

## Why Is Benzene Stable? – The Origin of Aromaticity: Conceptual Explanation for Organic Chemists

Organic chemists tend to esteem concepts more than numerical formulas. I (Tanuki) think this is right scientifically, since if one cannot explain the theory by words, it can't be said true theory. Relativity and quantum mechanics can be explained on their concepts by words. Of course, help of mathematical formulas is necessary for precise description of the theory though. I tried easy-word explanation of the origin of aromaticity, where I used some mathematics but it is the level of high school. The task was not difficult and it is shown hereafter. The original literature is,

Ichikawa, H.; Sakata, K. "Aromaticity/Antiaromaticity in Cyclic Conjugated Hydrocarbons," *Int. J. Quantum Chem.*, 2002, 87, 135-144.

### What Is Aromaticity?

Most organic chemists seem to grasp the concept of aromaticity. A typical compound with aromaticity is benzene. Although benzene is a compound with multiple double bonds, it is very stable. There are two of meanings for stability. One is the meaning that the compound resists against chemical reaction. The other is that the heat of formation is low.<sup>1</sup> In case of benzene, the comparative compound is a hydrocarbon with the same number of double bonds (hexatriene).

Benzene resists the attack of a reagent and when the reaction is forced to take place, the substitution reaction results instead of addition reaction. This may be understood as an addition reaction happens once, but it follows a reaction to recover the aromaticity with immediate elimination of H. Both phenomena surely show that a circular  $\pi$  electronic system which consists of 6  $\pi$ -electrons in benzene is stable or energetically low.

### What Is Anti-Aromaticity?

Then, how about cyclobutadiene which has the same cyclic conjugation system? It is very unstable. As soon as cyclobutadiene is generated, it results in polymerization. The life expectancy in molecular state (half-life) is usually said to be below  $10^{-6}$ sec. Why it is unstable like that?

The phenomena of aromaticity and anti-aromaticity can be explained sufficiently by

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<sup>1</sup> Heat of formation: The calorie which generates when a target matter (benzene) generates from the elements which exist in the standard condition. The heat of formation of benzene corresponds to the calorie of generation of liquid benzene from carbon element (graphite) and hydrogen gas at the standard condition.

the uncertainty relation and the Hund rule. First, the uncertainty relation and the Hund rule will be explained by words although easy mathematical formulas are used there.

### **The Uncertainty Relation**

The uncertainty relation is also called Heisenberg's uncertainty principle that is expressed as the product of the uncertainty of position ( $\Delta x$ ) and that of the kinetic momentum ( $\Delta p$ ) must be less than the constant related to the Planck's constant ( $h$ ).

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad \left( \hbar = \frac{h}{2\pi} \right) \quad 1$$

Although according to the Newton mechanics (classical mechanics), the kinetic momentum is defined as mass ( $m$ ) multiplied by velocity ( $u$ ), in quantum mechanics the concept is a little different from the classical one. The concept is also applied to wave movement as light. Light does not have the mass, but it has the momentum. When strong light is beamed at an object, the object receives force. Thus momentum may be considered as the cause of force which acts on an object. The momentum ( $p$ ) of electro-magnetic wave like light is expressed by  $p = \frac{h}{\lambda}$  where  $\lambda$  is the wavelength. This is called de Broglie's formula.

Uncertainty or "ambiguousness" is like the following. I will explain the concept using location ( $x$ ). The exact position of an object is set  $x_0$ . Ambiguousness is the average of the absolute values of  $x - x_0$  when measuring  $x$  more than one times. For example, let us assume the right position of an object as 3.0 (the unit is not considered here). Assume when the location is measured 5 times, then values 2.5, 2.3, 3.3, 1.8, and 4.0 are obtained. The absolute values of the error are 0.5, 0.7, 0.3, 1.2, and 1.0 respectively. Ambiguousness is those mean  $(0.5 + 0.7 + 0.3 + 1.2 + 1.0) / 5 = 0.74$ .

Since it is not generally possible to know the exact location ( $x_0$ ), the mean of measurement ( $x$ ), is set  $x_0$ . When the infinite times of measurement are carried out,  $x_0 = \bar{x}$  will holds.

### **The Uncertainty Relation Is Deeply Concerned with Organic-Chemical Phenomena**

This title is a little away from the main subject. But even if I accentuate this idea, I do not accentuate it too much. So I will explain this in some detail.

The variables which appear in the uncertainty relation are the position ( $x$ ) and the momentum ( $p$ ) (We can easily change it to the relation between time and the energy, but it is unnecessary in organic chemistry.) See that these amounts are vectors with

directionality.

Suppose that one measures the momentum ( $p$ ) of a particle (an electron) constrained in some area  $L(=\Delta x)$ .<sup>2</sup> In area  $L$ , if rightward movement is defined positive and leftward one negative, positive and negative values are observed at the same percentage, so the average of the momentum, ( $\bar{p}$ ), will be null. The uncertainty of momentum ( $\Delta p$ ) is the difference between the observed value and the average ( $p - \bar{p}$ ), and thus the following relation may hold.

$$(\Delta p)^2 = \overline{(p - \bar{p})^2} = \overline{p^2} \quad 2$$

This relation should be fully understood.

Using the uncertainty relation,  $\Delta p L \geq \frac{\hbar}{2}$ , the new relation,  $(\Delta p)^2 = \overline{p^2} \geq \left(\frac{\hbar}{2L}\right)^2$  is

derived. Here, let us estimate how much the kinetic energy of the particle by means of the Newton mechanics.

$$E = \frac{mu^2}{2} = \frac{p^2}{2m} \quad \left(\because u = \frac{p}{m}\right) \text{ is re-expressed by the new relation, the average of the}$$

kinetic energy ( $\bar{E}$ ) turns out to be,

$$\bar{E} = \frac{\overline{p^2}}{2m} \geq \frac{\hbar^2}{8mL^2} \quad 3$$

Right way of solving this problem is to solve the Schrodinger equation of a particle in a box, giving similar relation as Eq. 3.<sup>3</sup>

Look at Eq. 3, it is understood that at  $L \rightarrow 0$ ,  $\bar{E}$  will be infinitive. It means that  $L$  is made small, in other words, the movement area of an electronic is limited, the average electronic kinetic energy increases, i.e., the electron runs vigorously in classical sense. This result is entirely due to the uncertainty relation. Then, what is the character of the uncertainty relation then at all? Concerning this please refer to "Why does resonance/conjugation happen?" of this HP-> Solution.

### **The Lowest Energy of Cyclic Movement of Electron Is Null!**

By the way, the cyclic movement includes no beginning and no end. This means  $L = \infty$ . Therefore,  $E = 0$  comes out. That is, the lowest energy of cyclic movement of a particle is null: the particle does not move! This is not true in the higher energy levels because

<sup>2</sup> The particle exists somewhere between 0 and  $L$ , so ambiguousness of the location of the particle will be  $L$  itself for.

<sup>3</sup> See This HP->Tutorial->Fundation of Organic Chemistry->Part 1->Nucleus, The Uncertainty Priciple->1220

they involve phase inversions of the wave ( $L$  is not infinitive).

In an actual compound, for example, benzene, the potential from the nucleus is not constant but is different between on the atom and between atoms. So the kinetic energy appears in the lowest level, but it is found that the energy of the lowest orbital is extremely low as those compared with other orbitals. This is explained by the literature indicated first.

Next let us see other orbitals higher than the lowest energy level. The kinetic energy is not 0, so when thinking classically, movement (circular motion) exists. Moreover, the movement has two degrees of freedom, right-hand circulation and left-hand one. This indicates that two orbitals at the same energy-level should degenerate.

In conclusion, only one lowest-energy orbital must appear and doubly degenerated orbitals appear for other energy-levels in the  $\pi$  electron orbital system.

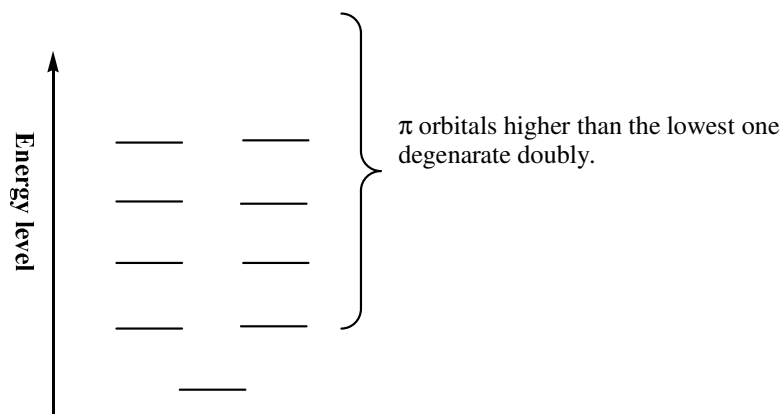


Fig.1. In cyclic conjugate system of  $\pi$  electrons,  $\pi$  orbitals higher than the lowest one degenerate doubly.

### How Electrons Occupy Orbitals in the $4n/4n+2$ Systems

Cyclic conjugation systems are classified into  $4n+2$  and  $4n$  systems according to the number of  $\pi$  electrons which occupy  $\pi$  orbitals.  $n$  takes any value of 0, 1, 2,  $\dots$ . Concretely, in the  $4n+2$  system, the number of  $\pi$  electrons is 2, 6, 10, 14,  $\dots$  and benzene's  $\pi$  electrons are 6. The number of  $\pi$  electrons in the  $4n$  system is 4, 8, 12,  $\dots$  and typically cyclobutadiene has 4  $\pi$  electrons.

$\pi$ -Molecular orbitals are shown in Fig. 2, where the orbitals are arrayed as increasing the energy-levels. When  $\pi$  electrons of  $4n+2$  occupy those orbitals, the highest occupied molecular orbitals are all doubly occupied by electrons. Where, all  $\pi$  electrons are paired and "paired electron" means a formation of chemical bond. Of course, we do not think of lone-pair electrons here.

The kinetic energy of  $\pi$  electrons in the lowest orbital is originally zero and they are the lowest in energy. The energies of other  $\pi$  electrons are considerably low as they are in

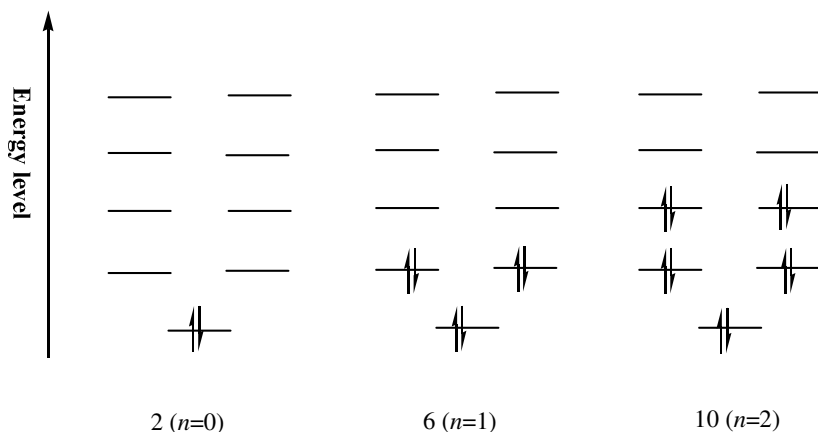


Fig.2. How  $\pi$  electrons occupy  $\pi$  orbitals in  $4n+2$  systems.

chemical bonds. Thus the energy of  $\pi$  electrons in benzene is extremely low and the system is stable.

Let us see the case of the  $4n$  systems. Concerning the stability, inconvenient situation takes place: inevitably 2 electrons must go into doubly degenerated  $\pi$  orbitals. The Hund rule tells that when electrons occupy degenerated orbitals, the spin quantum number must be largest of all possible configurations.

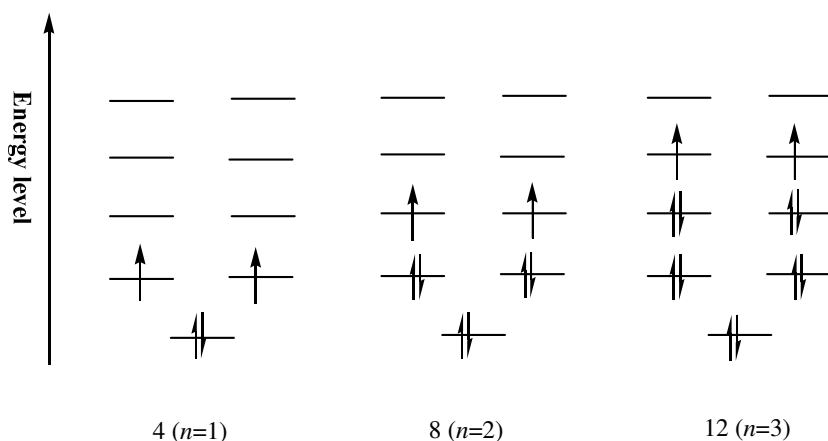


Fig.3. How  $\pi$  electrons occupy in  $4n$  systems.

$\alpha$  spin has  $+\frac{1}{2}$  and  $\beta$  spin has  $-\frac{1}{2}$  quantum number. Sum of all spin quantum numbers of all electrons in a system is called the total spin quantum number ( $S$ ) of the

system. The number,  $2S+1$ , is called multiplicity and when the system is put into a magnetic field,  $2S+1$  number of energetic states appear. Usual compounds, for example, those shown in Fig.2 have same number of both spins yielding  $S=0$  and therefore  $2S+1=1$ . They are called singlet state. Contrary to this, compounds which have configuration like shown in Fig.3 have  $S=1$  and  $2S+1=3$ . They are called triplet state compounds.<sup>4</sup>

The electronic state shown in Fig. 3, two electrons do not form a spin pair, so one chemical bonding is missing. That means that at least as much as one chemical bond, the energy of such system is higher if compared to the corresponding system in Fig. 2.

A triplet system has two unpaired electrons. In other words, the system has two radicals in it. A radical is highly reactive because it does not have the transition state of the reaction. Thus radicals react easily with other molecules and/or radicals consuming themselves. They are chemically very unstable.

The reasons of aromaticity/anti-aromaticity may be summarized as follows.

### **Aromaticity**

The origin of aromaticity found in those like benzene is that there exists the  $\pi$  orbital with no kinetic energy because of cyclic conjugate systems. Chain conjugation systems do not have such an orbital.

### **Anti-aromaticity**

The appearance of anti-aromaticity like that in cyclobutadiene is that in spite of the fact that the  $4n$  systems have the lowest energy orbital with null kinetic energy, they have two parallel-spin orbitals at the highest occupied orbitals losing the energy of one chemical bond. This makes the system higher in energy and in addition such a system has two radicals causing it chemically reactive, i.e., unstable.

## **Supplementary Explanation**

It is understood that the Hund rule and high reactivity of radical are concerned with realization of anti-aromaticity. As supplementary explanation, the Hund rule and the cause of high reactivity of radical are explained.

### **1. The Hund Rule**

The following description is based on that from Tutorial (1320) of this HP.

When an electron is regarded as a particle as considered by classical mechanics, it seems able to pack many electrons in one state, for example, in an atomic orbital.

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<sup>4</sup> A singlet state molecule has only one state in a magnetic field. But a triplet state molecule splits into three energetically different states in a magnetic field.

However, it is not always true in the microscopic world. It is known that there are two kinds.

### Bose Particle and Fermi Particle

One kind of particle is like that more than one particle can take one state. They are called bosons (Bose particles). Examples of boson are, photon,  $\pi$  meson and helium atom. (A super-flow phenomenon of liquid helium is caused because helium atoms are bosons.)

The other kind of particle shows the character that only one particle can take one state, i.e., the configuration of one particle being in one state is allowed. Such particles are called fermions (Fermi particles). The character of boson or fermion is given to the particle as an inherent one. The reason for this is unknown and is unnecessary to know to explain chemical phenomena. Let us accept this fact! The (electronic) state includes both spatial (orbital) and the internal (spin) state (to be given next) of the particle. Examples of fermion are electron, neutron, proton, and so on.

### Electron's Spin and Spin Quantum Number

It is known that an electron has two kinds of internal states. When it is adapted to a classical model, it corresponds to electron's rotation along the axis of movement. It called spin. Since it is easy to catch the concept, I will explain it using the classical model.

Let us assume an electron "ball" as shown in Fig. 4. The quantity of the rotational moment was measured and was found to possess  $+\hbar/2$  or  $-\hbar/2$ . One of them is called an  $\alpha$ -spin electron and the other a  $\beta$ -spin electron. Here,  $\hbar$  is a constant  $h$  (Planck's constant) divided by  $2\pi$  and has the value of  $1.054572 \times 10^{-34}$  J·s. The coefficients placed before  $\hbar$  i.e.,  $1/2$  and  $-1/2$  are called spin quantum numbers.

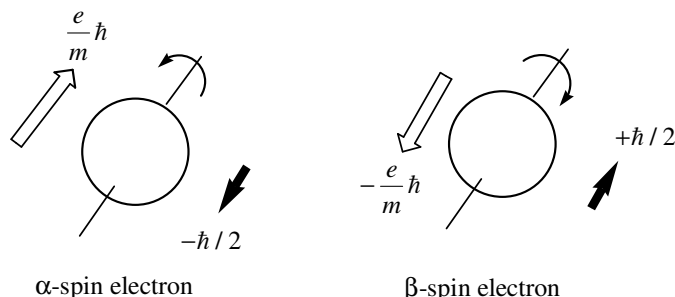


Fig.4. Electron's angular momentum and magnetic moment,  $e$  is elementary charge ( $1.6022 \times 10^{-19}$ C) and  $m$  is the mass of electron ( $9.109 \times 10^{-31}$ kg).

### The Pauli's Exclusion Principle

Including spin state, one orbital can accept two electrons and not more than two. This called Pauli's exclusion principle.

Atomic orbital,  $\chi$ , is described by the space coordinate as well as the spin coordinate: the space coordinate is usually expressed in de Cartesian or polar coordinate. Since the spatial and spin coordinate are independent each other, the total electronic state is expressed by the product of spatial and spin functions. For example, if an electron has  $\alpha$ -spin and occupied  $\chi$  orbital, the electronic state is mathematically  $\chi(1)\alpha(1)$ , likewise, for the  $\beta$ -spin electron 2,  $\chi(2)\beta(2)$  is given.

### Electron's Spin and Magnetic Momentum

As Fig. 4 shows, a ball with electric charges generates a magnetic moment by rotation. This causes an energy difference due to spin under a magnetic field.

### Hund Rule

Let us consider the cases of "how to enter" when more than one electron occupy the degenerated atomic orbitals. This way of occupation is called "electronic configuration". Considering the Pauli's principle, the possible configurations are shown in Fig. 5, when two electrons occupy the doubly degenerated orbitals,  $\chi_a$  and  $\chi_b$ .

The states [A and A'] and [B and B'] are reasonably considered to be equivalent in energy. Similarly, the energy with C and D is also equal.

Without magnetic field, the energies of F and E are equal. The problem is, which is the most stable state among A, C, and E when no magnetic field is applied.

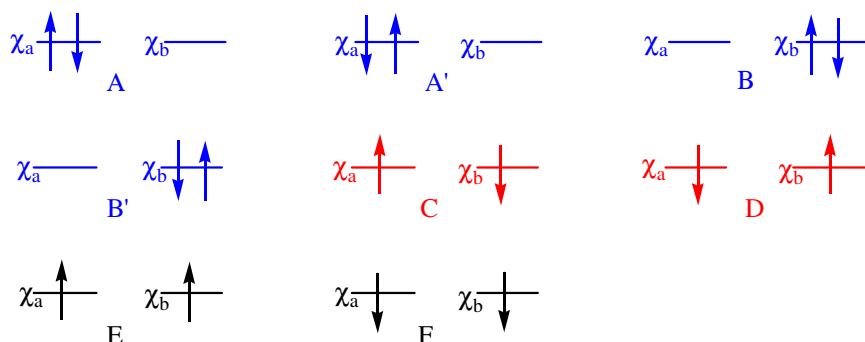


Fig. 5. Possibilities of configuration when two electrons occupy doubly degenerated orbitals.



It is easily expected that the energy of state **A** is the highest. For two electrons occupy the same orbital; in this state there is much chance for the electrons to become close and because of this, the electronic repulsion energy becomes higher than other cases.

Let us compare **C** and **E**: the difference is only in spin state. Remember that the shape and size of an orbital are not defined clearly and when the size of the orbital is said strictly, it is infinite. This means that the space is shared by the two orbitals: there is some possibility that some part of the electron that belongs to  $\chi_a$  becomes very close to another electron that belongs to  $\chi_b$ . This produced a large electron-repulsion energy between them.

In state **C**, such a case is really true, but in **E**, the repulsion-energy is much reduced because according to the Pauli's exclusion principle, mutual approach of electrons,  $\chi_a$  to  $\chi_b$  or  $\chi_b$  to  $\chi_a$ , is forbidden resulting is less energy in **E**. Conclusively, configuration **E** is the most stable.

### Total Spin Quantum Number

As we already saw, electron has either +1/2 or -1/2 spin quantum number. Let us consider the sum of spin quantum numbers of multiple electrons. If two electrons have  $\alpha$  spin, the sum of every spin quantum number is  $1/2+1/2=1$ , while one electron has  $\alpha$  spin and the other has  $\beta$  spin, then the sum is  $1/2-1/2=0$ . The sum of spin quantum numbers of all electrons in the system is called "total spin quantum number" ( $S$ ). This is shown by,

$$S = |s_1 + s_2 + \dots + s_n| \equiv \left| \sum_{i=1}^n s_i \right|$$

where  $s_i$  is the spin quantum number of electron  $i$ .

The way how to occupy the degenerated orbitals is so done as the total spin quantum number ( $S$ ) becomes as large as possible. This way is called the Hund's rule. The Hund's rule can apply to atomic orbitals as well as molecular orbitals.

### Spin Multiplicity

There are  $2S+1$  numbers of magnetic states for  $S$ , that is,  $2S+1$  numbers of energy states appear under a magnetic field. This number,  $2S+1$ , is called "spin multiplicity". For 1, 2, 3, ... of  $2S+1$ , one calls singlet state, doublet state, triplet state, and so on. For example, hydrogen atom has one electron, so,  $S=1/2$  and the multiplicity is  $2 \times (1/2) + 1 = 2$ , doublet state. The ground state of He has two electrons with  $\alpha$  and  $\beta$  spins giving  $S=-1/2+1/2=0$  and  $2S+1=1$  the singlet state. Most of usual organic compounds are in the singlet state ( $S=0$ ), Radicals are in the doublet state and biradical are easily expected to be singlet or

triplet.

## 2. Concerning the Reactivity of Radicals

The reaction rate of a radical reaction will be generally very high if compared to ionic reactions. This is because the radical reaction involves only the electron movement and because the mass of electron is very small. In addition, a radical easily reacts with other molecule(s) to generate a new radical. Therefore, chain reaction takes place in most cases.

The rate-determining of a radical reaction is in the movement of an electron, so the effect of the steric hindrance is very smaller than that of ionic reaction. (See a transition state exists because of the steric hindrance of the reactants.)

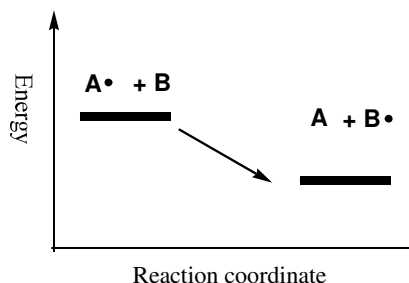


Fig.6. A radical reaction simply depends on the difference of energies.

The unpaired electron binds easily with another unpaired electron or paired electron in chemical bond. Reaction of  $A \cdot$  with molecule  $B$  produces radical  $B \cdot$ . As Fig.6 shows, if the total energy of the resultant system is lower than that of the reacting system, the reaction will go, simply because there is no transition state. The energy of system  $A + B \cdot$  is higher, the reaction will not go.

Figure 7 shows the case when the mixture of methane and chlorine is exposed to light.

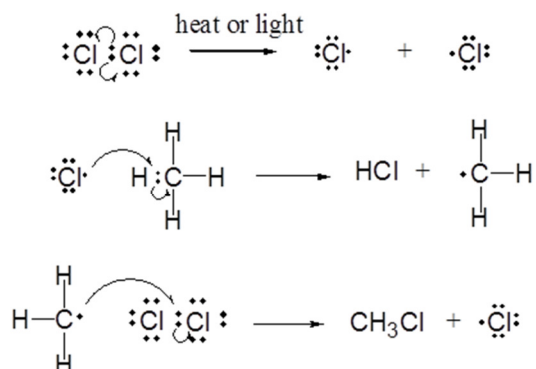


Fig.7. An example of radical reactions.

The reaction of the mixture does not take place without light, but light causes an

explosive reaction. The reaction path is: a chlorine radical ( $\text{Cl} \cdot$ ) is formed by light. The radical reacts with a near-by methane molecule to produce methyl radical ( $\text{CH}_3 \cdot$ ). Methyl radical reacts with chlorine molecule to give chlorine radical. Repeating this process is the chain-reaction.