With What Does It Mean the Organic Chemical Phenomena Are Solved?

Let me explain the meaning of this title quoting a simple example. Aniline has ortho and para orientation nature and nitrobenzene has meta orientation one to an electrophilic substitution reaction (SE). Explanation of the text level of organic chemistry, using an arrow electron theory, comes to show to Fig. 1.

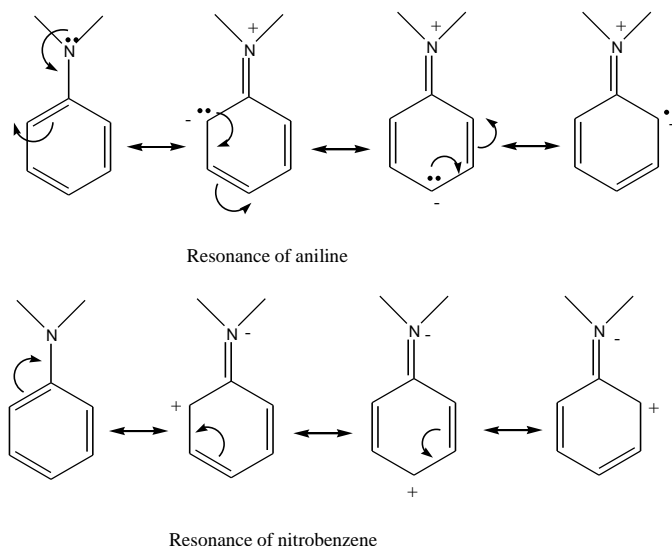Resonance of aniline

Resonance of nitrobenzene

Fig. 1. Organic chemical expression of resonance in aniline and nitrobenzene

That is, since the unshared electron pair of the N atom gather at ortho and para positions according to the arrows in aniline and π electron density of those positions becomes large, an electrophilic reagent is brought nearby those positions. On the other hand, in nitrobenzene, in order for π electrons of ortho and para positions to decrease and those positions are avoided by an electrophilic reagent for those positions tend to be positively charged.

Almost all organic chemists are satisfied with such an explanation. However, does it mean that one understands these reactions truly? Let's consider some points below. (1) What these arrows mean? (2) If the arrows mean the route to which the electron movement is expressed, why are they so? (3) Especially in aniline, why electrons flow into C with low electronegativity from N with high electronegativity? (4) What on earth is the cause of deciding atomic electronegativity, and so on. The arrow electron theory cannot explain anything of chemical phenomena at all.

Owing to the spread of molecular orbital calculation programs, the electron density in a molecule and the energy of a reaction process can be easily calculated by organic chemists as well, and they can show validity of a reaction. However, it is not in charge of the analysis of a phenomenon at all. The problem is why it brings such a result. Then, what kind of explanation is the real explanation of a chemical phenomenon? This is the meaning of the title.

See the Fact that a Chemical Phenomenon Belongs to Natural Phenomena

A chemical phenomenon is regarded as one of the natural phenomena. Nobody may object this idea. If so, one should also explain a chemical phenomenon from natural basic principles and this may be a natural conclusion.

The particle physics says that there are four sorts of force which govern nature. In order of strength, they are strong force, electromagnetic force, weak force, and gravitational force. Among them, the force related to chemical phenomena is only electromagnetic force. The range which acts although strong force is very strong but its action is limited to a nuclear domain (10^{-15}m). The weak force commits only at the time of collapse of a nucleus. Gravitational force is about 10^{-40} time weak compared with electromagnetic force, and can be disregarded completely.

The Natural Principles that Govern Chemical Phenomena

The idea that the electromagnetic force is the complete basis to understand chemical phenomena is not right. In atoms and molecules, the wave character of electrons plays important roles. The wave nature of a substance inevitably accompanies the Pauli uncertainty relation (principle). In addition, an electron has the important character: elementary particles belong to either the group to which only one can exist in one state (fermion) or the group called boson in which many particles can exist in one state. Here, a state refers to the stationary energy state (it does not change in minute time) specified by all the coordinates including internal ones. For example, if it is an electron, they are space coordinates and internal coordinates (the spin, the coordinates of rotation in classic understanding). An electron belongs to a fermion. The question why an electron is a fermion is not a problem which chemistry asks like the problem why an electron has an electric charge: let's accept these as a fact. The fermion character of an electron appears concretely in chemistry as the Pauli's exclusion principle.

After all, the factors which govern the atomic and molecular worlds will be (1) the electromagnetic force, (2) the wave character of an electron (or the principle of superposition), (3) the uncertainty relation, and (4) the Pauli's exclusion principle. Although 3 is a factor derived from 2, a chemical phenomenon becomes easier to understand by considering 2 and 3 separately. The electron's wave nature serves in understanding the way of electron distribution and expansion and shrinkage of electron distribution by orbital interactions. The uncertainty relation is convenient for qualitative understanding of the relationship between the electron's existence range and its kinetic energy.

How to Understand Chemical Phenomena on Natural Principles Using Molecular Orbital Theories

Explanation based on the electromagnetic force, the wave nature of electrons, the uncertainty relation, and the Pauli's principle may be true understanding of chemical phenomena. Next, let us

consider the concrete ways to understand chemical phenomena from those basic principles. This is comparatively easy. We use molecular orbital theories in order to explain chemical phenomena. Just use the molecular orbital theories appropriately.

Let me explain using the Hartree-Fock (HF) method as a molecular orbital theory. Although there are fellows who dislike this method because of not taking the electron correlation, I (tanuki[3)]) think it the excellent molecular orbital theory for which the virial theorem is materialized; this is basic requirement as a theory when it is applied to the mechanical analysis. Besides, the defect that electron correlation is not taken into account is easily removed by adding various electronic states. Although it is a digression, it should be mentioned that the density functional theories cannot be used for the mechanical analyses of chemical phenomena.

Although the details of the molecular orbital theory are omitted, let me point out an important fact. The coefficient (c_i) of the expansion function of a molecular orbital (ψ) is decided using the variation principle.

$$\frac{\partial E(c_1, c_2 \cdots c_i \cdots c_n)}{\partial c_i} = 0 \qquad 1$$

Here, E is the total electron energy. The point is that c is optimized to the total electron energy. It is never optimized to the energy of atom or between atoms. Although it is a digression, this shows that it is a mistake to divide the energy of a molecule into those of atoms and between atoms. Moreover, there is no theoretical guarantee on any kind of partitioning of energy and electron distribution into atoms ad between atoms, such as electron density population, and bond order, which have been currently and traditionally performed. Using them also turns into unsuitable application of a molecular orbital theory.

(1) An Appropriate Energy Partitioning

The Hamiltonian (H^{el}) of a system consists of operators of the kinetic energy of electrons (T) and the potential energy (V^{el}). V^{el} is partitioned into operators of 1-electron potential energy (V_{eN}) and 2-electron potential energy (V_{ee}). The expectation values of these operators are theoretically appropriate.

$$H^{el} = T + V^{el} = T + V_{eN} + V_{ee} \qquad 2$$

$$E^{el} = \int \Psi^* H^{el} \Psi d\tau = \int \Psi^* T \Psi d\tau + \int \Psi^* V^{el} \Psi d\tau$$
$$= \int \Psi^* T \Psi d\tau + \int \Psi^* V_{eN} \Psi d\tau + \int \Psi^* V_{ee} \Psi d\tau \qquad 3$$

The first , second, and third terms of the right-hand side of the lower formula of Eq.3 respectively correspond to expectation values of the kinetic energy of electrons, 1-electron potential energy, and 2-electron potential energy.

If the LCAO expansion is used (Eq. 4), each term of Eq. 3 is, in terms of atomic orbitals (χ_r) and

their coefficients (c_r), expressed as shown in Eqs. 5 to 7.

$$\psi^i = \sum_{r=1}^{n} c_r^i \chi_r \qquad 4$$

$$\int \Psi^* T \Psi d\tau = \sum_r \sum_s P_{rs} \int \chi_r^*(1) \left(-\frac{1}{2}\nabla^2(1)\right) \chi_s(1) d\tau_1 \qquad 5$$

$$\int \Psi^* V_{eN} \Psi d\tau = \sum_r \sum_s P_{rs} \int \chi_r^*(1) \left(\sum_Q - \frac{Z_Q}{r_{1Q}}\right) \chi_s(1) d\tau_1 \qquad 6$$

$$\int \Psi^* V_{ee} \Psi d\tau = \frac{1}{2}\sum_r \sum_s P_{rs} \left\{ \sum_t \sum_u P_{tu} \left[(rs/tu) - \frac{1}{2}(rt/su) \right] \right\} \qquad 7$$

In these formulas, P_{rs} is the bond-order between atomic orbitals χ_r and χ_s while, (rs/tu) is,

$$(rs/tu) = \int\int \chi_r^*(1)\chi_s^*(1)\left(\frac{1}{r_{12}}\right)\chi_t(2)\chi_u(2) d\tau_1 d\tau_2$$

Although repeated, Eq. 5 gives the kinetic energy of electrons which originate from the uncertainty relation and Eq. 6 does the electromagnetic (coulombic) energy of electrons and nuclei.

Eq. 7 corresponds to the interaction energy between electrons which includes simple coulombic energy and the effect of avoiding the existence of the same spins by the Pauli's exclusion principle. The effect of the Pauli's exclusion principle is expressed by $-\frac{1}{2}(rt/su)$ in Eq.7. The detail may be referred to literatures 5 to 8.

Here, let us make sure of some technical terms.

Coulombic interaction: the interaction between two charges

Electronic interaction: the interactions between two electrons including the Pauli's exclusion principle.

Electron correlation: the effect of electrons in which movement of a certain electron affects movement of other electrons. Since electron has a negative electric charge, other electrons move avoiding the electron. The Hartree-Fock method does not include this effect, since the interaction between electrons is taken in as the average value.

As described in the "Proposition" of this HP, no information is acquired only by looking at the energy value. By seeing the energetic changes accompanying with changes of nuclear position, one can know what will participate in the chemical phenomenon from the basic principles of nature.

(2) Some Examples of Fundamental Analysis

The analyses of the chemical phenomena by such a view have appeared for many years, although there are not many examples. In 1962, Ruedenberg examined the kinetic energy of electron and the potential (nucleus interaction is also included) energy of the H^+ -- H system as a function of internuclear distance between H^+ and H.[9] In conclusion, diffusion of the electron to H^+ from H atom takes place at first causing a fall of the kinetic energy. At the same time a fall of the potential energy

happens in connection with it. This continues until the nuclear-nuclear repelling Coulomb energy and decrease of the kinetic and one-electron potential energy are balanced to reach the equilibrium distance. In this case, since the number of the electrons of the system is one, the effect by the Pauli's exclusion principle does not enter, but it is clarified how the electronic kinetic energy which arises according to the uncertainty relation, and coulombic energy are correlated.

The problem of conjugation of the aniline and nitrobenzene shown at the beginning has already been dealt with.[8] Let me show the conclusion.

The method is, as shown in Fig. 2, to analyze the changes of the partitioned energies when the substituents are rotated along the C-N axis.
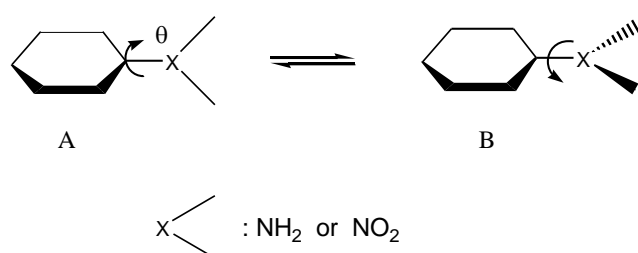

Fig.2. Rotation of substituents along the C-N axis.

The conclusion is as follows. In an electron-donative substituent group like an amino group, due to the relief of the kinetic energy pressure of the unshared electron pair of the N atom, the electrons flow into the benzene ring, causing a fall of the kinetic energy. On the other hand, in the electron-withdrawing substituent group like nitrobenzene, π electrons of the benzene ring move to the N atom due to the strong potential of the N atom of the nitro group. The authors have advocated that one calls the former kinetic-energy origin and the latter, the potential-energy origin.

The physical meaning was given to the conventional concept of electron-donative and electron-withdrawing natures of substituents, and inconsistency of the concept in the chemistry that electrons flow into the small C atom from the large N atom of electronegativity in aniline is solved with the concept of relief of kinetic-energy pressure. "Kinetic-energy pressure" is the concept which Reudenberg introduced, and since the electron confined in narrow space has a large kinetic energy (due to the uncertainty principle), electrons have a tendency to spread. Although it is a concept seldom used, since it is more direct than using the uncertainty relation, the use of "kinetic-energy pressure" seems suitable for an understanding of chemical phenomena.

Proposition

Since chemical phenomena belong to the natural phenomena, an understanding from the natural basic principles turns into the fundamental understanding. The factors which sway the world of atoms and molecules are (1) the electromagnetic force, (2) the wave character of electron (the principle of superposition), (3) the uncertainty relation, and (4) Pauli's exclusion principle, and since those

quantities are calculable with molecular orbital methods, one can understand the cause of a chemical phenomenon from those roles to obtain the true understanding. Moreover, the use of the concept of "kinetic-energy pressure" is appropriate for the character in which the electron tends to spread due to the uncertainty relation.

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1. It is not contained in the text of organic chemistry although the cause of deciding atomic electronegativity is well understood.
2. Relation between the uncertainty relation and the wave nature of electron may be referred to "Why Conjugation Takes Pace" in the Proposition of this HP.
3. Takuki is a raccoon-like mountain dog who sometime jokes human beings. Be aware!
4. Virial Theorem: the theorem that the ratio of kinetic energy (T) to the potential energy (V) is -2 in the system in a stationary state (V/T=-2). This theorem is an important one which is materialized in both classical and quantum mechanics. If this theorem is not theoretically fulfilled in a molecular orbital theory, such a theory is not suitable for the mechanical analysis of a phenomenon.
5. H.Ichikawa and Y. Ebisawa, *J. Am. Chem. Soc*., *107*, 1161 (1985)
6. H. Ichikawa, Y. Ebisawa, K. Sameshima, *Bull. Chem, Soc. Jpn*., **61**, 659 (1988)
7. H. Ichikawa, Y. Ebisawa, A. Shigihara, *J. Phys. Chem*., **92**, 1440 (1988)
8. H. Ichikawa, K. Sameshia, J. Phys. Org. Chem., 3, 587 (1990)
9. K. Reudenberg, *Rev. Mod. Phys*., **34**, 326 (1962). See also, M.J. Feinberg, K. Reudenberg, *J. Chem. Phys*., **54**, 1495 (1971)