギーを求めることができる。

*日本化学会編,「化学便覧（基礎編II）」,改訂2版,丸善(1975),p.1057

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Fig. 19.5 Determination of activation energy in the electronic textbook material, the student could actually measure the apparent activation energy from the product yield at different temperatures, in the advanced section of the experiment (Fig. 19.5). The obtained activation energy of 56.5 kJ mol^{-1} agreed with the literature value of ca. 60 kJ mol^{-1} [16].

19.4 Conclusions

The CG teaching material of the esterification of acetic acid and ethyl alcohol was made based on the semi-empirical molecular orbital calculation. The CG teaching material could simultaneously display realistic shapes and electrostatic potentials of the molecules on the way from the state of reactants to that of products. The teaching material could demonstrate images of dynamical reaction mechanism of the esterification. We have integrated the teaching material with the laboratory manual of chemical experiments for University students to develop an electronic textbook. The textbook in the tablet PC could display not only experimental procedure but also the reaction mechanism by the CG teaching material. After studying the concept of activation energy, students could actually measure the apparent activation energy. The textbook could be used to encourage students to integrate the observable level experiment and the molecular world of the esterification.

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