Quantum Chemistry

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Chapter 6

Molecular orbital and chemical reaction

Chemical reactions are phenomena in which systems of nuclei and electrons undergo changes of geometrical configurations and compositions. As we have studied, binding or antibinding forces are caused by electrons. In this chapter, we will study basic quantum chemical principles of chemical reactions based on functions of electrons.

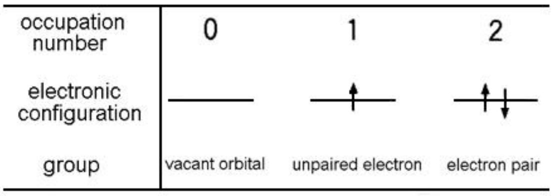
6.1 Orbital theory of reactivity

In Chapter 5 we studied composition of new molecular orbitals and energy levels based on orbital interactions. However, whether really new bonds are formed or not depends on electron configurations. In this section, let us first study relationships between electron configurations and reactivity as well as relationships between unpaired electrons and reactivity, and then we will study the HOMO-LUMO principle and the frontier orbital theory.

6.1.1 Electron occupation number and reactivity

Occupation numbers of electrons in one energy level are limited to be either of $2, 1, 0$ according to the Pauli exclusion principle, and they are classified into three cases listed in Table 6.1.

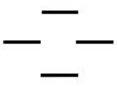
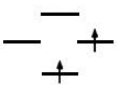
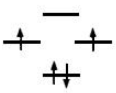
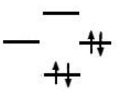
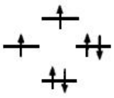
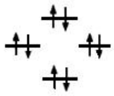
Table 6.1: Classification of electron energy levels



occupation number	0	1	2
electronic configuration	—	↑	↑↓
group	vacant orbital	unpaired electron	electron pair

Orbital interactions can also be classified into six patterns shown in Table 6.2. Pattern(1) is an interaction between vacant orbitals with no electrons leading to an occupation number of zero, which results in no bond formation. An example is interactions between 2s vacant orbitals of a pair of He atoms. Pattern(2) is an interaction between a vacant orbital and an unpaired electron, and in this case an electron in the bonding orbital yields one-electron bond with a bond-order of 1/2. A real example of this type is a production of $H_2{}^+$ ion from H and H^+ already studied in Chapter 5. The next Pattern(3) is an interaction between two unpaired electrons, which gives an electron-pair (covalent) bond with a bond-order of unity, as can be seen from a typical example of $H + H \rightarrow H_2$. An electron-pair bond can also be produced via Pattern(4), an interaction between a vacant orbital and an electron-pair, and an example is $H^+ + H^- \rightarrow H_2$; it is of note that H^- can exist, since the electron affinity of the H atom is positive.

Table 6.2: Fundermental patterns of orbital interactons and bond-order

pattern	(1)	(2)	(3)	(4)	(5)	(6)
electronic configuration						
bond order	0	1/2	1	1	1/2	0

Pattern(5) involving an interaction between an unpaired electron and an electron-pair gives an electron in the untibonding orbital in addition to two electrons in the bonding orbital, and thus the bond-order becomes $(2-1)/2 = 1/2$ equivalent to the one-electron bond. A typical example of this sort is $He^+ + He \rightarrow He_2{}^+$. As shown in Table 5.3, the dissociation energy and the bond length of $He_2{}^+$ are very similar to those of $H_2{}^+$, because the bond-orders are 1/2 in both cases. The last Pattern(6) includes interactions between electron-pairs, and in this case the bonding character of the bonding electron-pair cancells out with the antibonding character of the electron-pair in the antibonding orbital to result in no bond formation. Interactions between 1s electron-pairs in two He atoms belong to this type. The reason for no production of a He_2 molecule can be given by Patterns (1) and (6) in Table 6.2.

In the above arguments, we assumed that two orbitals effectively interact with each other. In real problems, we should consider whether the orbital interactions are effective or not, especially the conditions concerning with the principles of the energy difference and the overlaps between the interacting orbitals.

A careful analysis of electron occupation numbers and bond-orders for the six patterns in Table 6.2 leads to a conclusion that reactivity is governed by combinations of electron ocupation numbers, as summarized as follows.

(1) No reaction occurs between vacant orbitals or between electron-pairs. [Pattern (1) (6)]
(2) Unpaired electrons can react with any types. [Pattern (2) (3) (5)]
(3) A vacant orbital and an electron-pair can react. [Pattern (4)]

Atoms and moelcules with unpaired electrons are called redicals. When radicals meet with other species, they usually react promptly to yield other species. Therefore, radicals are chemically unstable. Radicals are often produced by dissociation of smoe cahmical bonds in stable chemical compounds. The chemial stability of compounds is thus not to react easily and to keep themselves unchanged longtime, even if they meet with other species. The stability of molecules by themselves is the physical stability, which is different from the chemcial stability. Under special conditions, where probabilities making contact with other species are supressed to be very low, as under high vacuum or at very low temperature, radicals can survive as they are. When the level of the unpaired electron has a very large energy separation or a negligibly small overlap with other orbitals, radicals do not interact with others to be able to exist with a good chemical stability.

Reactions by Pattern(3) and Pattern(4) will stop in most cases because of no unpaired electrons in the products. On the other hand, products of Pattern(2) or Pattern(5) also have unparied electrons, and further reactions wiil occur in many cases. Through such mecanisms, radicals produced by thermal decomposition, photolyses, or radiolyses of molecules often arouse chain reactions or even explosion.

One-electron bonds by Pattern(2) or Pattern(5) have the lower physical stability because of the lower bondo-order than electron-pair bonds by Pattern(3) or Pattern(4). One-electron bonds are chemically unstable because of the unpaired electron. In usual textbooks for the introductory chemistry, chemically stable bonds are considered to be formed by a bond of an electron-pair. In this sense, the important stability is the chemical stability. Even if the system is physically very stable, it is not necessarily chemicaly stable. No unparied electron can be considered as a necessity condition for the chemical stability except for some special cases. However, no unpaired electron does not necessarily mean the chemical stability, since Pattern(4) give reaction possibilites without unpaired electrons. Systematic considerations of conditions governing the chemical stability will be made afterward.

Here, we should note the physical stability in more detail. The physical stability becomes larger, when the dissociation energy((bond energy) - (zero-point energy)) becomes larger. Qualitatively, the higher the bond-order, the higher the physical stability. If the bond energy is too small, the system becomes getting out of the potential well by the zero-point vibration. This means that even if the bond energy is positive, the bond may be physically unstable unless the bond energy is larger than the zero-point energy. Furthermore, the bond may become unstable, when the thermal energy is larger than the bond energy. The thermal energy depends on the absolute temperature T, and it is approximately an order of kT, where k is the Boltzmann constant. Themal decompositiom may occur, when a thermal energy getting into the system is large enough to dissociate a bond. It follows that a bond with a high bond energy is thermally stable. In addition, the higher the bond energy brcomes, the lower the probability that undergoes exchange of chemical bonds becomes. In a thermal equilibrium, the lower energy has the higher possibility; the probability for a state of an energy E is proportional to $\mathrm{e}^{-E/kT}$. Thus, the larger bond energy means that the state is more stable and that the probability changing into other higher energy state is less probable.

In Pattern(4) for interactions between a vacant orbital and an electron-pair, a vacant orbital is coordinated with an elctron-pair, and the electron-pair is donated to the vacant orbital. This mecahnism corresponds to interactions of vacant orbitals of $\mathrm{H^+}, \mathrm{Zn^{2+}}, \mathrm{BF_3}$ with unshared-electron-pairs of $\mathrm{NH_3}, \mathrm{H_2O}, \mathrm{CN^-}$ leading to comlex formation by coordinate bonds or dative bonds. This pattern of bond formation is associated with an electron distribution transfer from an electron-pair to a vacant orbital. A phnomenon accomanied with an electron distribution transfer due to orbital interactions is called the cahrge transfer, and compounds or complexes formed by the charge transfer are called the charge-transfer compounds or the charge-transfer complexes. In charge transfer, a substance giving an electron is called the electron donor, and a substance receiving an electron is called the electron acceptor. The bond formation via interactions between a vacant orbital and an electron-pair, an electron reception of a vacant orbital as well as an electron donation of an electron-pair are associated. Key factors governing the formation of new chemcial bonds via this Pattern(4) are very important and will be studied in more detail in the last part of this section.

6.1.2 Number of unpaired electrons and the valency

The number of unpaired electrons and the number of stable bonds to be produced are closely related, because unparied electrons can be paired to produce an electron-pair bond via Pattern(3) in Table 6.2. This is also related with the number of valnce electrons and the valence. Table 6.3 lists the number of the outermost electron shell, the number of valence elecrons, the number of unpaired electrons, and the ususal valency for atoms with atomic numbers smaller than 11. The number of unpaired electrons may change depending on electron configurations of the atoms. When we only

Table 6.3: The number of unpaired electrons and valency

Atom	Number of electrons		Number of unpaired electrons		Usual
	Outermost electron shell	Valence electron	Ground electron configuration	Valence state	Valency
H	1	1	1	1	1
He	2	0	0	0	0
Li	1	1	1	1	1
Be	2	2	0	2	2
B	3	3	1	3	3
C	4	4	2	4	4
N	5	5	3	3	3
O	6	6	2	2	2
F	7	7	1	1	1
Ne	8	0	0	0	0

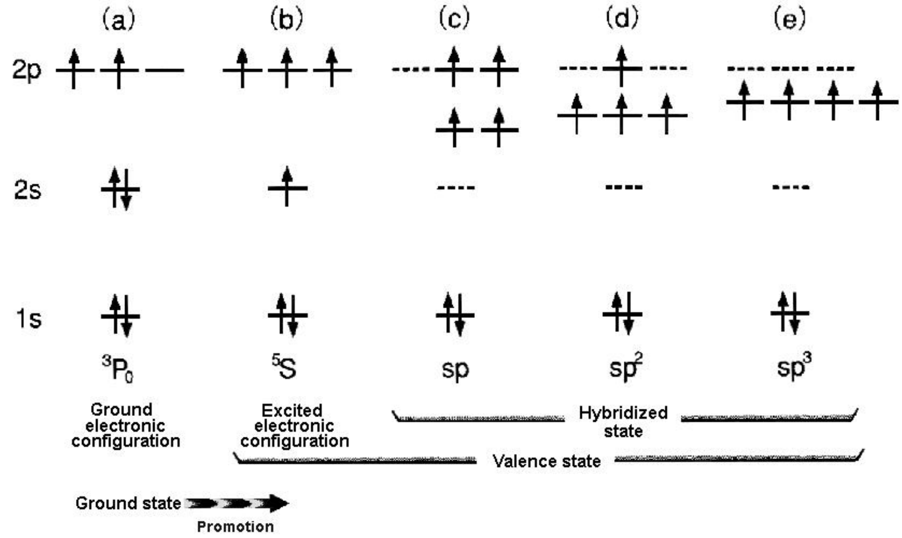


Figure 6.1: Valence states of the C atom and promotion

consider the ground electronic configuration, some discrepancies from the conventionally used will be found for C and Be atoms. This problem will be solved by considering valence states introduced below.

In the case of the C atom, the electron configuration is $(1s)^2(2s)^2(2p)^2$, and the C atom has only two unpaired electrons as shown in Fig.6.1(a). If an electron is excited to an electron configuration (b) in Fig.6.1, then we have four unpaired electrons, which agree well with the usual valency of four. Similarly electron configurations using hybridization as shown in Fig.6.1(c)-(e) give four unpaired electrons in agreement with the usual valency. These electron configurations giving the usual valency are called the valence states. Therefore, in order to obtain the usual valency, valence states with a higher energy need to be made. Such a process is called the promotion, and energies required are called the promotion energies. Promotion energies for the above (b)-(e) are the same, since they are just to promote a 2s electron up to a 2p level. If the stabilization energy gained by the bond formation is larger than the promotion energy, the reaction via the valence state with promotion becomes possible energetically. Be, B, and C atoms really show usual valency via valence states, because of sufficiently large bond energies much greater than the promotion energies.

6.1.3 The HOMO–LUMO principle and the frontier orbital theory

Let us study reactions without unpaired electrons of Pattern(4) in Table 6.2. This type of interactions between a vacant orbital and an electron-pair need conditions with a sufficiently small energy separation as well as an enough overlap between the orbitals. In the ground electron configuration without electron pairs, electron-pairs occupy lower levels up to the HOMO, and upper levels from the LUMO are vacant as can be seen in Fig.6.2. Thus, the required condition with a sufficiently small energy separation leads to the following important conclusions.

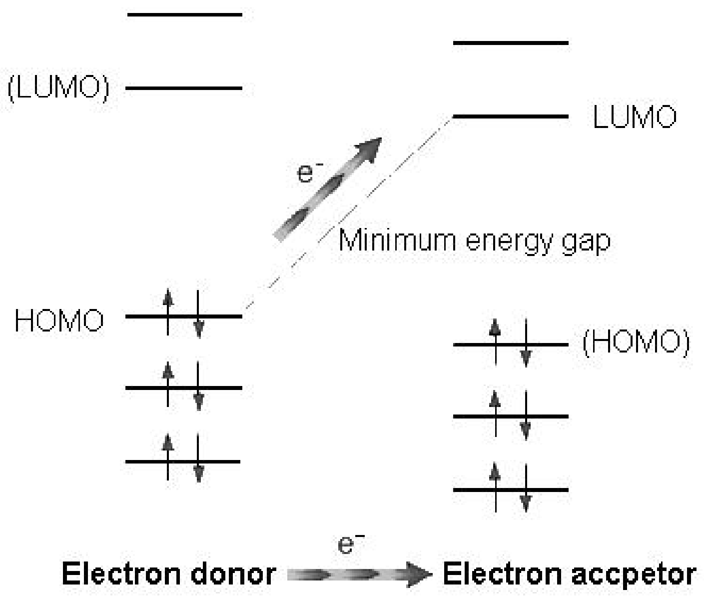


Figure 6.2: HOMO-LUMO interactions and the charge transfer

[The HOMO–LUMO principle]

> Interactions between a vacant orbital and an electron-pair occur most effectively between a HOMO of one species and a LUMO of the other.

This is denoted as the HOMO–LUMO principle, and an interaction between a HOMO and a LUMO is called a HOMO-LUMO interaction.

A comparison of HOMO–LUMO interactions among various compounds indicates that the higher MOMO and the lower LUMO give the smaller energy separation to become the better combination of an electron acceptor and an electron donor for the charge transfer or the electron transfer. This propensity can be summarized as follows.

[The principle of charge transfer interactions]

(1) The electron donation to the other species most easily occurs at the HOMO.

(2) The electron reception from the other species most easily occurs at the LUMO.

(3) The higher HOMO (the smaller ionization energy) gives the stronger ability of the electron donation to the other species.

(4) The lower LUMO (the larger electron affinity) gives the stronger ability of the electron reception from the other species.

(5) The higher LUMO and the lower HOMO result in the lower ability of electron donation and reception.

The occupation number of electrons in an unpaired electron orbital is unity, which is one half of the maximum occupation of electrons, and thus this type of orbitals is denoted as the singly-occupied molecular orbital (SOMO). The special reactivity of the unpaired electron orbital (SOMO) with arbitrary types of electron configurations in addition to the HOMO–LUMO principle and the principle of charge transfer interactions indicate that key roles in chemical reactions are played by HOMO, LUMO, and SOMO. These three types of orbitals are called the frontier orbitals, and the theory noting the roles of these orbitals is the frontier orbital theory proposed by Kenichi Fukui in 1951, who have developed quantum chemical theories of chemical reactions together with R. Hoffmann.

6.2 The chemical stability and the reactivity of rare gases

In this section, conditions for the chemical reactivity are summarized, and the reactivity of rare gases are discussed.

6.2.1 Conditions for the chemical stability

The chemical stability is not to change into other substances easily. This requires the physical stability, since the system should keep itself when it exits alone. In addition, the following four conditions for the chemical stability are important in order to keep itself even if it encounters with other species.

[**Conditions for the chemical stability**]

(1) No unpaired electrons

(2) HOMO is very low. (Almost no ability for the electron donation, because of the too large ionization energy)

(3) LUMO is very high. (No ability for the electron reception, because of the negative electron affinity)

(4) Spatial regions where HOMO and LUMO extend are not accessible by orbitals of other species.

If the above three conditions (1)–(3) hold, no reactions occur with other species having no unpaired electrons. The condition (4) can be satisfied when the system is placed under vacuum or in a solid matrix at low temperature (this technique is called the matrix isolation). This condition (4) can be fulfilled approximately, if the regions where HOMO and LUMO extend are protected physically from other species by a large functional group (such a technique is called the steric protection). Under the condition (4), reactions are suppressed even if the other species are radicals with unpaired electrons. When the condition (4) is not satisfied, an encounter with a radical having a large extension of SOMO may lead to reactions, even if the conditions (1)–(3) are satisfied.

In order to be chemically stable, the system needs also to be physically stable. Thus the system should be in the lowest electronic energy state (the ground electronic state). Further, except for monoatomic systems the bonding energy should be larger than the thermal energy. It is rather easy to maintain these physical conditions; we should only be careful not to introduce energetic actions by heat and light. When light is absorbed to give an electronic excitation to an excited state, the physical condition becomes unsatisfied, and simultaneously chemical conditions (1)–(3) also become unsatisfied.

In order to keep substances unchanged long time, those unstable thermally or photochemically should be saved under cold and dark places. Those reactive with water or oxygen should be kept in a nitrogen atmosphere or under a vacuum state. Special cares appropriate for each substance should be made considering the above conditions.

6.2.2 The reactivity of rare gases

Rare gas atoms in the ground state satisfy conditions (1)–(3) for the chemcal stability ((1) No unpaired electrons, (2) the ionization energy is too large, and (3) the electron affinity is negative), and thus their reactivity is very low. However, some reactions can occur if the conditions become partly unsatisfied. Although ionization energies of rare gas atom are large, their values decrease as He(24.6 eV), Ne(21.6 eV), Ar(15.8 eV), Kr(14.0 eV) in this order, and the ionization energy of Xe becomes 12.1 eV, which is smaller than the ionization energy of the hydrogen atom (13.6 eV). This indicates that the condtion (2) does not hold for Xe. Noting this propensity, N. Bartlet synthesized $XePtF_6$ from Xe and PtF_6 in 1962, and also N. H. Classen et al. obtained XeF_4 via thermal reactions of Xe and F_2 in 1962. Further, XeF_2, XeF_6, XeO_3, XeO_4 and some other rare gas compounds have been synthesized, and it follows that a hypothesis of (rare gases)=(nonreactive gases) has been rejected.

Ions and excited atoms (He*, Ne*, Ar*, Kr*, Xe:) of rare gases do not satisfy the conditions (1)–(3) for the chemcial stability, and it follows that the following reactons can occur.

(a) $He^+ + He \longrightarrow {He_2}^+$, $He^+ + H \longrightarrow (HeH)^+$, $He^+ + N_2 \longrightarrow He + {N_2}^+$

(b) $Ar^* + F \longrightarrow (ArF)^*$, $Kr^* + F \longrightarrow (KrF)^*$, $Xe^* + Cl \longrightarrow (XeCl)^*$

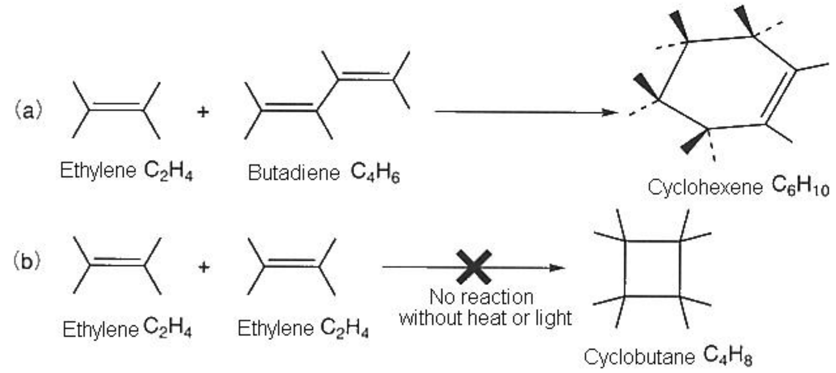
(c) $He^* + Ar \longrightarrow He + Ar^+ + e^-$, $Ar^* + H_2O \longrightarrow Ar + H_2O^+ + e^-$ In the reactions of (a), He^+ behaves as a very strong electron acceptor. Reaction products in (b) are called the excimers (the excited dimers), which are used for the laser oscilation. Reactions in (c) are ionization reactions associated with a collision between an excited atom and a molecule and called the Penning ionization.

6.3 Cyclic addition reactions and the exchange of chemical bonds

In this section, cyclic addition reactions will be studied as an example of chemical bond exchange mechanisms for reactions between species having no unparied electrons.

6.3.1 The Diels-Alder reaction

Addition of a compound having a CC unsaturated bond such as ethylene and acrolein to a diene such as butadiene yields a cyclic skeleton composed of six carbon atoms. This type of reaction is called the Diels-Alder reaction. A typical example is a reaction of butadiene and ethylene producing cyclohesene as shown in the next chart (a), which is easily occur.



On the other hand, another addition reaction (b) involving two ethylene molecules does not proceed without heating or irradiation of light. In order to elucidate the mechanism of the addition reaction (a), let us first study molecular orbitals and energy levels for ethylene and butadiene.

Molecular orbitals and energy levels for ethylene C_2H_4

As studied in section 5.6 and in Example 5.3, the moelcular skeleton of ethylen is on a plane, and the bond angles are about 120°. HOMO and LUMO of ethylene are a bonding π orbital π_b and an antibonding orbital π_a composed of the π type overlap of p orbitals vertical to the molecular plane as can be seen from Fig.6.3 and Example 6.1. In order to consider the mechanism of the Diels-Alder reaction, properties of these HOMO and LUMO are important.

Example 6.1 Compose molecular orbitals and their energy levels from two units of CH_2 (an application of the AH_2 molecule in Section 5.4).

(Solution) Place two units of bent CH_2 with a common central axis bisecting both units, and then get closer to each other (Fig. 6.4).

The lowest energy orbitals of each C_2H_2 unit is 1σ orbital almost purely composed of a C1s orbital, and an interaction of a couple of 1σ orbitals yields a σ orbital (1) due to their same phase mixture and another σ orbital (2) due to the opposite phase mixture. The energy levels become

(1)<(2). This difference is small, because the overlap between C1s orbitals is very small due to very tight electron distributions around the nuclei in the inner shell orbitals, though the energy difference is zero.

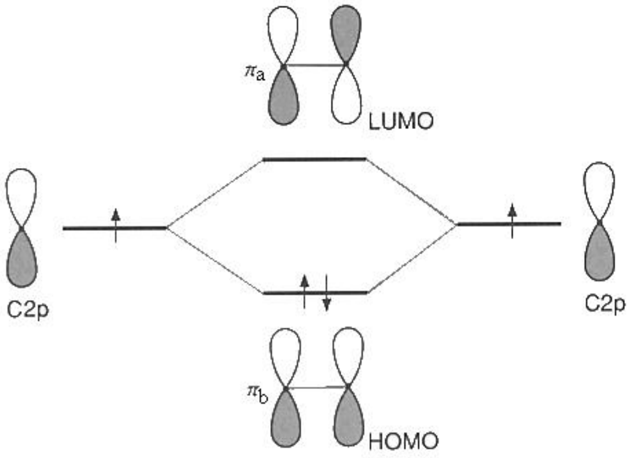


Figure 6.3: HOMO and LUMO of ethylene C_2H_4

Next, let us consider an interaction between 2s orbitals mainly composed of C2s. This interaction yields a C2sCC bonding σ orbital (3) due to the same phase mixture and a C2sCC antibonding σ orbital (4) due to the opposite phase mixture, and the levels become (3)<(4). In this case, the energy difference between (3) and (4) is significantly large because of a large overlap.

A paralell coupling of 3σ orbitals with strong CH bonding characters leads to an orbital (5) with a π bonding character together with an orbital (7) with an atibonding type, and the level ordering becomes (5)<(7).

Here, it should be noted that a same phase interaction at the CC bond region between 4σ orbitals with HH bonding characters yields a level of (6), which intervenes between the levels of (5) and (7). The interaction between 4σ is very strong because of the hybridization of 2s and 2p orbitals on the C atoms. It follows that an antibonding orbital produced by this interaction becomes the higher energy level than the forthcoming two π orbitals (8) and (9).

Since 1π orbital is composed of a p orbital vertical to the CH_2 plane, a bonding π orbital (8) and an antibonding π (9) are produced simply by π type interactions between the p orbitals.

A C_2H_4 molecule has 16 electtrons, and two electrons are accomodated in each orbital from (1)~(8). Thus, the bonding π orbital (8) is HOMO, and the antibonding π orbital is LUMO.

Molecular orbitals and energy levels for butadiene C_4H_6

A butadiene molecule can be constructed by an electron-pair bond between two radicals having an unpaired electron in each unit, which is produced from ethylen by taking away one H atom from a CH bond. The new CC bond thus produced has a double bond character a little by a reason mentioned below, and it follows that a butadiene molecule has a planar structure in which 10 atoms are placed on the molecular plane. Therfore, butadiene has two isomers, *cis* and *trans* forms (Fig. 6.5). Among them, the *trans* form is more stable. The Diels-Alder reaction of butadiene proceeds in the *cis* form, since this form is suitable to the reaction mechanism discussed below.

Example 6.2 Construct π orbitals and their energy levels of butadiene from p orbitals of four C atoms, starting from two sets of π orbitals of the ethylene type (Fig. 6.6).

(Solution) Let us suppose that π orbitals of butadiene are produced by an π type interaction of a pair of p orbitals at one end of each ethylene unit.

Based on the discussion for constructing A_2 type molecules in Section 5.5, let us consider interactions between bonding π_b orbitals and those between antibonding π_a orbitals. In-phase

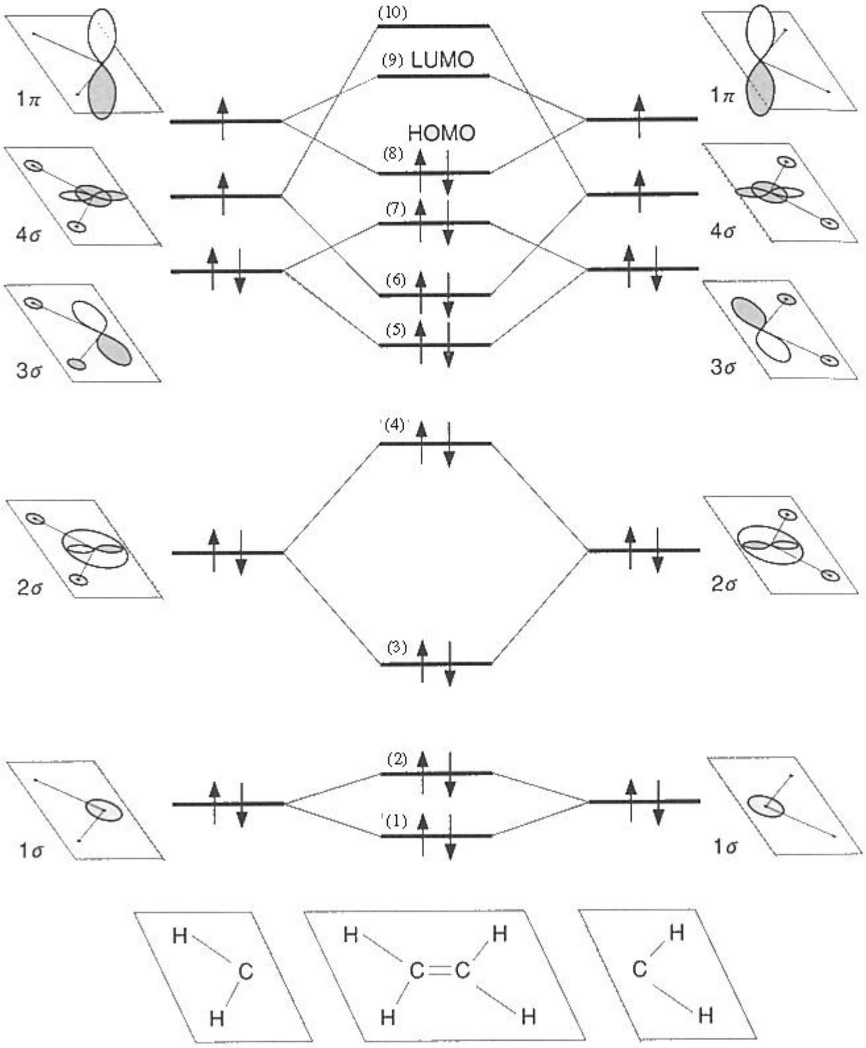


Figure 6.4: Moelcular orbitals of ethylene

interactions between π_b orbitals yield an orbital (1) which is entirely bonding for three CC bonds and expressed as bbb and another orbital (2) having antibonding character in the middle which is expressed as bab. The energy ordering of these orbitals becomes (1)<(2) as can be seen in Fig. 6.6(a). Similarly the same type interactions between π_a orbitals yield an aba type orbital (3) and an aaa type orbital (4). Thus, the energy level ordering becomes (1)<(2)<(3)<(4).

In the next step, let us consider interactions of a pair of orbitals, (1)(3) having a node and (2)(4) having no nodes at the central CC bond. Then, we obtain new orbitals modified by mixing effects shown in (b) of the figure. From the upward to the downward the bonding character is relatively strengthened, and from the downward to the upward the bonding character is relatively weakened.

The energy levels are numbered from the lowest as π_1, π_2, π_3, π_4, in which numbers of nodes are smaller than the numbering by one. This propensity is the same as the number of nodes in wave functions for a particle in a box. This similarity is due to the structure of the C-C-C-C skeleton which is one dimesional space where an electron is accomodated. Noting this similarity, characteristics of π orbitals in butadiene can also be deduced.

Since one electron is provided from a p orbital of each C atom, there are four π electrons in butadienem, which occupy π_1 and π_2 orbitals as electron-pairs. Thus, π_2 is HOMO, and π_3 is

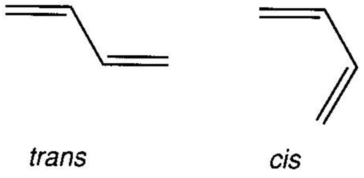


Figure 6.5: *trans* and *cis* forms of butadiene

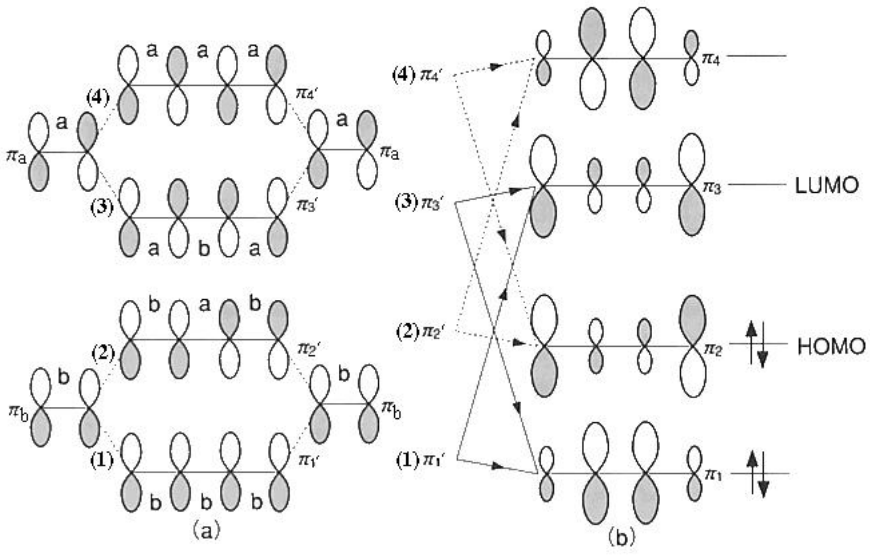


Figure 6.6: Molecular orbitals of butadiene

LUMO. At the central CC bond, the bonding contribution from π_1 is larger than the antibonding contribution from π_2, and hence this bond has slightly a double bond character (the bond length of the central CC bond in butadiene is 1.483 Å, which is a bit shorter than a pure single CC bond of ethane (1.536 Å) and longer than the pure double bond of ethylene (1.338 Å)).

6.3.2 HOMO–LUMO interactions and the symmetry of orbitals

Based on the above orbitals of ethylene and butadiene, let us consider HOMO–LUMO interactions of those orbitals. If ethylene and butadiene molecules are placed on the same plane, H atoms avoid mutual overlaps of π orbitals to result in insufficient interactions. Thus, two molecules should be placed on a pair of parallel planes, the upper and the lower, and we consider interactions of two orbitals, one extending from the upper plane to downward and the other from the lower plane to upward. In Fig. 6.7, ethylene is placed on the lower plane, and butadiene is placed on the upper plane. In this situation, C atoms 1 and 4 can interact with C atoms 6 and 5, respectively. When we place HOMO of ethylene and LUMO of butadiene to have in-phase couplings at the positions 1 and 6 as in Fig.6.7(a), the opposite ends at 4 and 5 can also have overlaps in the same phase. It follows that new bonds are simultaneously formed at $1\sim6$ and $5\sim4$.

Now, let us study effects of the above interactions in terms of changes in bonding characters associated with the electron transfer. Electrons in the electron-pair of ethylene flow into butadiene, and then bonding electrons around 5 and 6 go away to some extent to result in the decrease of the bonding between 5 and 6. This effect reducing the bonding can be denoted as (−) as shown in Fig. 6.8. As already mentioned, the electrons flow into the bonding regions of 1-6 and 4-5, where bonds are missing before the reaction. Thus, such an increase of the bonding in these regions can be denoted as (+). Also, the electrons flow into antibonding regions of 1-2 and 3-4 in

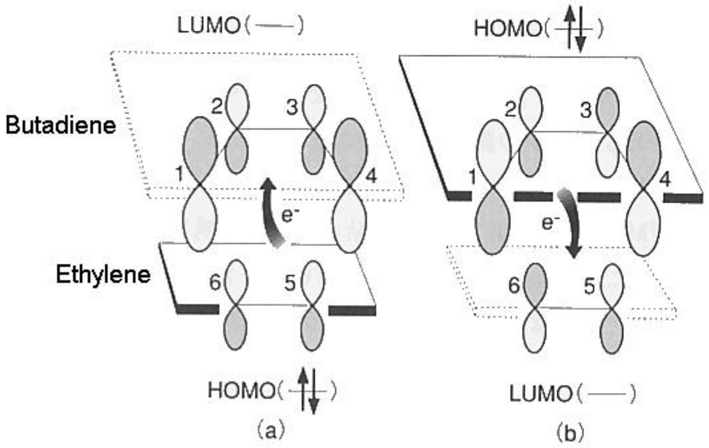


Figure 6.7: HOMO–LUMO interactions of ethylene and butadiene

LUMO, and these regions have (–) effects on bonding. The electron flow into the bonding region of 2-3 in LUMO gives a (+) effect. As summarized in the middle of Fig. 6.8, the above effects are alternating on the perimeter of the hexagon as +–+–+– to lead to bond-order changes of ±1 producing a skeleton of cyclohexene as shown in the right part of Fig. 6.8.

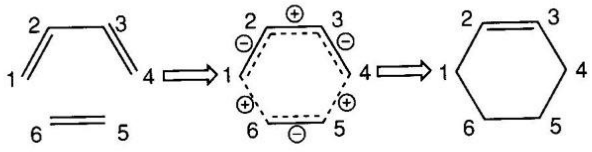


Figure 6.8: Bond-order changes in the Diels-Alder reaction

By the way, we should consider interactions between LUMO of ethylene and HOMO of butadiene as shown in Fig.6.7(b). Although this combination of orbital interactions has an opposite direction of the electron flow, associated changes in bonding characters are the same as those in Fig. 6.8. It follows that these effects of HOMO–LUMO interactions between ethylene and butadiene occur in a concerted way of bond-order changes to complete bond formation and destruction. It should be noted in two types of HOMO–LUMO interactions that one includes interactions between symmetric orbitals, and the other includes interactions between antisymmetric orbitals. Such a reaction with good symmetry combinations is called the symmetry allowed reaction.

In the case of two ethylene molecules, the cyclic addition reaction cannot proceed in a concerted way, because the symmetry matching at one end is not compatible with another symmetry matching at the other end, as can be seen in Fig. 6.9. Such a reaction without good symmetry combinations is called the symmetry forbidden reaction.

Example 6.3 Predict the stereo chemical structure of dichlorocyclohexene produced by cyclic addition reaction of *cis*-dichloroethylene and butadiene.

(Solution) Since Cl atoms of *cis*-dichloroethylene are on the same side of the plane of two C atoms in ethylene during the reaction process, two Cl atoms are also on the same side in the product cyclohexene ring with respect to C atoms 5 and 6 in Fig. 6.7, as can be seen in Fig. 6.10.

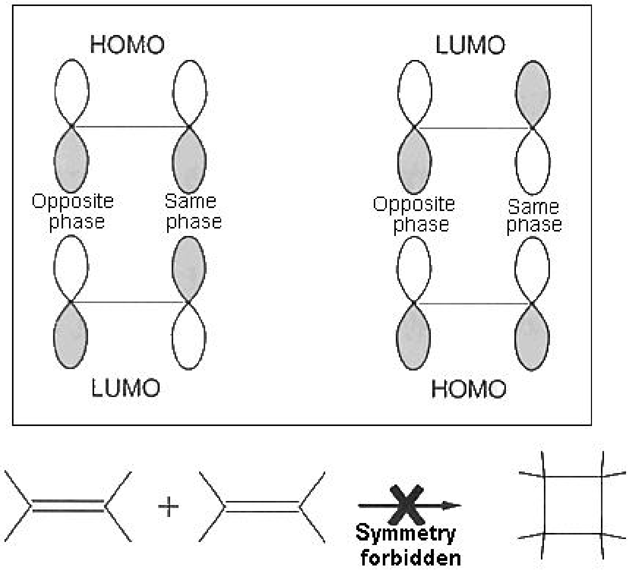


Figure 6.9: HOMO–LUMO interactions between two ethylene molecules

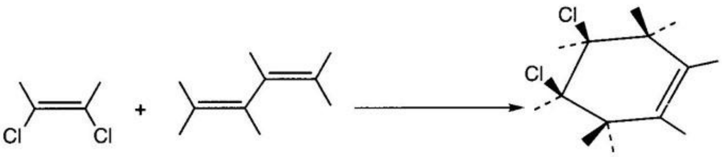


Figure 6.10: The structure of dichlorocyclohexene

6.4 Selectivity and substitution effects in chemical reactions

In view of obtaining chemical products utilizing chemical reactions, it is preferable to minimize the useless loss of the strating materials. For this purpose, by-products should not be produced. Production of by-products necessarily increases not only the useless loss of the starting materials but also additional efforts to separate and purify them from the aimed products. From actual needs for application, development of selective reactions as well as elucidation of their reaction mechanisms have been aroused interests of many chemists. In this section, we will study some selective reactions owing to introduction of functional groups.

6.4.1 Deformation effects of HOMO and LUMO by introduction of functional groups

When an electron accepting functional group X such as the formyl group CHO is introduced in ethylene, the vacant orbital of X interacts with π_{b} and π_{a} orbitals, and the shape of LUMO will have a substantially increased distribution at an end distant from X. This mechanism can be explained by interactions of π_{b} and π_{a} with X on the basis of the two to one orbital interactions as shown in Fig. 6.11. In the new LUMO, the higher π_{a} mixes with X in the same phase from the upward, and in addition the lower π_{b} slightly mixes with X in the opposite phase from the downward. It follows that the electron wave at the nearest part from X is weakened in the opposite phase, and that the electron wave at the distant part is strengthened in the same phase. Since the LUMO level becomes lower, the substituted ethylene becomes a stronger electron acceptor.

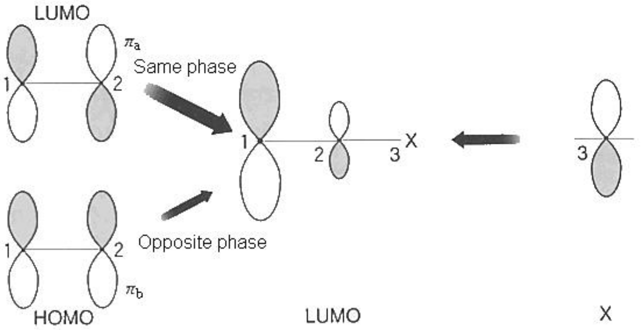


Figure 6.11: Deformation of LUMO by introduction of an electron accepting functional group X

When an electron donating functional group Y such as the methoxy group –OCH_3 is introduced in butadiene, the electron-pair of Y interacts with HOMO(π_2) and LUMO(π_3) of butadiene, and the shape of HOMO will have a substantially increased distribution at an end distant from Y. This mechanism can be explained by interactions of π_2 and π_3 with Y on the basis of the two to one orbital interactions as shown in Fig. 6.12. In the new HOMO, the lower π_2 mixes with Y in the opposite phase, and in addition the higher π_3 slightly mixes with Y in the same phase from the upward. It follows that the electron wave at the nearest part from X is weakened in the opposite phase from the downward, and that the electron wave at the distant part is strengthened in the same phase. Since the HOMO level becomes higher, the substituted butadiene becomes a stronger electron donor.

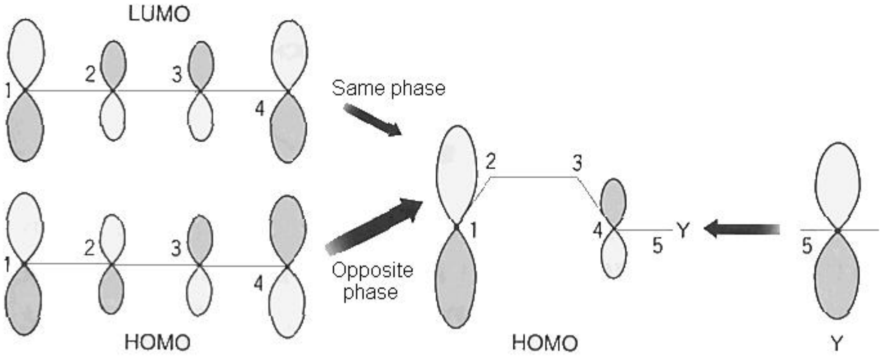
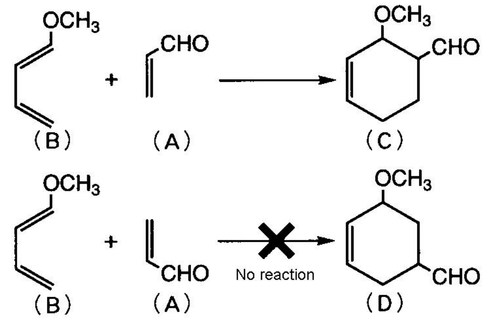


Figure 6.12: Deformation of HOMO by introduction of an electron donating functional group Y

As can be seen in the above examples, spatial extension of HOMO and LUMO can be modified upon introduction of functional groups, which changes the extent of overlaps in orbital interactions to result in variation of the reactivity. Whether accepting or donating power is aimed to be emphasized can be chosen by selection of the functional group. These techniques can be applied to selective control of reaction routes as can be seen in the following example.

6.4.2 Regioselectivity of reactions

Acrolein (A) is a compound produced by substitution of H in ethylene by the CHO group, and 1–methoxybutadiene (B) is a compound generated by substitution of H in one end of butadiene by the OCH_3 group. When (A) and (B) undergo addition reactions, a simple deduction neglecting effects of the functional groups leads to tow possible products, an *ortho*-adduct (C) and a *meta*-adduct (D) with the same probability. The substitution effects, however, emphasize the electron accepting ability of (A) as well as the electron donating power of (B). This means that LUMO in (A) and HOMO in (B) play dominant roles. It follows that only (C) is selectively synthesized without formation of (D).



Let us study the mechanism of the selective production of (C). As can be seen in Figs. 6.11 and 6.12, LUMO in (A) and HOMO in (B) have the substantial enlargement of orbital lobes at the distant end from the functional groups. On the other hand, at the nearest part from the functional groups the orbital lobes become smaller.

When orbital lobes for the most important parts of the orbital interactions are inequivalent to have different spatial extension, let us denotes the inequalities $a > b$ for one and $a' > b'$ for the other. Since the extent of an overlap depends on the overlap integral, we can estimate the magnitude of the interaction from the summation of respective products of the overlapping parts. Now let us compare pairs of the larger ones and smaller ones of $(aa' + bb')$ with combinations of different types, the larger with the smaller and the smaller with the larger, of $(ab' + a'b)$. The magnitude of the overlaps for the former case is always larger than the latter. This can be seen from the difference by the following equation.

$$(aa' + bb') - (ab' + a'b) = (a - b)(a' - b') > 0$$

Since the larger the overlap becomes the stronger the orbital interaction becomes, combinations of big ones together with those of small ones are selected in real chemical reactions. On account of this mechanism, new chemical bonds are formed at both of the nearest parts from the functional groups as well as at both of the distant ends. It follows that the *ortho*-adduct (C) in which the functional groups are placed in the adjacent positions is selectively produced.

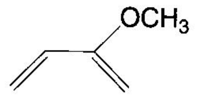
Exercises

6.1 A ground-state oxygen atom in the triplet state has two unpaired electrons, whereas an oxygen atom in the singlet state has a vacant p orbital among the valence p orbitals. Such a vacant orbital of an O atom can accept coordination of one of electron-pairs in a chloride ion Cl^- to yield a hypochlorous ion ClO^-. Noting this reaction as well as the similarity of electron configurations of S^{2-}, P^{3-}, Si^{4-} with the Cl^- ion, which have the same number of electrons (isoelectronic configuration), explain structures of the following compounds.

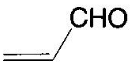
$$(ClO_4{}^-, SO_4{}^{2-}, PO_4{}^{3-}, SiO_4{}^{4-}, XeO_4)$$

6.2 Explain the reasons why rare gases are chemically inactive.

6.3 In 2-methoxybutadiene the electron donating ability of HOMO increases with the electron donating effect of the methoxy($-OCH_3$) group, and in addition LUMO of the butadiene skeleton slightly mixes with HOMO at the position 2. Considering these properties, predict the structure of the main product of the addition reaction of 2-methoxybutadiene with acrolein.



2-Methoxybutadiene



Acrolein