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Development of Teaching Material in Tablet PC for Experiment of Nitration of Benzene Based on Computer Graphics by Quantum Chemical Calculation

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Abstract: The change in the structure of reactants about the transition state after the π-complex in nitration of benzene was visualized by CG based on the semi-empirical molecular orbital calculation. Teaching material could demonstrate the structural change of reactants with both space filling and ball-and-stick models along with the reaction profile, which can provide image of energy change during the reaction. The teaching material was tried to integrate with an electronic textbook of chemical experiment for the student's laboratory.

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

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. Observable-level phenomena and molecular-level models are then represented in terms of mathematics and chemical equation, which is at the symbolic-level (Gilbert & Treagust, 2009). If these levels are introduced together, numerous opportunities should be given to relate them, so that linkages are formed in the long-term memory (Tasker & Dalton, 2010). Student's difficulties and misconceptions in chemistry are from inadequate or inaccurate models at the molecular-level (Kleinman et al., 1987). Visualization based on quantum chemical calculations is great help for students to have images at the molecular-level. It is our aim to produce CG teaching material, which provides realizable images of the nature of chemical reaction (Ikuo, Nagashima, et al., 2012). If the CG teaching materials were combined with chemical experiments of student's laboratory, students would observe the reaction from the three thinking levels. Our ultimate goal is to produce such an electronic textbook that can be used not only in the classroom but also in the experimental laboratory.

Nitration of benzene is one of typical reactions in organic chemistry, and the reaction is often adopted in teaching material on the curriculum of high school and the university, including many appropriate schemes (For example: McMurry, 2001). The scheme should be developed for student to acquire more realizable images of the nature of the reaction. The reaction proceeds *via* intermediates 1) π-complex and 2) σ-complex (Esteves et al., 2003. Queiroz et al., 2006.), and overall reaction is controlled by those intermediates. Recently, we developed CG teaching material of the reaction 2) σ-complex (Ikuo, Ono, et al., 2012). In this work, the change in the structure of reactants about 1) was followed by the semi-empirical molecular orbital method. Produced teaching material was tried to integrate with an electronic textbook of chemical experiment for the student's laboratory.

2. Procedure

a. Quantum Chemistry Calculation

The semi-empirical molecular orbital calculation software MOPAC (Stewart, 1989) with PM5 Hamiltonians in CAChe Work System for Windows (ver. 6.01, FUJITSU, Inc.) was used to find the transition state and the reaction profile of chemical reactions. The structure of the reactants on the transition state was searched by use of the optimized structure of reactants. 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) (Fukui, 1970) calculation was performed to verify the reaction profile.

b. Production of Teaching material of CG and Electronic Textbook

A movie of the reaction profile was produced by the software DIRECTOR (ver. 8.5.1J, Macromedia, Inc.) following the display of the structure of the reactants in each reaction stage, which was drawn by the CAChe (ver. 6.01, FUJITSU, Inc.). The movie file was converted to the Quick Time movie by the Quick Time PRO (ver. 7.66, Apple, Inc.). Electric textbook was produced with iBooks Author (ver. 2.0, Apple, Inc.) and was saved to iPad (Apple, Inc.) by using the iTunes (ver. 11, Apple, Inc.).

3. Results and Discussion

a. Validation of Teaching Material

From the result of the vibrational analysis of reactants on the transition state, single absorption peak in the imaginary region was observed at -343.29 cm^{-1}; therefore, the structure of the transition state was verified. The reaction path from the reactants to the product *via* the transition state was searched by the IRC calculation, and molecular configuration of each step on the reaction profile was obtained. The activation energy was 25.96 kJ mol^{-1}, which was within the estimated value (Esteves et al. 2003) of 29.29 kJ mol^{-1}. Furthermore, bond length, l, and angle of the product was in good agreement with reported value (Nihonkagakukai-hen, 1984) in parentheses, for example, l_{CN} = 149 (147) pm and l_{NO} = 122 (122) pm, and angle of N-O-N = 123.5 (122.8) degree. Therefore, it was confirmed that the reaction profile and the molecular configurations obtained by the calculation were appropriate. The Quick Time movie file was produced as teaching material.

b. Electronic Textbook

Selected pictures of teaching material are shown in the figure 1. Left part of the material shows the reaction profile, potential energy *vs*. reaction coordinate, which indicates the degree of the reaction progress by the red ball on the profile. Right part shows structural change shown in space-filling model, which exhibits the existence probability of the electron of 90 %. While choreographed animation of chemical reaction are common (For example, Tasker & Dalton, 2010), CG based on theory in the present study could provide not only images of energy change but also images of dynamical structure change with more realistic shape. When student touches the material in the tablet computer, 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

b

c

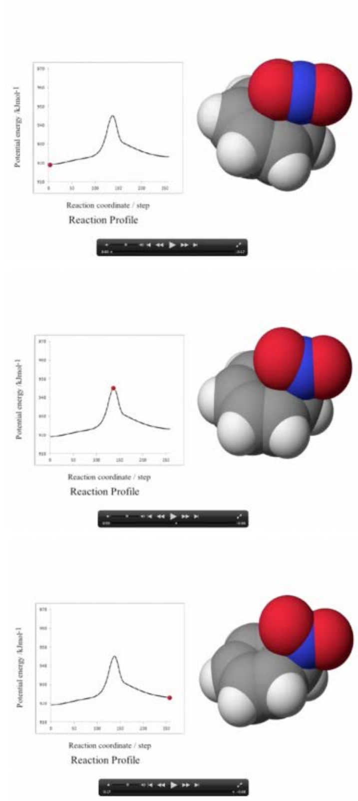

Figure 1 Teaching material
a: initial, b: transition state, c: product

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 of the reaction profile was also inserted. When student touches the icon on the profile, the teaching material appears to show image of the structural change during the reaction.

Tablet computer was covered with waterproof plastic-bag and was used for practice of five students of the third year in the chemistry course of the Tokyo Gakugei University. After explanation of usage of the tablet, 5 tablets were distributed to the students. Students were able to start the experiment smoothly by watching experimental procedure in the tablet, and after 60 minutes they were able to finish the reaction safely. During the reaction, students had time to watch the teaching material repeatedly. These results indicated that the electronic textbook was able to provide information about experimental procedure sufficiently and that students were interested in watching the teaching material during the experiment.

4. Conclusions

The change in the structure of reactants about the transition state after the π-complex in nitration of benzene was visualized by CG based on the semi-empirical molecular orbital calculation. Teaching material could demonstrate the structural change of reactants with both space filling and ball-and-stick models along with the reaction profile, which can provide image of energy change during the reaction. The teaching material was tried to integrate with an electronic textbook of chemical experiment for the student's laboratory. The electronic textbook was able to provide information about experimental procedure sufficiently and that students were interested in watching the teaching material during the experiment.

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