

Influence of Electron Effect on Electrophilic Addition

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Abstract

Electronic effects include induction effect and conjugate effect, which are the most important theoretical basis in organic chemical reactions. This paper expounds the concept and essence of these two effects, and gives theoretical elaboration and examples based on the effects on addition reactions. In addition, the position selectivity of addition reaction between asymmetric olefin and asymmetric electrophile is also discussed, which is markov rule. The effects of organic chemical reactions on electrophilic addition can be analyzed by using electron effect, and the products of organic chemical reactions can be judged.

Keywords

Conjugative effect; Induction effect; Markovnikov rule; Electrophilic addition reaction.

1. INTRODUCTION

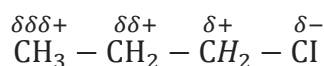
In organic reactions, the activity and reaction law of organic compounds determine how the reaction will proceed. Electronic effect is an important factor affecting the reaction, and even plays a decisive role in the reaction. The electronic effect in organic chemistry is more complex and profound than that in inorganic chemistry. A deep understanding of the electronic effects of organic chemistry can help us understand organic compounds more deeply and develop more and more rationally. Organic compounds have many kinds and complex structures, and the factors that affect their properties are often multifaceted. Only by understanding the influence of atoms or groups in molecules, can we better understand and grasp organic chemical reactions. These effects can generally be analyzed from two aspects: electronic effect and stereoscopic effect. This paper only describes the influence of electronic effect on electrophilic addition in organic reactions.

Electron effect refers to the influence of electron density distribution on molecular properties. Generally speaking, there are two or three effects that work together to affect the properties of substances. Next, we will introduce the types and significance of electronic effects, understand the expression, application conditions and scope of Markov rules, deeply explain the essence of Markov rules, and judge whether the reaction really conforms to Markov rules. Not all reactions conform to this rule.

2. ELECTRONIC EFFECT

2.1. Induced Effect

When two atoms combine to form covalent bonds, the electronegativity of each atom is different, so it will cause the electron cloud to lean to the side of the atom with greater electronegativity. The bond formed in this way is called polar covalent bond. This electric field generated by polar covalent bonds can cause the charge of adjacent valence bonds to move. For example:



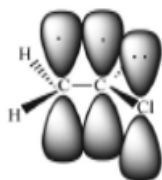
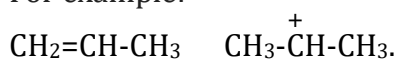
In this molecule, when the carbon atom combines with the chlorine atom, a polar covalent bond (C-Cl) is formed. Because the electronegativity of the chlorine atom is greater than that of the carbon atom, the second and third carbon atoms connected with the chlorine atom have partial positive charges, and the electronegativity decreases in turn. In an organic compound like this, the electronegativity of atoms causes the electricity to transfer along the carbon chain, shifting the bonded electron cloud to the side with greater electronegativity. Generally, the longer the carbon chain, the weaker this effect. We believe that the influence is very weak when passing through three carbon atoms, and disappears when passing through five carbon atoms. This effect is called induction effect, and affects other parts of the molecule through electrostatic induction. In general, I is used to indicate the induced effect- I refers to the electron absorption effect, which means that when the atom or atomic group forms a bond with the carbon atom, the bonding electron cloud deviates from the carbon atom. On the contrary, +I effect is the electron donor effect, and the induction effect of saturated C-H bond is specified as 0.

2.2. Conjugate Effect

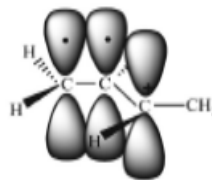
Conjugation effect, also known as delocalization effect, is an electronic effect that interacts between atoms in molecules due to electron delocalization. If in a conjugate system, all σ bonds are in the same plane of the system, the conjugation effect will occur. The reason is that when they are in the same plane, the p orbitals involved in conjugation are parallel to each other, so the molecular orbitals can be formed. If the p orbitals are not all parallel to each other, then this coplanar will be destroyed, and the degree of overlap will be reduced, so the conjugate effect will gradually weaken with the reduction of the degree of overlap, until it disappears completely. This effect is transmitted through π bond, which can be transmitted from one end to the other. Generally speaking, there are three kinds of conjugation effects: ① π - π conjugation effect: single and double bonds are distributed in turn, and the p orbitals forming π bonds alternately overlap each other on the same plane to form a conjugated system, such as $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$.

② P- π conjugation effect (as shown in the figure): one side of a single bond has a π bond, and the other side has atoms that do not share electron pairs, or has parallel p orbitals, such as $\text{CH}_2=\text{CH}-\ddot{\text{Cl}}$, $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2$, etc.

③ Superconjugation effect: if π bond and C-H σ Bond conjugation, that's it σ - π conjugation; If C-H σ Bond conjugation with p orbital becomes σ - P conjugate. because σ The orbital is not completely parallel to the π orbital, so the σ - π conjugation effect and σ - P-conjugation effect is much weaker than π - π conjugation and p- π conjugation, so it is called hyperconjugation effect. For example:



Multi electron p- π conjugation



Electron deficient p- π conjugation

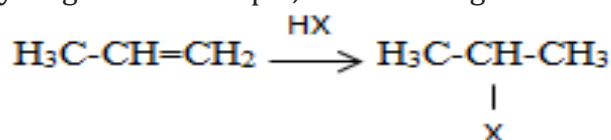
C is used to represent the conjugation effect, and -c represents the electron absorption conjugation effect, +c represents the electron donor conjugation effect. So what is electron attracting conjugation effect? What is electron donor conjugation effect? There are substituents on the conjugated system, such as -COOH, -CHO, -COR, etc., which are electron withdrawing groups; On the contrary, if the connected groups increase the density of the π electron cloud of

the system, they are called electron donating groups, and they have electron donating effect. For example, $-\text{NH}_2$, $-\text{OH}$, $-\text{R}$, etc.

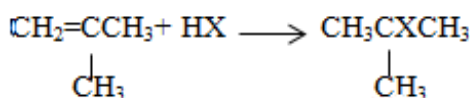
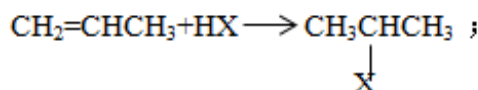
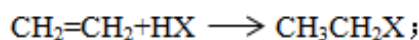
Both conjugation effect and induction effect have a great influence on organic compounds, and the influence is often not single, but affects compounds at the same time. An organic compound generally has both conjugation effect and induction effect, and the direction of these two effects can be consistent or inconsistent. Generally, the intensity of superconjugation effect is weaker than $\pi - \pi$ conjugation and $\text{P} - \pi$ conjugation, but stronger than induced effect.

3. TRADITIONAL EXPRESSION OF MARKOV RULE

Markov rule, namely Markov nikov rule, he summarized Markov rule after a lot of experimental research in 1869. That is, when asymmetric olefins and asymmetric reagents undergo electrophilic addition reaction, the positively charged group in the reagent (such as H^+ in acid) should be added to the double bond carbon containing more hydrogen, and the negatively charged group in the reagent (such as halogen) should be added to the double bond carbon containing less hydrogen. For example, the following reactions:



According to Markov's rule, in addition to adding hydrogen halide to ethylene to obtain the main halogenated alkanes, other alkenes can only obtain secondary and tertiary halogenated alkanes:



3.1. Essence of Markov Rule

3.1.1 explanation from the aspect of electronic effect

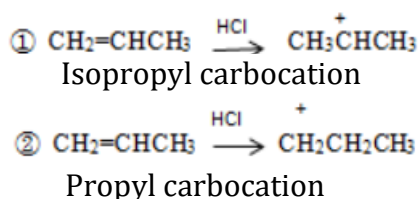
Generally speaking, the carbon atom in the methyl group is sp^3 hybrid, while the carbon atom in the double bond is sp^2 hybrid. The electronegativity of the carbon atom increases with the increase of the amount of s orbital in the mixed orbital. The closer the density of the electron cloud is to the nucleus, the greater the Electronegativity of the orbital. That is to say, the order of electronegativity is $s > \text{sp} > \text{sp}^2 > \text{sp}^3 > p$, so if methyl is connected with a group with strong electronegativity (such as $-\text{CH}=\text{CH}_2$), it means power supply, which makes the π electron cloud of $\text{C}=\text{C}$ move.

From the perspective of hyperconjugation effect, $\text{C}-\text{H}$ on methyl group σ Bond and π bond formation in $-\text{CH}=\text{CH}_2$ $\sigma - \pi$ hyperconjugation effect, which provides the polarization of carbon carbon double bonds. The final result is consistent with the induced effect of methyl.

3.1.2 explanation from the aspect of reaction process

In the example of the addition of propylene ($\text{CH}_2=\text{CHCH}_3$) with hydrogen chloride (HCl), the generation of carbon cations is the decisive step of the reaction. It is assumed that there are two possible additions of hydrogen ions in the addition reaction with hydrogen chloride. If hydrogen

ions are added to carbon 1 (C1) in the double bond, isopropyl carbon cations will be generated; If hydrogen ions are added to carbon 2 (C2) in the double bond, propyl carbon cations will be generated. The direction of addition depends on the relative stability of these two carbon cations. Stable carbon cations are easier to form in the reaction.



As an active intermediate, carbon cations are hybrid with sp^2 as the central carbon atom, and the hybrid orbital combines with three atoms or groups to form three σ Key, and three σ The bond is coplanar with the central carbon atom, and the p orbital of the remaining unfilled electrons is perpendicular to this plane. Based on the position of positively charged carbon atoms, alkyl carbon cations can be divided into primary (primary) carbon ions, secondary (secondary) carbon ions, tertiary (tertiary) carbon ions, and Quaternary (quaternary) carbon ions.

The distribution of the charge carried by a substance determines the stability of the charged system, that is, the more dispersed the charge, the more stable the system will be. Similarly, the charge distribution on matter also determines the stability of carbon cations. Carbon cations have empty orbitals, which can accept electrons, so when the central carbon atom is connected with the alkane group, if the hydrocarbon in the alkane group σ If the orbitals and the empty p orbitals of the central carbon atom are located in the same plane, only part of the two orbitals overlap, and the electrons will tend to delocalize into the empty p orbitals of the carbon cations, so that the positive charges of the central carbon atom are dispersed and the system tends to be stable. This delocalization function is called σ - P conjugate effect. participate in σ - The more the number of conjugated C-H bonds of P is, the easier the positive charge dispersion is, and the more stable the carbon cation is, the easier it is to generate. For example, there are 9 tertiary butyl carbon cations with σ - C-H bond of P conjugation effect; There are 6 in isopropyl carbon cations, 3 in ethyl carbon cations and 0 in methyl carbon cations. It is not difficult to understand that the more alkyl groups on positively charged carbon atoms, the more positive charge dispersion, and therefore more stable. Therefore, there is the following order of stability of carbon cations: $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{C}^+\text{H} > \text{CH}_3\text{CH}_2^+ > \text{C}^+$, that is, $3^\circ > 2^\circ > 1^\circ$.

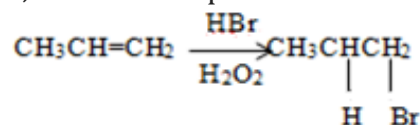
3.2. limitations of Markov rule

According to a large number of experimental facts, the Markov rule was born. The proposal of this rule is a major breakthrough in organic chemistry, especially for judging the main products of olefin electrophilic addition reaction. Secondly, when asymmetric olefins react with sulfuric acid, water and other reagents, we can know what substances are produced and infer the reaction orientation by using Markov rule. However, this rule is an empirical rule obtained from experiments, and there is no deeper theoretical study from the reaction mechanism. Only from the unilateral point of view, which part of the hydrogen atom is added to the double bond carbon in the reaction, it can not fully explain that all addition reactions comply with this rule, so the Markov rule has certain limitations.

When asymmetric olefins (such as propylene) react with electrophilic reagents (such as hydrogen halide), the product is inconsistent with the product judged according to the Markov rule, which is called the anti Markov nikov rule. Generally speaking, there are two situations that do not conform to the Markov rule:

- (1) the reaction condition is light or peroxide, and the free radical addition reaction occurs;

(2) The electronegativity of the hydrogen atom contained in the electrophilic reagent is larger than that of the atom or atomic group connected to the reagent. From the result form, the orientation does not conform to the Markov rule. For example, if there is a strong electron withdrawing group (such as $-\text{CF}_3$) attached to the double bond carbon of olefins, when reacting with electrophilic agents, due to the influence of induction, through σ The bond sends the electron extraction effect to the double bond, polarizing the double bond, and then hydrogen is added to the intermediate carbon, which is the product of the anti Markov rule.



Borohydride oxidation reaction is also a reaction that does not conform to Markov rules. Boron atom is electrophilic in this reaction (δ^+), And it tends to replace less bound to double bonded carbon, so the bound carbon atom has a partial negative charge, then another carbon has a positive charge, and part of it forms a more stable carbon cation. Partial reactions that do not use carbon cations as reaction intermediates are also inconsistent with Markov rules. For example, free radical addition reaction of olefins and hydrogen halide. Taking HBr as an example, when bromine is added to carbon with less hydrogen, the free radicals formed are stable. Its stability is similar to that of carbon cations. The more substitution, the more stable the group is. This free radical takes hydrogen from another HBr molecule. In general, hydrogen is added to carbon atoms that contain more hydrogen. The electrophilic addition reaction of alkynes, not only olefins, is also carried out according to the anti Markov rule. For example, phenylacetylene reacts with water. Due to the rearrangement of carbon cations, the products produced after rearrangement usually do not conform to Markov rules.

4. INFLUENCE DEGREE OF ELECTRON EFFECT ON ELECTROPHILIC ADDITION

It can be seen from the above that carbon cations are intermediate reactions, and their stability can determine the direction of olefin electrophilic addition reaction. At the same time, the determination of the direction of electrophilic addition reaction also reflects the stability law of intermediates. In addition, because Markov rules only reflect the law of expression rather than the essence. So we can express the decision rule in this way; The main product of olefin electrophilic addition reaction is the electrophilic Center (the positive part in the reagent), which is formed by adding double bond carbon atoms, which leads to more stable carbon cations. According to what we have learned, the electrophilic addition of alkynes and cycloalkanes is similar to the electrophilic addition of olefins. It is also a relatively stable intermediate carbon cation, which is regenerated into the main product. The essential laws followed by such reactions are consistent. Therefore, the judgment rules we described earlier also apply to alkynes and cycloalkanes.

5. CONCLUSION

According to the above discussion, it can be concluded that in the electrophilic addition reaction, some products are added according to the Markov rule, and some reaction products cannot be judged by the Markov rule. It can be seen that Markov rule is not a universal law, and it is not applicable to all electrophilic addition. When determining what kind of products are produced by electrophilic addition reaction, it is particularly important to correctly judge the stability of carbon cations. Negative electrophilic groups should attack the most stable carbon cations, so the products produced by the reaction are correct. In short, the electronic effect usually plays a major role. However, the chemical reaction of organic matter is not only related

to electronic effect, but also to its three-dimensional effect. The combined action of the two determines the chemical properties of substances. Of course, this is only in terms of the internal structure of substances. When discussing specific reactions, external factors should also be considered, such as solvation, reaction temperature, solvent properties, etc., in order to make a more comprehensive and demonstrative analysis.

In short, to understand the structure of matter, electronic effect is a very important foundation. The structure of organic matter determines its properties, and all applications are inseparable from its properties. Therefore, we should firmly grasp the electronic effect, which plays a very important role in learning organic chemistry.

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