

Minimum Change of “Shapes” of Molecular Orbitals in the Elementary Chemical Reactions and a New Perspective of Quantum Chemistry

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Chemical substances are highly diverse. Here, we discuss the regularities of chemical changes among the substances. As a typical example, the regularity of the change between benzene and its structural isomers, i.e. Dewar benzene and prismane, has been discussed in terms of molecular vibrational theory and orbital correlation diagrams. It has been shown that when a certain molecule changes to another one with a similar structure, the “shapes” of the original electronic states are transferred to the next ones with minimum change. Regarding this, it has been pointed out that Neumann-Wigner’s non-crossing rule need not be applied to orbital correlation diagrams. It has also been shown that changes of molecules are “quantized” and cannot be described continuously, i.e. the states which can be accurately described by the Schrödinger equation are limited to “quantum steady states”.

Key words: Elementary Reaction, Conservation of Orbital Phase, Dynamic Correlation Diagram, Non-crossing Rule, Schrödinger Equation

1. Introduction

Modern chemistry is based on theories such as Dalton’s atomic theory, Avogadro’s molecular theory, and Frankland’s atomic valence theory, etc. However, in order to understand the regularity that controls the world of atoms and molecules, we needed the discovery of the electron by Thomson in 1897, followed by the construction of quantum mechanics, the clarification of atomic structure, and the detailed study of the nature of atomic valence.

Furthermore, in 1861, the Russian chemist Butlerov proposed the concept that the nature of substances is dependent on their chemical structures, which is one of the most basic common recognitions among chemists today. Thus, the elemental compositions and the structural configurations of numerous substances have been clarified by many researchers, and such efforts for clarification are still ongoing. We keenly realize the perfection of this systematized theoretical framework when we search libraries of chemical compounds in the formula index.

The Chemical Abstracts Service of the American Chemical Society continuously compiles compounds which have confirmed structures. The number of such compounds was reported to be 50 million in October 2009, reaching 70 million in December 2012 (FoodWatchJapan/Science/15856). Here, such a compound is considered to maintain a stable chemical structure for a certain period of time.

Meanwhile, the concept of a chemical reaction is that certain stable compounds change into other stable ones over time. In such a chemical reaction, with what regularity or

over what period of time will the molecules change? Here, we discuss this issue from a new perspective.

2. The Rate of Chemical Reactions and the Elementary Chemical Reactions

It is generally said that inorganic chemical reactions are fast, while organic chemistry reactions are slow. For example, when a AgNO_3 solution is added to a NaCl solution, white precipitates of AgCl immediately appear. On the other hand, in the synthesis of acetanilide, aniline and acetic acid require heating for one to several hours. Moreover, for the synthesis of ethyl acetate from ethanol and acetic acid, a reaction time from several hours to several days is required. However, the reaction rate in these examples refers to the time taken for all or almost all of the Avogadro’s number of molecules to react. It should be noted that the reaction rate of elementary chemical reactions, in which one or several molecules change, is a different concept. Then, what time is needed for these elementary chemical reactions?

3. Structural Isomer of Benzene and the Rate of Mutual Conversions

It is generally understood that, as Kekulé thought, the structure of benzene consists of a hexagonal ring frame of six carbon atoms, each of which is attached to a hydrogen atom. When irradiating benzene with light under certain conditions, structural isomers of benzene, such as Dewar benzene, prismane, benzvalene and fulvene are formed, all of which have a molecular formula of C_6H_6 (Fig. 1).

Each of these compounds has a definite stable chemical structure. Here, we consider the change of Dewar benzene (2) to benzene (1), where there seems to be the smallest

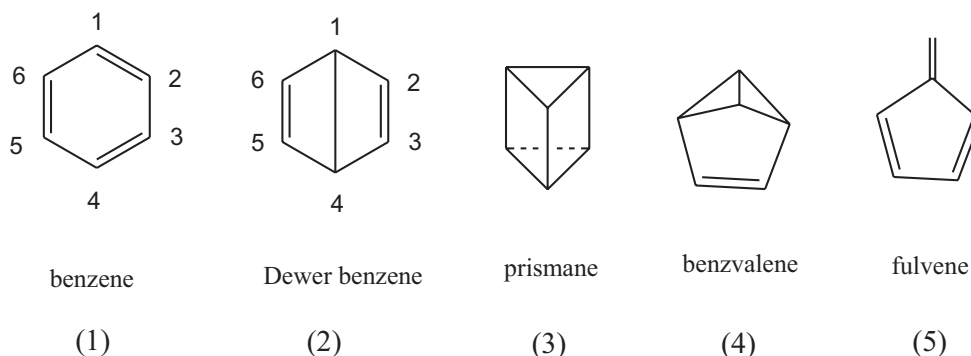


Fig. 1. Typical structural isomers of benzene.

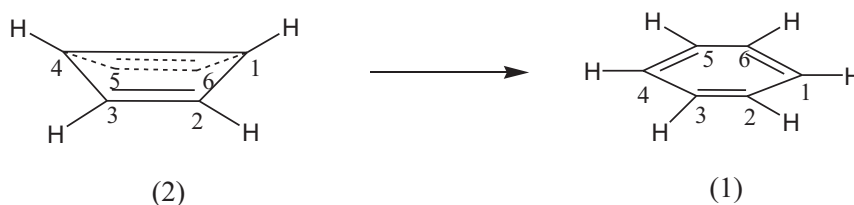


Fig. 2. The conversion of Dewar benzene to benzene.

change in terms of reorganization of atoms and atomic valences. That is, the bond between carbon 1 and carbon 4 of Dewar benzene (2) breaks to form benzene (1). Although Dewar benzene is a stable molecule, the constituent atoms are not prohibited to move from their static positions. Indeed, each atom actively moves in the vicinity of their static bond distances and angles.

According to the theory of molecular vibration, the degree of freedom for a nonlinear n -atom molecule is $3n - 6$. The number of vibrational degrees of freedom for Dewar benzene is, therefore $3n - 6 = 30$. Although the structure of Dewar benzene is expressed by the formula of (2) in Fig. 2, the actual molecule exists in complicated motion.

From the theory and the measurement of infrared absorption spectroscopy and Raman scattering spectroscopy, molecular vibrations are repeated at a frequency of 10^{13} – 10^{14} times per second. Since all the movements of constituent atoms of the molecule are regulated by its characteristic vibration, both much faster and much slower movements compared to the vibrational rates are forbidden. Even if the vibration is very large, the molecule should be recognized as the same molecule as long as the average coordinates are the same as the original one. It can be said that a chemical reaction occurs at the moment when a molecule cannot return to its original vibrational coordinates and passes to another vibrational state. Thus, we can conclude that changes of molecules in all chemical reactions proceed in durations of the order of molecular vibrational periods, i.e. 10^{-13} – 10^{-14} s.

In this way, we can define an elementary reaction as a one-step reaction that does not have any stable intermediate molecules or stable activated complexes (Nohira and Nohira, 2012). As a result, the elementary reaction is regarded as the minimum unit of chemical changes.

4. The Electronic Orbital Correlation Diagram for the Structural Isomer of Benzene

4.1 Dynamic correlation diagram and the minimum change of “shapes” of molecular orbitals

In a previous paper, we have proposed the dynamic correlation diagram method based on the idea of the minimum change of “shapes” (phases) of molecular orbitals. We have also pointed out that Neumann-Wigner’s non-crossing rule (Neumann and Wigner, 1929) need not be applied to the orbital correlation diagrams (Nohira and Nohira, 2012). Here, we explain the method of drawing the dynamic correlation diagrams. First, the approximate energy levels of the orbitals of the reactants are written from top to bottom on the left-hand side of each diagram, while those of the products are given on the right-hand side. Next, we consider the change of the key orbitals, in other words where bond cleavage occurs in the reactant, and where bond formation occurs in the product. Then, we can easily draw a correlation line by considering the changes in the “shapes” (phases) and energy levels of each molecular orbital. Finally, the remaining orbitals can be linked by applying the principle of minimum change of orbital “shapes” (phases). In the previous paper, we reported dynamic correlation diagrams for the Diels-Alder reactions of butadiene and ethylene, electrocyclic reaction of hexatriene to cyclohexadiene, and electrophilic substitution of naphthalene, which are explained by Fukui’s frontier orbital (FO) theory. With these diagrams, we succeeded in consistently explaining Fukui’s FO theory (Fukui *et al.*, 1952; Fukui, 1971) and Woodward-Hoffmann’s orbital symmetry conservation (W-H) theory (Woodward and Hoffmann, 1965, 1969).

4.2 Dewar benzene-benzene

Based on the same principle as above, we report the dynamic correlation diagram and the corresponding state diagram for the conversion of Dewar benzene to benzene

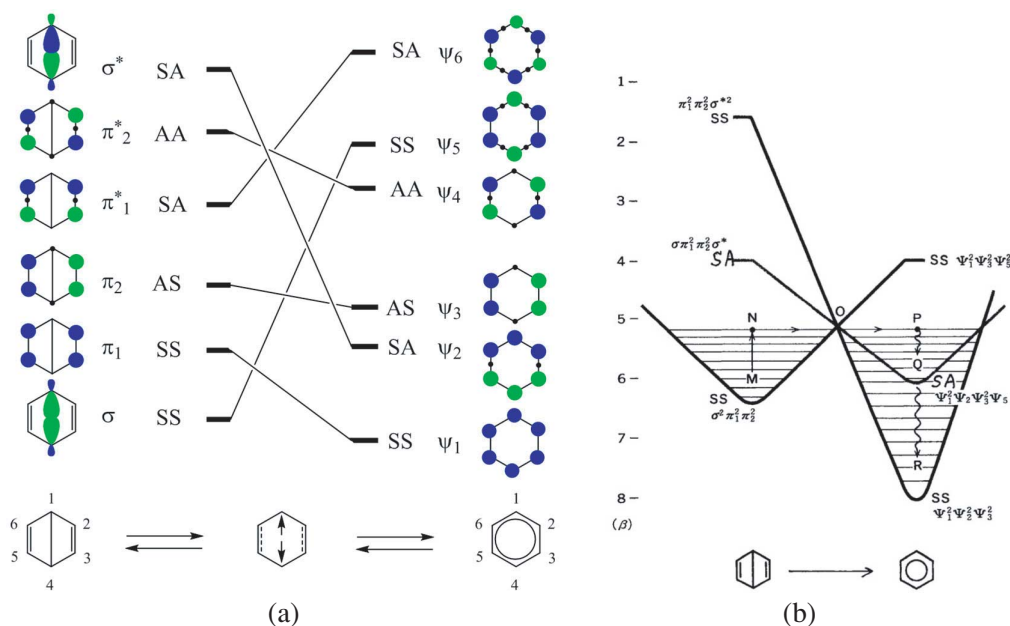


Fig. 3. The dynamic correlation diagram (a) and the corresponding state diagram (b) for the conversion of Dewar benzene to benzene.

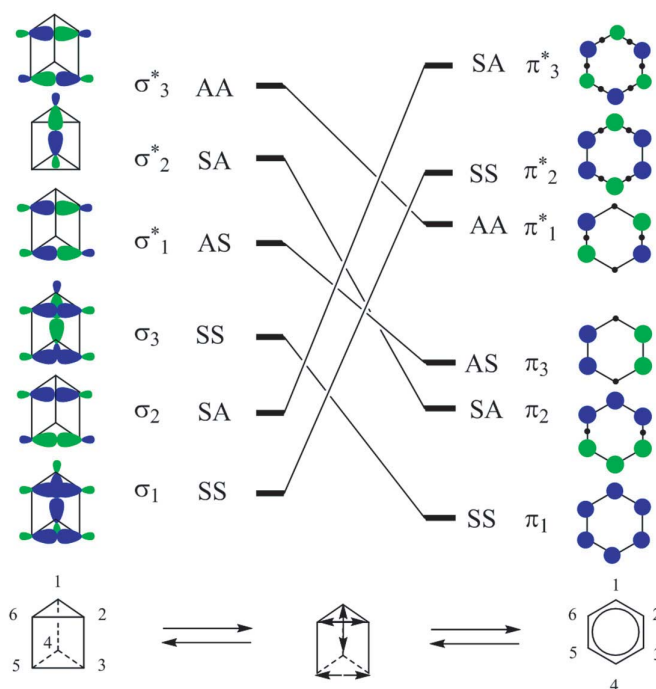


Fig. 4. The dynamic correlation diagram for the conversion of prismane to benzene.

in Figs. 3(a) and (b) (Nohira and Nohira, 2013).

The diagrams have been drawn in the same style used in the previous paper (Nohira and Nohira, 2012). The meaning of each symbol in Fig. 3 (also in Fig. 4) is as follows. σ : σ bonding orbital, σ^* : σ antibonding orbital, π : π bonding orbital, π^* : π antibonding orbital, SA: laterally symmetric and vertically antisymmetric, AS: laterally antisymmetric and vertically symmetric, SS: both laterally and vertically symmetric, AA: both laterally and vertically antisymmetric. Here, the shapes of π orbitals and the corresponding energy levels for the reactants and products are the same

ones that were used for the correlation diagram by Woodward and Hoffmann. They used the simple Hückel method to estimate the shapes and energy levels (Streitwieser, 1961; Rauk, 2001). Since this method is generally sufficient in terms of accuracy for present purposes, it has also been adopted in this study. Although we assumed that the energy level of an ordinary C–C σ bond was 1.3β in our previous paper (Nohira and Nohira, 2012), we assigned that of Dewar benzene to 1.2β , considering the effect of ring strain. From Fig. 3(b), we can easily explain the phenomenon that thermal isomerization of Dewar benzene to benzene pro-

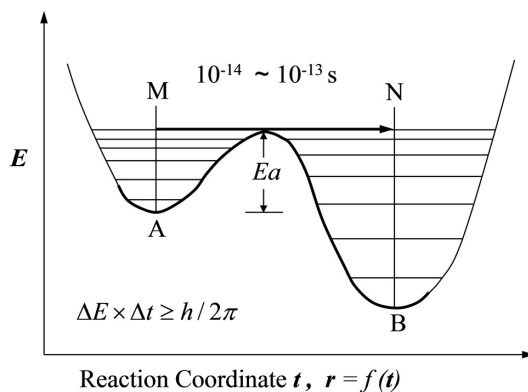


Fig. 5. The energy surface for an elementary reaction.

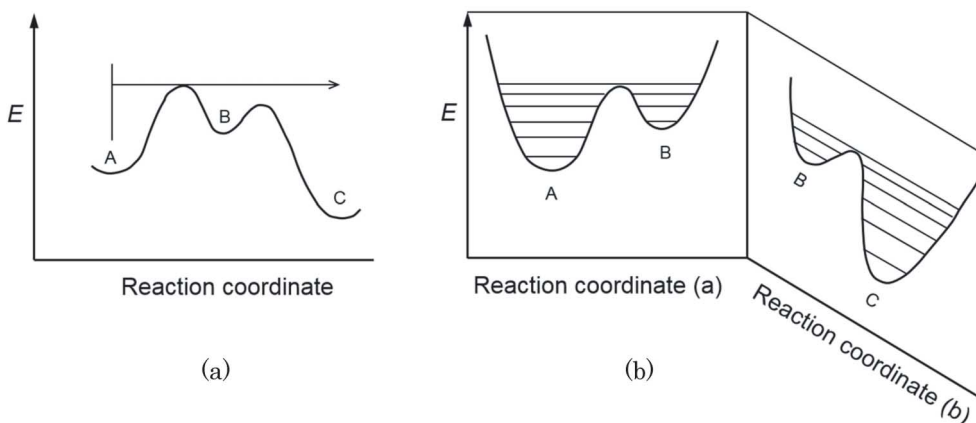


Fig. 6. Exemplified energy profiles for a two-step reaction: (a) commonly used figure; (b) proposed one showing clearly the situation consists of two elementary reactions.

ceeds via the formation of an excited state of benzene, accompanied by chemiluminescence.

4.3 Prismane-benzene

Woodward and Hoffmann have indicated a reasonable relation between the orbitals of reactant and product for the conversion of prismane to benzene (Woodward and Hoffmann, 1969). In their figure, however, the orbitals have not been drawn in the order of energy level, because the crossing of the correlation lines, which have the same symmetry, cannot be avoided. As the result, they have not provided a complete correlation diagram.

If we are not restrained by the non-crossing rule, then we can complete the diagram for this conversion as shown in Fig. 4. This figure clearly shows that the σ_1 and σ_2 bonding orbitals of prismane are linked to the π_2^* and π_3^* antibonding orbitals of benzene. Thus, this reaction is forbidden in the ground state.

5. The Validity of the Schrödinger Equation for the Midway State of Elementary Chemical Reactions

As mentioned earlier, we have defined an elementary reaction as a one-step reaction that does not have any stable intermediates. This means that the electronic structure of the intermediate state is continuously changing over time, and that there is no steady state. As stated in Section 3, a typical elementary chemical reaction proceeds in time

intervals of 10^{-14} – 10^{-13} s.

Figure 5 shows a schematic of the potential energy surface for an elementary reaction. The horizontal axis is the reaction coordinate, r , and the vertical axis is the energy level of the electronic system of the molecule, E . We assume that the stable state of molecule A changes to another stable state of molecule B. M and N denote the centers for the position coordinates of A and B, respectively.

The moment of elementary reaction from A to B is the point at which the reaction coordinate changes from M to N. In conventional discussions of a potential surface diagram, time, t , is not considered. For elementary reactions, however, t should be considered, because the state changes with time, i.e. r is a function of t :

$$r = f(t). \quad (1)$$

Meanwhile, there is an inherent uncertainty in the energy levels of the midway states of chemical reactions according to the Heisenberg uncertainty principle (Heisenberg, 1927):

$$\Delta E \times \Delta t \geq h/2\pi = \hbar \quad (2)$$

where, h is the Planck constant and \hbar is the reduced Planck constant. This principle clearly states that “a state that only exists for a short time cannot have a definite energy”.

We have previously pointed out that the midway state of a chemical reaction cannot be accurately described within the

framework of the time-independent Schrödinger equation (TISE) of Eq. (3) (Nohira and Nohira, 2012).

$$E\psi(r) = \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r) \right\} \psi(r). \quad (3)$$

Regarding this issue, a general opinion is that the time-dependent Schrödinger equation (TDSE) of Eq. (4) should be applied.

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r,t) \right\} \psi(r,t). \quad (4)$$

A standard approach to solve Eq. (4) is shown by Eq. (5) (Schatz and Ratner, 1993, 2002; Tannor, 2007).

$$\psi(r,t) = \sum_n C_n(t)\phi_n(r)e^{-iEt/\hbar}. \quad (5)$$

Since Eq. (5) is a linear combination of steady states, it is obvious that it cannot express the states which are changing rapidly with the lapse of time.

Originally, the TDSE for a moving electron was derived from the analogy of the traveling light wave (Schiff, 1968), where r and t are essentially inseparable. Even if we use the TDSE, therefore, we cannot accurately describe the electronic states $\psi(r,t)$ by independently designating r and t .

In conclusion, as Schrödinger himself mentioned in his papers (Schrödinger, 1926, 1935), it is reasonable to consider that the states which can be accurately described by the Schrödinger equation are limited to “quantum steady states”, which have lifetimes longer than one vibration period described by the following time-dependent term:

$$\exp(-iEt/\hbar). \quad (6)$$

To summarize, when we investigate a reaction pathway in detail, it is most important to examine whether the objective pathway is an elementary process or not. If the pathway is a multistep reaction, the most realistic and effective approach should concentrate only on “quantum steady states” and not on “quantum unsteady midway states”.

6. The Energy Profiles of the Multistep Reactions

Figure 6(a) shows a conventional energy profile for a two-step reaction in which state A changes to C via B. Here, we assume that the energy barrier between A and B is higher than the barrier between B and C. In this case, if state A acquires the vibrational energy higher than that of the former barrier, the state A will go directly to state C because the energy level is higher than the barrier between B and C, as shown by the arrow. Although this can actually occur, the situation is described more properly as follows. If state B is a stable intermediate, there must be a barrier which stops

the chemical change there. Then, if state B further changes to C, it is natural that there is another reaction coordinate different to the one from A to B. Such a situation is clearly described by Fig. 6(b), in which two reaction coordinates are drawn independently.

7. Conclusion

As described herein, the changes for the elementary chemical reactions should be regarded as “quantized”, as well as for atoms and molecules. That is, the states which can be described by the Schrödinger equation exist discontinuously. As a natural consequence, we do not have to apply Neumann-Wigner’s non-crossing rule to electronic state correlation diagrams and potential energy surfaces of chemical reactions. When a molecule changes to another one via an elementary reaction, the “shape” of the original electronic states is transferred to the adjacent ones with minimum changes, owing to the variational principle. We expect that these new aspects of chemical reactions will open up a new field of quantum chemistry including quantum molecular dynamics.

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