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AN INVESTIGATION INTO REPRESENTATIVE MODELS FOR INDENTIFYING ORGANIC REACTION MECHANISMS

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Abstract: This article investigates representative models for determining organic reaction mechanisms. These models could be applied to identify a possible mechanism of an organic reaction because they are systematic, logical, and easy-to-remember. The representative model contains three modules including a recognition module, a mechanism writing module, an analysis and a conclusion module. The recognition module provides necessary information, identifying what kind of mechanism a reaction could follow. The representative models of several types of organic reactions, such as substitution reaction (S), addition reaction (A), elimination reaction (E) were investigated. The representative models might be used as a new teaching method, making the learning of organic reaction mechanism of not only high school students but also bachelor students easier and more efficient.

Key words: organic reaction mechanism; the representative model; the recognition module.

1. Introduction

An organic reaction mechanism provides fundamental information on the direction of a reaction, and factors that impact on the reaction; hence appropriate adjustments to the given factors could be made for three main purposes: to obtain desired results, enhance reaction performance, and lower the cost. Since the mechanism is abstract, it is a challenge for lecturers to illustrate the theory briefly and clearly as well as for students to have an insight into it. In the current context, although the illustrations for reaction mechanisms are various and dependent on different authors, these illustrations obey the same approach for analyzing each of functional groups. For example, the S_R (Radical substitution) mechanism is introduced in the lesson of alkane and the A_E (electrophilic addition) mechanism is introduced in the lesson of alkene. These methods of illustration reduce the creativity of students in researching this subject. For example, the vast majority of students confuse that reaction of alkyne follows the A_E mechanism, or all reactions of aldehyde and ketone follow the A_N (nucleophilic addition) mechanism. Modeling factors that decide the mechanism of an organic reaction provides students with a general picture, and an easy-to-understand perspective; hence students could determine the possible reaction as well as determine what kind of mechanism this reaction follows.

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2. Proposal of illustration models of reaction mechanism

The illustration model of mechanism consists of 3 modules: a recognition module (including reactants and reagents, and conditions), a mechanism writing module, and an analysis module.

2.1. Reaction Recognition

One of the most challenged obstacles of writing a reaction mechanism is to determine its type of mechanism. Recognition module provides primary information to solve this problem.

2.1.1. Reactants

This method uses the hybridization structure of a carbon atom (sp, sp^2, sp^3) to recognize the reactants. Reactions of a substance which contains sp, sp^2

hybridized carbons are predicted to obey the mechanism of electrophilic addition to break the bonds while a reaction is predicted to obey the principles of substitution mechanism and elimination mechanism if it contains sp^3 hybridized carbons.

For example, alkenes, alkynes, aldehydes, etc. tend to undergo electrophilic addition reactions, whereas halogen derivative, alcohol, etc. tend to undergo substitution and elimination reactions.

2.1.2. Reaction reagents

The recognition of reagents is mainly based on the characteristics of a polar bond or polarization between two atoms forming the bond. Non-polar compound X:X benefits the hemolytic bond cleavage to produce radical reagent such as halogen, peroxide. In contrast, polar compound Y→X has its advantage in taking place in heterolytic fission to produce nucleophilic or electrophilic reagents.

2.1.3. Reaction condition

Reaction condition decisively impacts on the probability for a reaction to occur, its mechanism, reaction rate, and the characteristics of resulting products.

In reaction recognition, the condition that affects bond cleavage is the most important factor. A reaction, which occurs in an inert and non-polar solvent at high temperature, tends to undergo a radical mechanism. On the contrary, a reaction, which is catalyzed by an acid or a base in a polar solvent at low temperature, tends to undergo electrophilic or nucleophilic mechanisms. They are signs to determine reaction mechanism.

2.2. Mechanism writing

Reaction mechanism is written based on intermediate steps that were proved strictly and logically. After the mechanism is determined, mechanism writing is performed following the proved models.

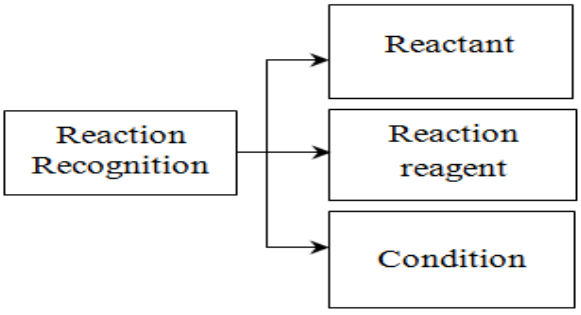
2.3. Mechanism analysis

An organic reaction often occurs in many directions, yielding many different products. Reaction mechanism recognition and writing only clarify the process and basic steps occurring in a reaction. The step of analyzing the reaction mechanism can systematically predict the priority order among reaction directions as well as characteristics and features of resulting products. Understanding the similarities and distinctions between reaction mechanisms learned from these bases aims to adjust the relating factors to control the reaction for yielding the necessary products and adapting required demands. Hence, the three modules are tied together and dependent on each other. In detail, determining the type of reaction mechanism is required for mechanism writing, and mechanism writing is a compulsory factor to analyze and examine the resulting products. The main point of this article is to analyze the recognition module, which is a decisive factor for organic reaction mechanism models.

3. Reaction mechanisms recognition

The recognition modules of S_R, S_E, S_N, A_E, A_R, A_N and E mechanisms include three factors: reactant, reaction reagent, condition, which are shown as follows.

3.1. Radical substitution S_R [1]

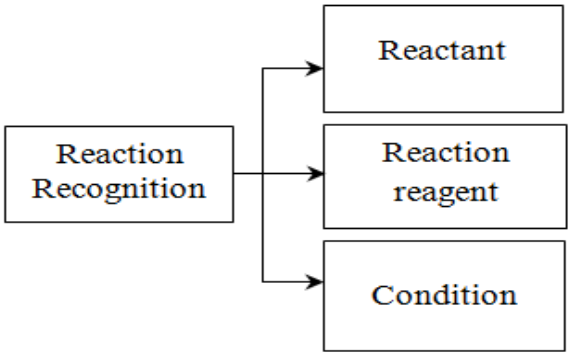


- sp^3 C of saturated hydrocarbon

- Free radical

- High energy (heating, sunlight exposure, lighter)
- Catalyst: peroxide
- Solvent: non-polar such as ether, CCl_4, CS_2, cyclohexane,…

3.2. Electrophilic substitution S_E [2]

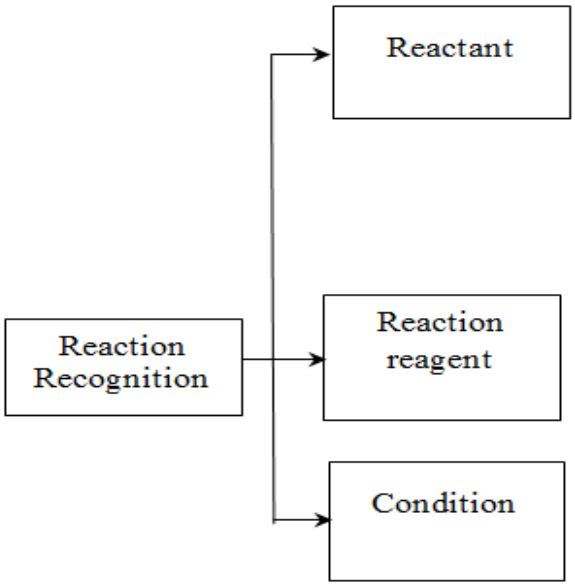


- Compounds with a high electron density center such as arenes, unsaturated compounds or saturated compounds that consist of an electron donor group.

- Compounds with empty orbitals such as positive ion, or unfilled orbital.

- Reactions occur at normal temperature.
- Solvent: polar solvent
- Catalyst: Lewis acid

3.3. Nucleophilic substitution S_N [1]

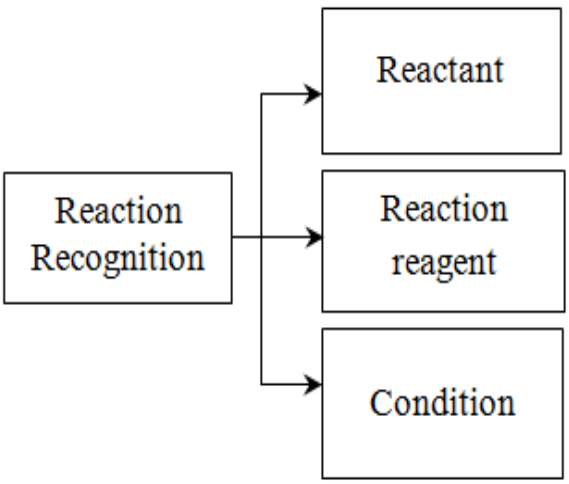


- Polar compounds: $R \overset{\delta+}{\rightarrow} X^{\delta-}$
- R: all kinds of C (sp^3, sp^2, sp), O, S, N. S_N typically associated with sp^3 hybridized Carbon with the lowest electron density, with no nuclear hindrance, which is easy to be approached by a reaction reagent.
- X: negatively charged groups: Hal, OH, OR, OSO_2R, OCOR,… or positively charged groups: N^+R_2, S^+R_2…

- Anion: C^-, H^-, O^-, S^-, N^-…
- Neutral molecules:
* H : Y eg. HOH, H-Hal, H-OR, H-NH_2, …
* Cl : Y eg. Cl : PCl_4, Cl : PCl_2, Br : PBr_2, …

- Reactions occur at normal temperature.
- Solvent: polar solvent
- Catalyst: acid or base, depending on the reactant or the reaction reagent.

3.4. Nucleophilic addition A_N [5]



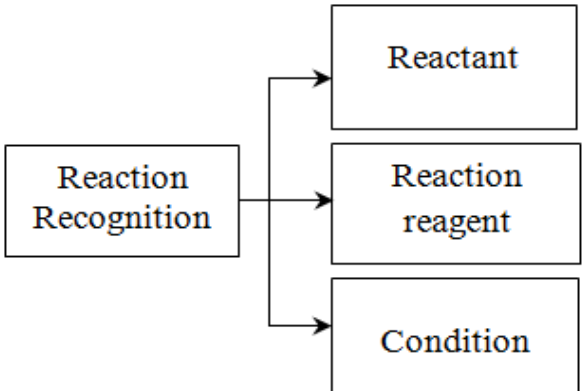
$-\underset{|}{C}=X$ (O,N,...)

- Aldehyde, ketone, acid, ester, amid, nitrile. C=C bond of a compound that contains a strong electron withdrawn group that could participate in the A_N reaction.

- $Z^{\delta+} : Y^{\delta}$ → Z: H, RO, Hal… ; Y: OH, Hal, NH_2…

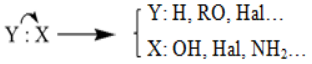
- Reactions occur at normal temperature.
- Solvent: polar solvent
- Catalyst: acid or base, depending on reactant or reaction reagent.

3.5. Electrophilic addition A_E [4]



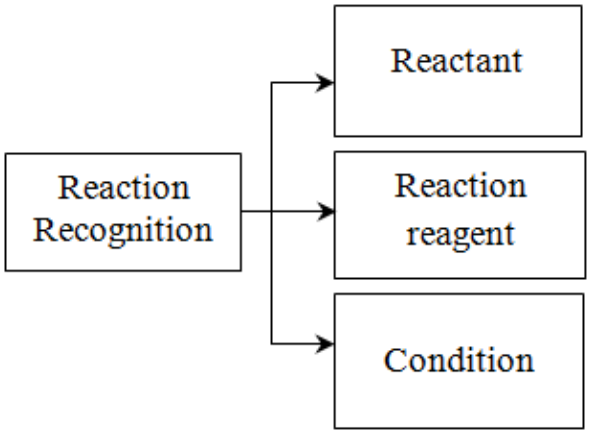
- Unsaturated compounds that contain multiple bond. The most common case are alkens and alkynes.

- Compounds that have empty orbital as cation or neutral molecules.



- Reactions occur at normal temperature.
- Solvent: polar solvent
- Catalyst: Lewis acid

3.6. Radical addition A_R [1]

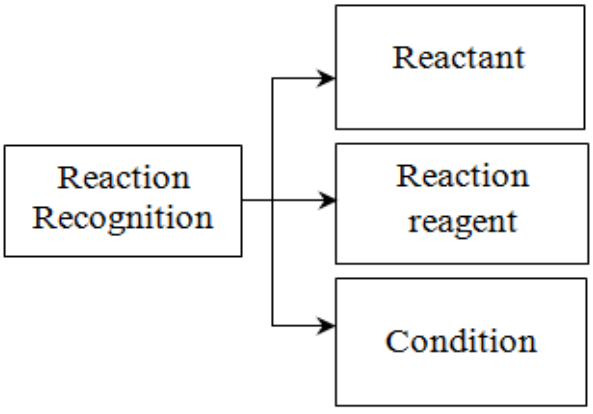


- Compounds containing C=C bond.

- XY: halogen, HBr, H_2S, HSR, poly-halogen methane (CCl_4, $CHCl_3$, CBr_4), …

- Reactions occur at high temperature or with the assistance of light.
- Solvent: polar solvent
- Catalyst: compound that can generate free radical, such as oxygen, peroxide

3.7. Elimination reaction E [1]



$\overset{\delta+}{-R} \rightarrow \overset{\delta-}{X}$ X: F, Cl, Br, I, OSO_2R,…

- Compounds that have an opposite property to Reactant.

- Reactions occur at high temperature
- Solvent: polar solvent

4. Examples of applying the model of reaction mechanism recognition

4.1. Example 1

Consider the following reaction:

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

- Reactant: CH_4 is a saturated hydrocarbon, so it participates in the substitution reaction. The sp^3 hybridized carbon and the nonpolar bond C-H in CH_4 facilitate the homolysis.

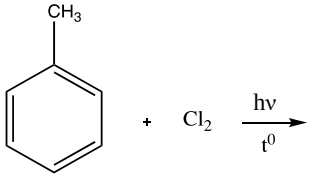
- Reagent: Cl-Cl forms free radical Cl· under light exposure.

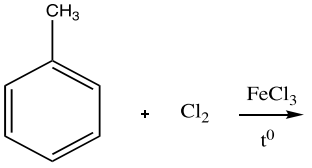
- Condition: this reaction occurs under the condition of diffused sunlight.

Compared with the aforementioned models of the reaction mechanism, the given reaction corresponds to the S_R mechanism.

4.2. Example 2

Consider two following reactions:

a) 

b) 

* Reaction a:

- Reactant: C of $-CH_3$ group in toluene is a sp^3 C. Like C in saturated hydrocarbon, this C could take part in a substitution reaction and homolysis.

- Reagents: Cl-Cl forms free radical Cl· under light exposure.

- Condition: this reaction occurs under the condition of diffused sunlight.

→ S_R mechanism can be written for this reaction.

* Reaction b:

- Reactant: the compound containing phenyl group with a high electron density center can participate in the substitution reaction as an electrophilic reagent.

- Reagent: Cl_2 reacts with $FeCl_3$ to form an electrophilic reagent $Cl^+ \ldots FeCl_4^-$.

- Condition: Lewis acid catalyst $FeCl_3$.

→ S_E mechanism can be applied for this reaction.

4.3. Example 3

a) $CH_3 - CH = CH_2 + Br_2 \xrightarrow{peroxide}$

b) $CH_3 - CH = CH_2 + Br_2 \xrightarrow{H_2O}$

* Reaction a:

- Reactant: contains C=C bond therefore it is easy to undergo an addition reaction.

- Reagent: free radical Br· is formed with the presence of peroxide catalyst.

- Condition: peroxide catalyst.

→ A_R mechanism can be applied to this reaction.

* Reaction b:

- Reactant: the compound has C=C bond, so it is preferable to take part in an addition reaction. In addition, the electron density of C=C bond is high enough to react with an electrophilic reagent.

- Reagent: H_2O is a polar solvent, so Br_2 reacts with water to form electrophilic reagent $Br \overset{\delta+}{\rightarrow} Br \overset{\delta-}{.}$

- Condition: a polar solvent (H_2O).

→ A_E mechanism can be written for this reaction.

Discussion: In practice, there are various reactions sharing the similarities between reaction factors and reactants; however, they occur with different mechanisms, depending on their reaction conditions. Hence, it is necessary to determine the three factors simultaneously including reactants, reaction factors, and reaction conditions to lay a solid foundation for reaction mechanism writing.

5. Conclusion

This article has provided a new method for teaching the organic reaction mechanism. In fact, representative models of some reactions such as substitution, addition, elimination were investigated. These models were applied to propose some example reactions. Representative models of mechanism could be widely used, making the organic chemistry mechanism more accessible to leaners.

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NGHIÊN CỨU MÔ HÌNH HOÁ ĐỂ NHẬN DIỆN CƠ CHẾ PHẢN ỨNG HỮU CƠ

Tóm tắt: Bài báo này công bố kết quả nghiên cứu mô hình hóa cách nhận diện cơ chế phản ứng hóa học hữu cơ. Ưu điểm của việc xác định cơ chế phản ứng theo hướng mô hình hóa là có thể áp dụng cho mọi cơ chế, có tính hệ thống, logic và dễ ghi nhớ hơn. Mô hình cơ chế được trình bày gồm 3 module là nhận diện phản ứng, viết cơ chế và phân tích, nhận xét. Trong đó module nhận diện phản ứng sẽ cung cấp bước đầu thông tin cơ bản để biết phản ứng xảy ra theo cơ chế nào. Dấu hiệu nhận biết các cơ chế phản ứng thế S, phản ứng cộng A, phản ứng tách E đã được đưa ra. Đây là phương pháp mới có thể sử dụng để giảng dạy cơ chế phản ứng tại các trường phổ thông và đại học giúp học sinh và sinh viên dễ hiểu và dễ nhớ hơn.

Từ khóa: cơ chế phản ứng hóa học hữu cơ; mô hình cơ chế; module nhận diện phản ứng.