Should We Use Force Instead of Energy in the Analysis of Chemical Phenomena? -1 Cause and Result

Energy is frequently referred to as a quantitative evaluation value in chemistry. It is used to determine the stability of a system and the reaction path. Compared with energy, the concept of force has not been much referred to. Here, I would like to point out that much information is acquired from force and explains the validity of using force for the analysis of chemistry phenomena. Let us begin with considering “cause and result”.

Cause and Result

It is said that the system which is changeless in time is in a stationary state. For example, the usual molecule is in a stationary state. In the process in which the system is in the non-stationary state results in a stationary state, a certain force works on the system as it makes the unsteady state face to the stationary state. This means that a stationary state is the result of forces which are applied to the system. Let's explain somewhat concretely.

The C-C bond in the ground state of ethane is 1.522(±0.002) Å. Let us set this distance to r_0. Now, let us consider the case that the bond distance is extended by 1.6 Å. Since this is a non-stationary state, the forces work on both carbons as the bond distance becomes r_0. The factor which generates the forces turns into the cause of forcing the system to the stationary state. The summation of these forces worked on the system is the energy. That is, "energy" simply shows the "result."

1. Energy Is the Quantity Given to Whole System

Energy is a scalar quantity. Since it does not have elements like vector, energy is given to a specific state of the whole system. Accordingly, the energy of a system is not the quantity which can be divided into the portion of the system. Some may refute as “Isn't bond energy is given to a specified bond?” As a matter of fact, some theoretical chemists lead discussions by assigning the total energy by the molecular orbital method to atoms and between atoms. This is a clear mistake although such confusion is caused by improper expression as if bond energy were the direct energy of the bond. The truth is that the bond energy of A-B is the energy difference of system (A-B) and system (A + B) (A and B are an atom or an atom group) and is never the energy of the bond of A and B in the system. Let us explain this concretely using ethane molecule.

Ethane has the structure shown in figure 1-A in the most stable state. The C-C bond dissociates and generates two methyl radicals. The most stable structure of methyl radical is planar (figure 1-B). Dissociation of the bond does not follow the way that the pyramidal structure of two methyl groups is maintained, but with dissociation, the structure changes a lot and eventually turns into a planar structure. Bond energy does not contain the energy of this structural change.

Bond energy is a difference of twice the free energy of B and the free energy of A in the standard condition. When enthalpy and entropy are not considered, the bond dissociation energy corresponds to the difference between the twice of the total energies of B and the total energies of A. Anyway, in the state of **A**, the energy of structural change of the methyl group after dissociation is not reflected at all.

A B

Fig.1. Geometries of ethane and methyl radical

2. Make Sure that Energy is the Quantity of Result

Since the entitled concept is very important, I would like to reconfirm that energy is the result of force exerting on a system using a simple example. Let us consider the case where the object of the mass *m* is lifted to height *h*. When acceleration of gravity is expressed by *g*, the force (*F*) works on the object is *mg* (*F=mg*). If the object is at the height of *h*, it has the potential energy[1] of *mgh* (work-done energy is the distance (*x*) × the force which is applied to the object). This appears as a result of putting force on the object (*m*).

Hydrogen atom has energy of -2,620kJ/mol. The negative sign means that the system released the energy of that amount. What is the standard of energy? The energy usually set to 0 in the state where the proton and the electron dissociate completely (the distance between the proton and the electron is infinity).

When the distance of two-point charges Q_1 and Q_2 is *r*, the Coulomb force carried out is given by the following formula.

$$F(r) = k\frac{Q_1Q_2}{r^2}$$

$$k = \frac{1}{4\pi\varepsilon_0} \qquad \varepsilon_0 = 8.8537\times10^{-12}\,\mathrm{C^2N^{-1}\,m^{-2}}$$

Here, ε_0 is the dielectric constant of vacuum[2].

When the infinitive distance of a proton and an electron becomes *s* (0.529Å) to form hydrogen atom, the energy is, since the force depends on the distance (*r*), expressed by Eq.1

$$V = \left[k\frac{Q_1Q_2}{r}\right]_{\infty}^{s} = k\frac{Q_1Q_2}{s} \qquad \left(V(r) = k\frac{Q_1Q_2}{r}\right) \qquad 1$$

[1] The energy which is determined by positional coordinates is called "potential energy".

[2] In the cgs unit system, *k*=1. 1/(4πε_0) is the conversion factor to the MKSA unit system.

The average distance of proton and electron of hydrogen atom is ca. 0.53Å. The potential energy (*V*) is,

$$V = k\frac{Q_1Q_2}{r} = \frac{1}{4\times 3.14\times 8.85\times 10^{-12}\mathrm{C}^2\cdot\mathrm{N}^{-1}\cdot\mathrm{m}^{-2}}\frac{-1.6\times 10^{-19}\mathrm{C}\times 1.6\times 10^{-19}\mathrm{C}}{0.53\times 10^{-10}\mathrm{m}}$$
$$= -4.35\times 10^{-18}\, N\cdot m(\equiv J) \qquad 2$$

If this value is converted to that of per mol, it would be -2.62×10^{6} J or -2620 kJ. The negative sign means that the system worked out by that amount. That is, when an electron in infinity from the nucleus approaches to the distance of 0.53Å, the energy of Eq. 2 is released outside the system[3]. Equally, it will be said that the electric charge of a proton and an electron carried out negative work to the system of a proton and an electron.

As the above two examples show, energy is the resultant quantity of force having acted on the system. This is completely the same in a complicated molecule. As for the energy of a molecule, the standard is the energy of the state that the electrons and the nuclei of all the atoms which constitute the molecule are completely separated. And the energy of the molecule is the resultant energy that the negative force worked on the system to form the molecule from the system of completely separated particles. That is, energy is a result and is not the cause.

3. Force is the Cause of Energy

Although this title is a matter of course in physics, the importance is seldom recognized by chemistry. Probably, there is no objection to what "the elucidation of a chemical phenomenon is searching for the cause of the phenomenon." The cause is unknown forever if one looks only at the result. The cause of a phenomenon becomes clear by investigating the forces committed in a system. Energy has long been considered as an important factor in chemistry and it is very strange that force has not been taken into account.

Force is equivalent to partial differential of the energy with respect to coordinates. Let me explain this using a molecule as an example and using de Carte coordinate system. The energy of a system is given by the function of the coordinates of the nuclei which constitute the molecule, and E (x_i, y_i, z_i). x_i, y_i, and z_i are coordinates of nucleus *i*. Energy is differentiated with respect to the position of nucleus *i*. Since partial differentiation is carried out with respect to each coordinate, the following three formulas are obtained.

$$F_x^i = \frac{\partial E}{\partial x_i}, \quad F_y^i = \frac{\partial E}{\partial y_i}, \quad F_z^i = \frac{\partial E}{\partial z_i}, \qquad 3$$

[3] Although it is a digression, when there is no medium which receives the energy released, an electron is not brought close to a proton (since all the potential energy generated turns into kinetic energy and electronic movement becomes intense). In space, since the concentration of substance is extremely thin, a nucleus and an electron do not join together but are in the state (plasma) where they are dissociated.

It is easily understood that the force has components that show direction. This direction has problem-solving power in the analysis of chemical phenomena.

Proposition: Use Force in the Analysis of Chemical Phenomena

Detailed observations and calculation results show that benzene is a very stable substance compared with other unsaturated hydrocarbons: benzene is thermodynamically stable compared with other unsaturated hydrocarbons. However, the reason for "why to be stable" is unknown only if one looks at the energy value.

Let me bring up an example which may be a problem solver. Benzene has the structure of the regular hexagon (D_{6h}). If one wants to investigate the reason why benzene is D_{6h}, he strongly suggested that he analyzes the ingredients of the force exerted on carbon atoms at the non-stationary state as the D_{6h} structure of benzene is made to, for example, D3h structure.

The total energy of a molecule can be divided into electronic kinetic energy (T), one-electron potential energy (V_{Ne}), two-electronic potential energy (V_{ee}), and nuclear repulsion energy (V_{NN}) (this is possible since it is not division to portions of the system). If partial differential is taken with respect to the position of these nuclei, the forces for the partitioned energies will be acquired. By investigating them, the reason for the D_{6h} structure of benzene will be known fundamentally. Using the force analysis in chemical phenomena seems to make great progress in theoretical chemistry.

How to compute force using a molecular orbital theory will be explained next time.