Calculation of Potential Energy Concerning 
"H + Cl₂ → HCl + Cl" and Production of CG Movie for Learner to Acquire Its Image with Structures of Reactants and Reaction Profile

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Geometries and potential energies for reactants of "H-Cl-Cl" around the transition state in the reaction of H + Cl₂ → HCl + Cl were calculated. The reactant on the transition state was formed at incident angle of 180°. This reactant was supported by the method of the intrinsic reaction coordinate (IRC). We produced a movie, which displays CGs of potential energy surfaces in 2-D and 3-D for reactants on the way of the reaction. The reaction profile with potential energy and structures of the reactants are also displayed. The profile was synchronized with the structures. The CG movie was tried, and it was improved through the application to student's learning on the Web. It was effective for students to acquire images of the reaction from the standpoint of its potential energy and molecular structure.

Keywords: Potential energy surface, HCl formation, Incident angle, Visualization, CG movie

1 Introduction

The reaction of hydrogen atom and halogen molecule and related reactions have played a fundamental role in the development of chemical kinetics and theoretical chemistry [1,2]. For example, a study on the reaction of Cl + H₂ or D₂ has been reported by calculating potential energy (PE) surface [3]. Arrhenius parameters were computed in the reaction of H + Cl₂ [4], and an empirical value of activation energy in the reaction was reported [5]. However, the reaction of H + Cl₂ has not been clarified enough in details such as PE surface in three-dimension (3-D) especially from the standpoint of incident angle. The incident angle of atom approaching to halogen molecule decides the reaction [6].

Visualization of computer graphics (CG) is a great help to realize not only images of molecules but also images for dynamical reaction mechanism. The visualization has been tried and reported, for example, the interactive movie of hydrogen atomic orbital based on the atomic orbital calculation [7,8] and molecular structures of 215 organic compounds in the field of life science based on the molecular mechanics calculation [9,10]. It is our aim to produce programs, which provide images of chemical reactions. A CG movie of chemical reaction of carbon dioxide and water based on molecular orbital calculations was reported [11]. The reaction was energetically favored compared to that with one molecule of water. The CG with two molecules of water has been demonstrated. The CG movie of esterification of acetic acid and ethyl alcohol has also been reported [12].

Reaction profile is generally used to represent relationship between PE and reaction coordinate. This is often used in high school chemistry textbooks [13]. It is sometimes difficult for the learner to realize the meaning of reaction coordinate. Visualization of PE surface in 3-D could clearly provide images of reaction coordinate from the standpoint of subject on energy. A Figure of PE surface in 2-D or contour diagram is often used in

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university physical chemistry textbooks [6]. A limited number of images on PE surface in 3-D is used in these textbooks. In this paper, we report the calculation of the PE at various incident angles in the reaction of H + Cl₂ and produce PE surface in 3-D. A CG movie, which provides images of potential energy and reaction profile, was produced and was tried in undergraduate laboratory class. Although energy difference is relatively small it may provide image of the simple reaction.

2 Procedure

2.1 Calculation based on quantum chemistry

The semi-empirical molecular orbital calculation software MOPAC in the CAChe Work System for Windows ver. 5.04 (former name of SIGRESS, Fujitsu, Inc.) with PM5 Hamiltonian was used in all calculations for optimization of geometry by the Eigenvector Following method, for search of potential energies of various geometries of reactants by use of the program with Optimized map, 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 calculation of the intrinsic reaction coordinate (IRC) [14].

2.2 Production of potential surface

Data of potential energies and geometries of reactants were extracted from the "energy.map" file from the calculation of Optimized map, and these were pasted on the worksheet of Excel (Microsoft). Potential energy surface in 3-D was drawn by the Excel.

2.3 Production of CG movie

A CG was drawn by the CAChe (former name of SIGRESS, Fujitsu, Inc.), and both CG movies by Quick Time (Apple, Inc.) and by Shockwave were produced by the DIRECTOR 8.5 J software (Macromedia, Inc.). The Web page was produced by the Homepage builder software (IBM, Inc.).

3 Results and discussion

3.1 Optimization of states of reactant Cl₂ and product HCl

The reaction of H + Cl₂ shown in the Scheme 1-a is well known [6]. An attack of a hydrogen atom to a chlorine molecule leads to form hydrogen chloride.

Appropriate geometry of chlorine molecule and hydrogen chloride was calculated by the Eigenvector Following method in MOPAC with PM5 Hamiltonian. The calculation was carried out until the cutoff value of less than 1.0 in gradient of root mean square (RMS). The optimization of Cl₂ was started at the point of initially defaulted value of inter-atomic distance. Tentative heat of formation, ΔHᵓ, was obtained by MOPAC calculation. ΔHᵓ on the state of Cl₂ was obtained. Gradient of RMS was initially acceptably small, and the self-consistent field (SCF) was achieved. Geometry of Cl₂ can be considered as the lowest in the energy. The ΔHᵓ value of Cl₂ was 7.8311 kcal mol⁻¹. Similarly, the optimization of HCl was started at the point of initially defaulted value. The ΔHᵓ value was decreased from −30.06345 to −30.41859 kcal mol⁻¹ in 3 cycles of optimization. Finally, the value of RMS gradient of 0.73810 was obtained. The value was also acceptably small, and the SCF was achieved. Geometries of both Cl₂ and HCl in the lowest energy were determined by these optimizations.

3.2 Inter-atomic distances of Cl₂ and HCl

Inter-atomic distances of Cl₂ and HCl obtained from the calculation in the above section are listed in the Table 1 besides references of empirical values in parentheses [15]. Inter-atomic distances of Cl₂ and HCl were 1.969 Å (1 Å = 100 pm) and 1.232 Å, respectively. These values show good agreement with empirical values, Cl₂ and HCl are 1.988 Å and 1.275 Å, respectively [15]. PM5 Hamiltonian was used for calculation of PEs hereafter.
Table 1. Inter-atomic distances of Cl₂ and HCl calculated by MOPAC/PM5.

| Method  | Interatomic distance / Å |
|---------|--------------------------|
| Cl-Cl   | 1.969 (1.988)³          |
| H-Cl    | 1.232 (1.275)³          |

³ Determined by ultraviolet spectroscopy and microwave spectroscopy cited in Kagakubinran Kisoen II, p. 797*, p. 798*, respectively: Maruzen (2004).

3.3 Approaching route of H to Cl₂

3.3.1 Dependence of incident angle of H approaching to Cl₂ on potential energy

Image of incident angle, θ, of H approaching to Cl₂ is shown in the Scheme 1-b. Reactants for calculation of the PEs were produced as follows. Inter-atomic distance of Cl₂ obtained in the previous section was adopted for the reactants. The incident angle was changed in a range from 90 to 270° at intervals of 2°. Inter-atomic distance of H-Cl was changed from 1.9 to 3.9 Å at intervals of 0.03 Å. PE of each reactant described above was calculated by MOPAC with PM5 Hamiltonian. The PE expressed with color is shown in 2-D in the Figure 1-a along with Figure legend of color boundaries for PE. The incident angle is drawn as a horizontal axis and inter-atomic distance of H-Cl is drawn as a vertical axis. Distribution of the PE can be seen by the colors. For example, PE was the highest around incident angles of 90° and 270° which is exhibited clearly on PE surface in 3-D in the Figure 1-b. PE was the lowest at the angle of 180°, which indicates path of the lowest energy via the saddle point. Energy difference between states of the reactants and the transition state was ca. 5 kcal mol⁻¹ which was ca. 5 kcal mol⁻¹ lower than that of angle of 90° or 270°. This difference in energy is large for radical reaction in which activation energy is generally 4.7 to 7.7 kcal mol⁻¹ [16]. For the reaction, the incident angle of 180° is energetically favored. This reaction path is supported by the method of the IRC [14]. The result is also supported by the observation of orbital overlap of HOMO-LUMO, which was large at incident angle of 150° to 210°.

3.3.2 Potential energy of wide range of incident angle

The range of the incident angles was extended from former mentioned range of 90 to 270° to 0 to 360° and shown in the Figure 2-a in 2-D and the Figure 2-b in 3-D. As the incident angle decreased from 90 to 0°, PE increased drastically. Similar change was observed in the range of 270 to 360°. From the dependence of incident angle of 0 to 360° on PE, the reaction occurs most easily when the incident angle is 180°.

The reaction path by the IRC calculation leads to the steepest path to reach product of stable state in energy, and when it is reached to the stable state, the calculation is terminated automatically. This procedure is fast but view of path is limited to the steepest path. The PE surface as shown in the Figure 2-b provides not only the steepest path but also other paths, which may require more energy. This birds-eye view of PE surface provides the way of thinking as to which path reaches the product. This method could provide a global image of the reaction path although application is limited to simple reactants.

3.4 Application to education by CG movie

3.4.1 Production of CG movie

A Web-based CG movie was produced in order to provide images of potential energy and reaction path. Selected examples of CGs are shown in the Figures 3 to 6. Dependence of
The inter-atomic distances of H-H and H-Cl on PE is shown in the Figure 3. Distribution of PE can be seen by the colors. In the Figure, valley of low energy can be recognized. PE surface in 3-D is shown in the Figure 4. The Figure clearly demonstrates areas of high PE and low PE. Combination CGs of PE surfaces in 2-D and 3-D with structure of reactant is shown in the Figure 5. This CG demonstrates change of PE and the structure simultaneously. The reaction profile and structure of the reactant can be seen in the Figure 6. Structural change and progress of the reaction are synchronized.

3.4.2 Evaluation of CG movie

A questionnaire survey was carried out to investigate whether understanding of potential energy and the reaction path was improved by showing the CG movie mentioned in the previous section. The survey was conducted on 73 first and second year students in science major, class A to C of Tokyo Gakugei University. The contents of the questionnaire including six questions a through f in both English and Japanese are listed on Table 2. At first, students were asked to answer the questionnaire, which was printed on the front side of the questionnaire sheet as a pre-test. Second, after filling out the questionnaire, the CG movie was shown to the students. Finally, students were
asked again to answer the questionnaire of the same contents as a post-test, which was printed on the reverse side of the sheet.

Results are shown in the Table 3. Before the CG movie was shown, 100%, 89%, and 87% were correctly answered in questions of e (1), e (2), and f, respectively, while 19% and 22% in questions of (c) and (d) were correctly answered. Results indicate that students understood the concept of transition state well but not about PE and reaction path. Percentage of the correct answer was generally improved after showing the CG movie. The students acquired images of PE and the reaction path. Percentage of correct answer for the question of b decreased after showing the CG movie. It was thought that the student misread as the transition state is the lowest in the PE because other part of the surface appeared to have large PE when the PE surface was seen in the CG movie in the Figure 5.

3.4.3 Evaluation of revised CG movie

The CG movie was revised to prevent the misreading mentioned in the previous section. The reaction profile was added in the way that its height of the potential energy was enhanced. Screen capture of the CG movie is shown in the Figure 7.
achieved by showing the revised movie. This movie could be used as a supplemental material to the Figure of reaction profile often used to teach "structure and the chemical equilibrium of the material" that are a unit of senior high school chemistry II [13]. The CG movie could be applied in the high school not to mention in the university. The CG can be seen at http://www.u-gakugei.ac.jp/~ikuo/cm/HCl.html.

4 Conclusion

Geometries and PE for reactants of "H-Cl-Cl" around the transition state in the reaction of H + Cl₂ → HCl + Cl were calculated. The reactant on the transition state was formed at incident angle of 180 °. The transition state was supported by method of the IRC. The movie displays CGs of potential energy surfaces in 2-D and 3-D for reactants on the way of the reaction. The reaction profile with potential energy and structures of the reactants are also displayed. The profile was synchronized with the structures. The movie was tried, and it was improved through the application to student's learning on the Web. It was effective for students to acquire images of the reaction from the standpoint of its potential energy and molecular structure.

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