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CHEMICAL REACTIVITY THEORY——ITS PRAGMATISM AND BEYOND

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Abstract - The development of the theory of chemical reactions is sketched. The use of a perturbation molecular orbital theory, the primordial frontier orbital theory, is stressed in view of the reaction design. Examples of the frontier orbital polarization approach are shown. A theory of chemical reaction path, called the IRC (intrinsic reaction coordinate) approach, is mentioned. It is shown that this approach is useful for making the chemical reactivity theory go beyond the perturbation method. Several applications of the IRC approach are discussed.

INTRODUCTION

Since G. N. Lewis introduced the concept of "sharing of electrons" in 1916, the electronic theory had been developed by a number of chemists. Particularly R. Robinson and C. K. Ingold contributed much to establish the electronic theory so as to be suitable for discussing the chemical reactivity of organic compounds(Ref. 1 & 2). In that theory, the electron density distribution and its change in a compound played a principal role. Various chemical concepts were understood in terms of the electronic charge. The position of attack in chemical reactions was discussed by the electrostatic principle. In this fashion, the electronic theory was able to explain a majority of complicated experimental results in a unified manner.

The success of the electron density criterion was great. However, a weak point also existed. It was involved in the substitution reaction of non-substituted aromatic hydrocarbons. For instance, naphthalene reacts with both electrophiles and nucleophiles at the same position 1. Evidently, the simple electronic theory was not well qualified for explaining this result. So, Coulson and Longuet-Higgins considered the change of electron density under the influence of the attacking reagent(Ref. 3). Wheland calculated the energy required to localize electrons to the reaction site(Ref. 4). These two papers successfully interpreted the experimental results.

A PERTURBATION THEORY——FRONTIER ORBITAL APPROACH

In this connection, another attempt was made to approach this problem. The principal role of valence electrons in the formation of a molecule from constituent atoms was noticed. By analogy, the density distribution of the highest occupied molecular orbital(HOMO) was calculated for the attack of an electrophilic reagent. An agreement was obtained between the position of attack and the site of the largest density of this particular orbital. For a nucleophilic attack, the distribution of the lowest unoccupied MO(LUMO) was calculated and a correlation with reactivity was found. In the radical substitution the distribution of (HOMO + LUMO) possessed a correlation with reactivity(Ref. 5 & 6). The reasoning for these results was simply made by a perturbation theory(Ref. 7).

These selected orbitals, HOMO and LUMO, were called "frontier orbitals," and the reactivity criteria using the frontier orbitals were soon extended to other compounds than conjugated molecules and to other reactions than aromatic substitutions. Such an extension was made with no essential difficulty, since the method was based upon the electron delocalization between the frontier orbitals of the substrate and the reagent and there was no reason

to put any limitation with respect to the molecule and the reaction(Ref. 8 & 9). Some reactivity indices were derived from this delocalization picture. The method showed its usefulness in the field of the hydrogen abstraction from hydrocarbons by radicals, the S_N2 and the E2 reactions in halogenated hydrocarbons, the nucleophilic abstraction of hydrogen in olefins, and so forth. These results were collected in a single volume(Ref. 9). All of other reactivity theories then available were applicable only to conjugated molecules.

FRONTIER ORBITAL SYMMETRY

The usefulness of the theory was much more broadened when the symmetry of the frontier orbitals was employed in the discussion of the reactivity in Diels-Alder reaction(Ref. 10). By this work, the orbital symmetry was connected to the selective occurrence of chemical reactions. It was shown that the symmetries of HOMO and LUMO of dienes and dienophiles were in a situation favourable for a concerted cyclic interaction between them. The electron delocalization from the diene HOMO to the dienophile LUMO causes the weakening of the double bonds of both diene and dienophile and the formation of new bonds between the two molecules and also inside the diene. The nodal structure of diene HOMO and the dienophile LUMO is satisfactorily adapted for the formation of two new independent bonds. These circumstances simply explain why diene normally behaves as an electron-donor and dienophile as an electron-acceptor(Ref. 11). The bond exchange takes place smoothly by the aid of such a favourable situation of orbital symmetry. The orbital symmetry relationship in actually occurring Diels-Alder reaction is always favourable in the sense mentioned above.

The "selection rule" for the occurrence of concerted two-centre reactions seemed to be the conformity of the symmetries of HOMO and LUMO at the reaction centres. But one should not be too hasty in concluding so with only one example. In fact, it was after the proposal of a more general rule by Woodward and Hoffmann(Ref. 12) that the selection rule was systematized in the foregoing style(Ref. 13).

After the discovery of the Woodward-Hoffmann rule, the recognition of the frontier orbital theory became more rapid than before. It was therefore particularly fortunate for the development of the reactivity theory based mainly on perturbation methods that the Woodward-Hoffmann rule independently appeared just in time.

In process of time, the nature of chemical reactions had gradually been disclosed. The electron delocalization between HOMO and LUMO was found to be the principal factor. So, the easiness of a chemical reaction was controlled by the favourableness of the HOMO - LUMO interaction. It also determined the stereoselective path. Intramolecular processes were discussed similarly to intermolecular processes. A number of chemists contributed much to develop the HOMO - LUMO interaction approach(Ref. 14-21).

It is often useful to discuss the interaction energy divided into its constituents——the coulomb, the exchange, the polarization, and the delocalization energies. Such a partitioning technique is based on a perturbation or non-perturbation evaluation of the interaction energy(Ref. 22 & 23). Several examples are given(Ref. 24-31).

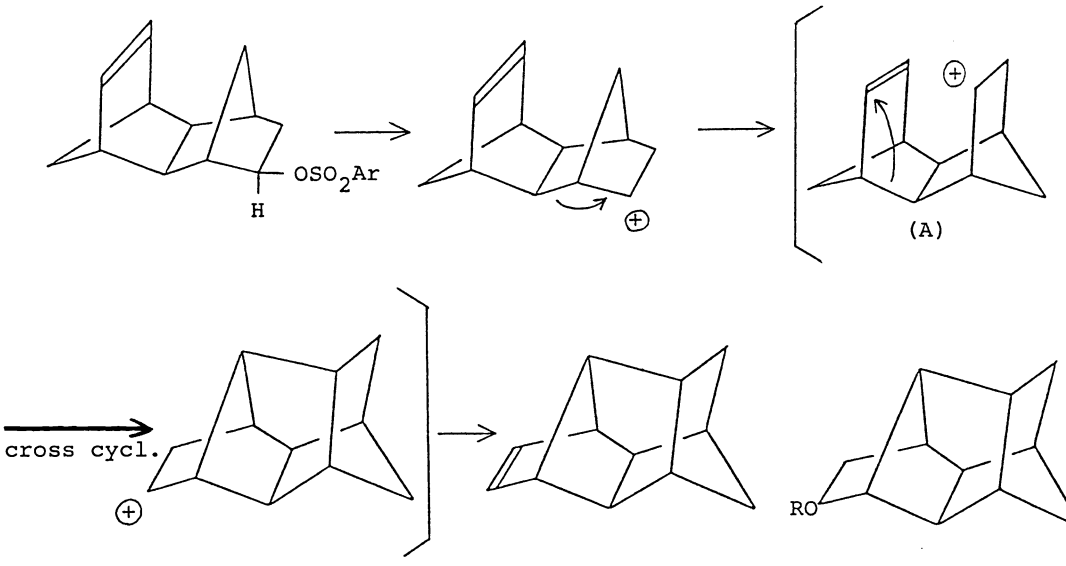
ORBITAL POLARIZATION APPROACH

The usefulness of the HOMO - LUMO interaction criterion in chemical reactivity problems has been shown. An effective discussion is in some cases possible even without quantitative calculation of molecular energy. A qualitative theory of orbitals for that purpose is most nicely mentioned in a lovely and unique book of Jorgensen and Salem(Ref. 32).

In relation to such a qualitative reactivity theory the frontier orbital polarization approach is frequently convenient for the reaction design. The orbital interaction causes orbital polarization in the course of reaction. Such as regioselectivity in cycloadditions, various subsidiary effects in cycloadditions, substituent effects, d-orbital effects, lone-pair orbital effects, plane-asymmetric stereoselective reactions, and other selective reactions were interpreted(Ref. 9, 13, 19-21, 33-37).

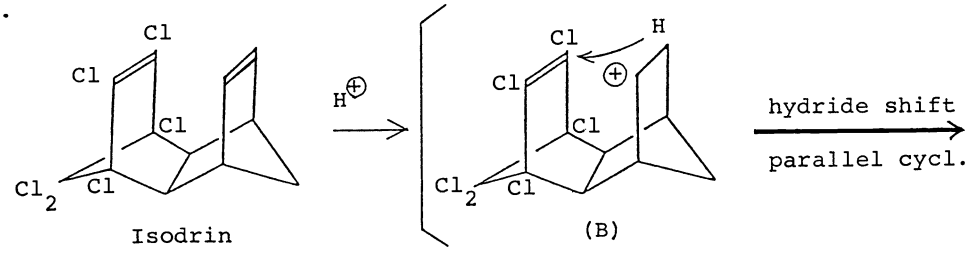
An interesting application of orbital polarization approach is the explanation of transannular cross- and noncross-bond formations. The following four cases are to be explained:

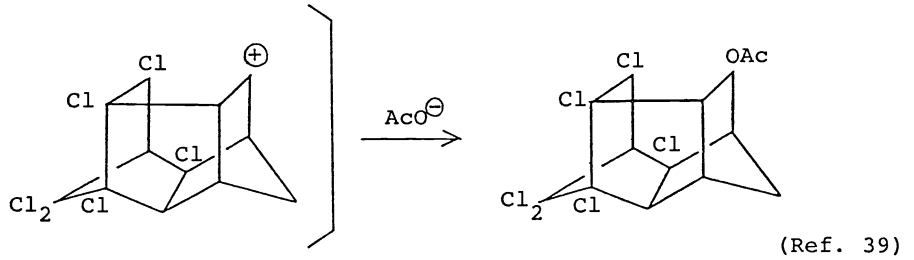
Case I.



(Ref. 38)

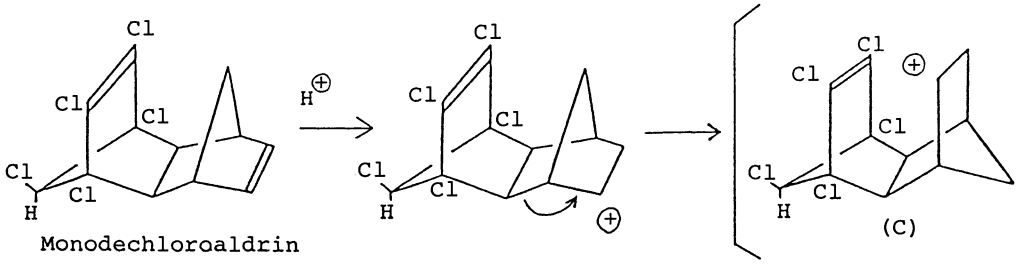
Case II.

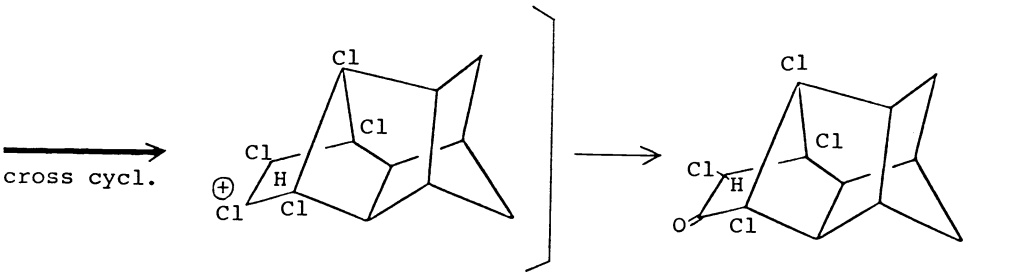




(Ref. 39)

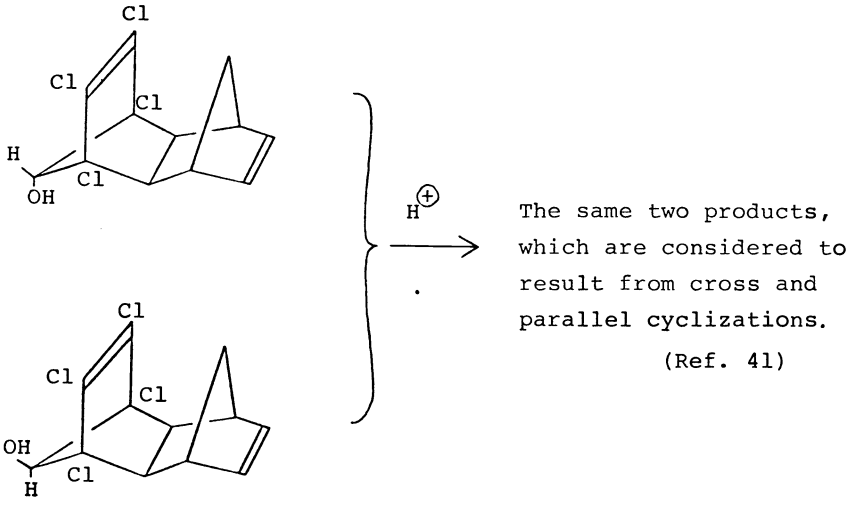
Case III.





and epimer about Cl-C-H

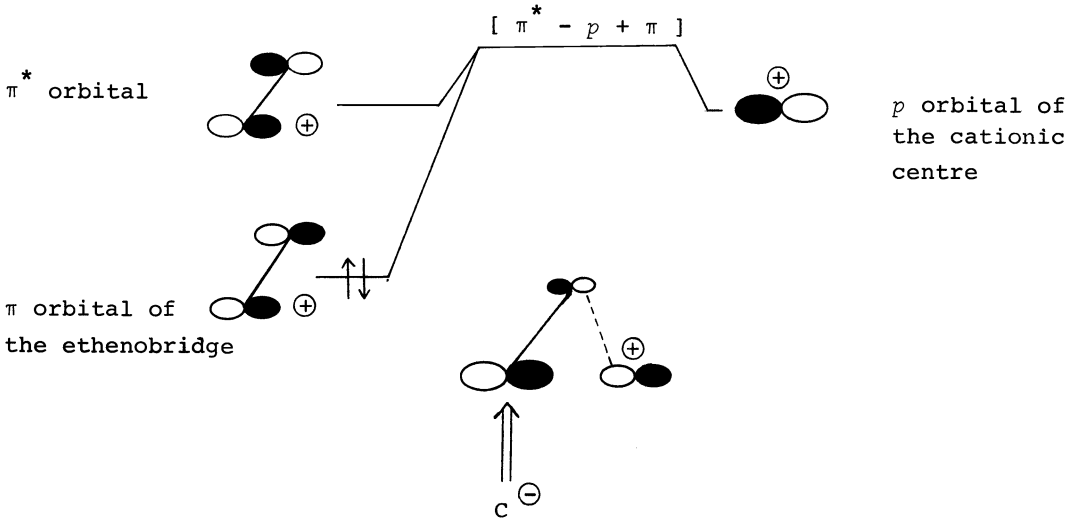
(Ref. 40)



The same two products, which are considered to result from cross and parallel cyclizations.

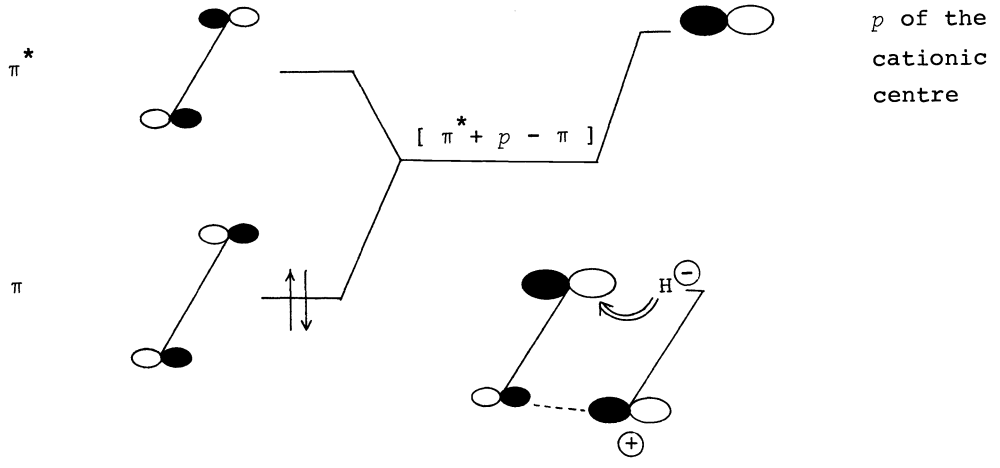
(Ref. 41)

The direction of polarization in the π^* orbital of the etheno-bridge due to the cationic charge in (A) can easily be given(Ref. 37).



The path of the Wagner-Meerwein rearrangement is thus understood.

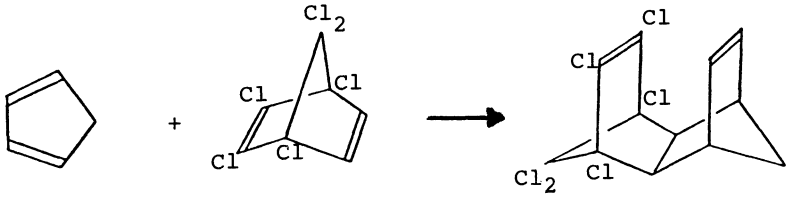
In contrast, the direction of orbital polarization is opposite in (B), in which the effect of polyhalogenation brings about a lowering of π orbital energies, so as to cause the shift of the hydride.



In the hypothetical ion, (C), the lowering of π levels could be insufficient to cause the hydride shift, since the strong participation of the axial C-Cl bond to absorb electrons disappears in this case, so that the cross cyclization occurs again like in (A). The result of Case IV indicates that the effect of OH substituent instead of axial-Cl at the methylene bridge might make the cross and parallel cyclizations compete.

Next example is the stereospecificity in the Diels-Alder reaction.

Case I.

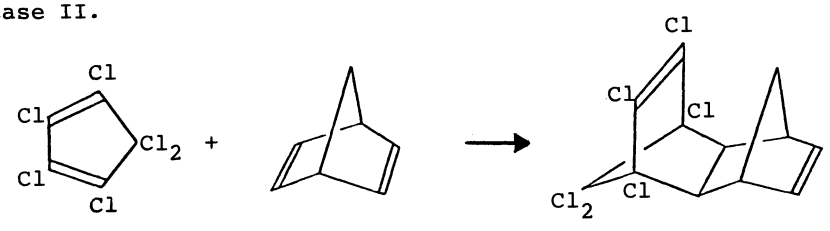


(Ref. 42)

Isodrin

(endo-endo adduct)

Case II.

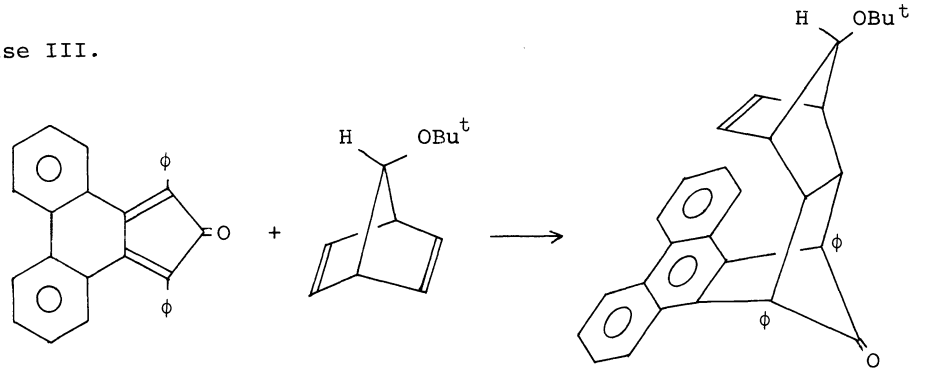


(Ref. 43)

Aldrin

(endo-exo adduct)

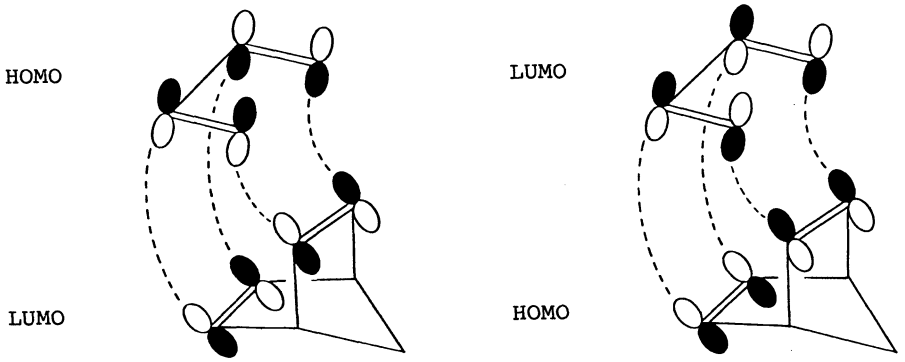
Case III.



(endo-endo-anti-Bu^{t}O adduct)

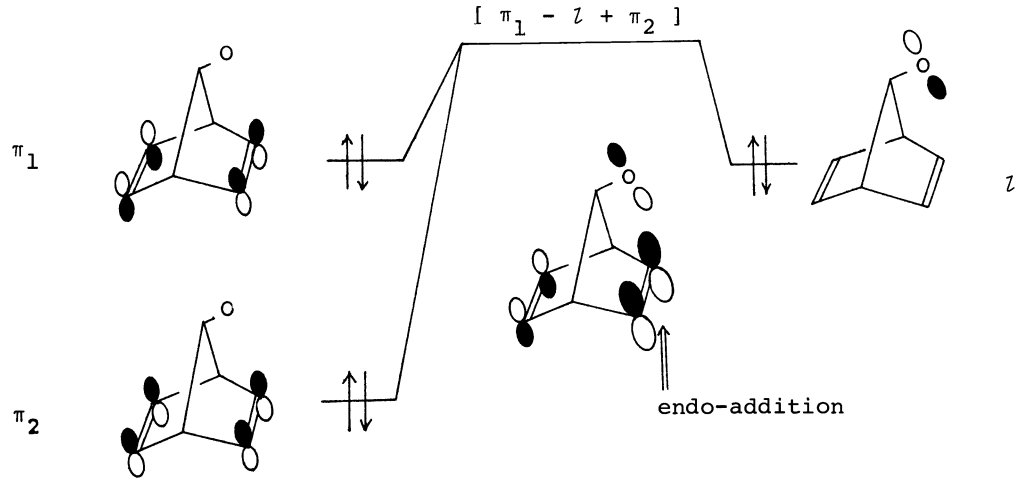
(Ref. 44)

Case I is an example for the case occurring in normal electron demand. The regioselection in hexachloronorbornadiene could be attributed to the interference of the antibonding p lobes at the adjacent chlorine atoms in the LUMO of the dichlorinated ethylenic bond. The endo-endo terminology of the product implies that the first "endo" criterion relates to the two remaining double bonds and the second "endo" corresponds to the norbornadiene double bond. The dominance of endo-adduct in all these cases with respect to remaining double bonds is easily understood by considering the auxiliary orbital effect which is favourable for the "endo" configuration.



In the formation of exo-adduct there is no favourableness like this.

The exo-endo selectivity with respect to the norbornene double bond is the next problem. Usually the exo addition is predominant as in Case II. Case I and Case III must involve particular reasons to produce 'endo' adducts. Such a reason for Case I could be the steric circumstances at the methylene chlorine substituents. In Case III the regioselection in norbornadiene is the first problem to be solved. The influence of the tert.-butoxy substituent at the methylene bridge could be interpreted as an orbital polarization which follows:



The direction of polarization of two double bonds is in conformity with endo-syn(with respect to Bu^tO) adduct, resulting in anti-Bu^tO(with respect to the remaining double bond) isomer. Such an explanation is only possible in regard to the HOMO of the parallel ethylenic bonds. The repulsive effect of oxygen atom would raise the energy of the dienophile, which in consequence comes to act as a donor. In this way the Diels-Alder addition will take place in inverse electron demand, as is pointed out by Mackenzie(Ref. 44).

THE PATH OF A CHEMICAL REACTION

In the papers already referred to(Ref.24-31),the change of geometry of reacting molecules is treated. The range of the change discussed there is sufficiently wide, so that the theory may be called as going beyond the perturbation method. But in this series of works the determination of the geometry of reacting molecules is not yet theoretically complete. It was in pace with the development of the theoretical calculation of the potential energy function that the fundamental idea to decide the change of geometry of reacting molecules proceeded.

The adiabatic potential of a chemically reacting system is now theoretically available, in principle, as a function of the variables which can determine the atomic arrangement. Such a potential function, say V, possesses several equilibrium points where all of their derivatives vanish. Among these equilibrium points, those of interest are the initial stable point, the transition-state point, and the final stable point of a reaction.

The reaction path is a chemical concept involving an ambiguity or flexibility. It was attempted by many authors to formulate the classical reaction path mathematically(Ref. 45-47). Two different approaches are introduced here. One is the trajectory approach and the other is the reaction coordinate approach. The trajectory of a reaction varies with the initial condition of the reacting system while the reaction coordinate is not affected by the initial condition. The trajectory approach is essentially compared to solving the classical Newtonian equation of motion directly, and was successfully developed in particular by Karplus and other chemists(Ref. 48). But here the focus is put on the reaction coordinate in view of the connection with the perturbation theory of reactivity.

The reaction coordinate is determined by integrating Newton's equation of motion with respect to the time considering an infinitely slow change of the atomic configuration. The following relation holds every moment:

$$M_i(dX_i / d\tau) = \partial V / \partial X_i \quad (i = 1, 2, \cdots 3N)$$

where X_i are the space-fixed cartesian coordinates of atom i of mass M_i, and N is the number of atoms of the reacting system. The parameter τ plays the part of "time" in the quasistatic motion. The solution which is determined by this differential equation and passes the transition-state point and a stable point is referred to as an intrinsic reaction coordinate (IRC) (Ref. 49). The IRC is the locus of infinitely slow motion of the reacting system along a chemical reaction, keeping the significance to represent the "centre-line" of the reaction path which is of empirical origin and never a simple concept. This differential equation may be called the IRC-equation.

The first application of the IRC-equation is to obtain the continuous change of the geometry of reacting molecules by a successive plot starting from the transition-state point to a stable equilibrium point——"reaction ergodography" (Ref. 52).

The method was successfully applied to the following reactions:

i) The hydrogen migration in enol-form malonaldehyde (Ref. 50)

ii) $T + CH_4 \longrightarrow CH_3 + H$

$T + CH_4 \longrightarrow CH_3 + HT$

$T + CD_4 \longrightarrow CD_3T + D$ (Ref. 51, 52)

$T + CD_4 \longrightarrow CD_3 + DT$

iii) $HNC \longrightarrow HCN$ (Ref. 53)

iv) $H^- + CH_4 \longrightarrow CH_4 + H^-$ (Ref. 53, 54)

v) $HFCO \longrightarrow HF + CO$ (Ref. 55)

vi) Isomerization of triplet butadiene (Ref. 56)

vii) $CH_3CH_2F \longrightarrow CH_2CH_2 + HF$ (Ref. 57)

viii) $H_2CO \longrightarrow HCOH$

$H_2CO \longrightarrow H_2 + CO$ (Ref. 58)

The sixth example refers to an excited state. The IRC equation can be equally applied to the geometry change from any non-equilibrium point.

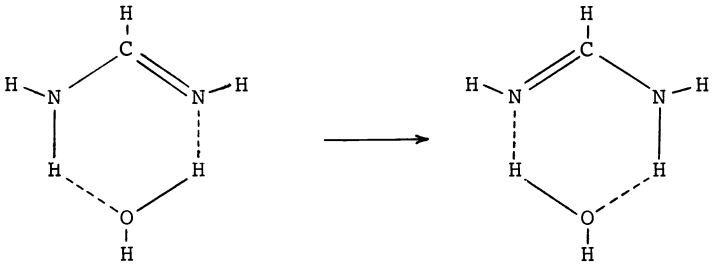
The determination of the geometry of reacting molecules along the IRC supplied information on various properties of a chemical reaction. First of all, one can obtain the energy of each point on the IRC, which gives the shape and height of potential barrier. The activation energy of the Eyring-Polanyi theory is obtained together with the breadth of the barrier. In some favourable cases one can discuss or guess the effect of isotope exchange simply by the broadening of the barrier breadth (Ref. 52). Similarly, one can calculate the force acting on each atom at any point on the IRC to promote the change of geometry directly from the IRC equation.

The IRC plot makes it possible to correlate any molecular constant which is calculable along the reaction path. For instance, one can obtain a quantitative orbital correlation diagram, which makes the Woodward-Hoffmann correlation diagram quantitative if it is so desired. Also one can obtain a vibrational correlation diagram in which all normal vibrations and vibrational frequencies are correlated to the geometry along the IRC (Ref. 55, 58, 59). This diagram can be correlated with the curvature of the IRC path so that one can discuss the composition of the reaction coordinate with regard to normal vibrations and the contribution of each normal vibration to the vibrational energy transformation. Such a discussion is no doubt useful in relation to laser chemistry, in particular to mode-selective chemical reactions. Yamashita et al. (Ref. 58) treated the asymptotic behaviour of the IRC in the vicinity of the stable equilibrium points of the reacting system. The vibrational correlation diagrams for the isomerization and decomposition of formaldehyde were obtained to discuss the strategy to give rise to a mode-selective reaction.

The energy (Ref. 59, 60) and the density partitioning techniques (Ref. 61) along

the reaction path are applied to discuss the detailed reaction mechanism. One can apply various quantum-chemical methods to analyze submolecular or electronic processes involved in the reaction based on the calculated geometry.

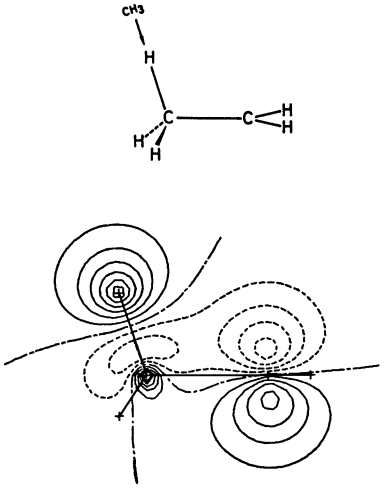
An attempt to use the IRC approach was made to treat the role of solvent molecules in a chemical reaction(Ref. 62). A powerful effect of one water molecule hypothetically relaying the 1, 3-hydrogen shift in formamidine on the reduction of the potential barrier was theoretically disclosed(Ref. 63). Such a model will be useful in discussing biomolecular phenomena.



The IRC approach is useful for the purpose of visualization of the mode of proceeding of a chemical reaction. This can be done by constructing a sort of localized orbitals which represent the intermolecular interaction most effectively. Such localized orbitals are mathematically obtained by diagonalizing any quantity which corresponds to that intermolecular interaction. If one uses the magnitude of delocalization energy as the quantity to be diagonalized, one gets interaction frontier orbitals(IFO)(Ref. 64). If one takes the intermolecular overlap population instead of the delocalization energy one obtains interaction hybrid molecular orbitals(IHMO)(Ref. 65).

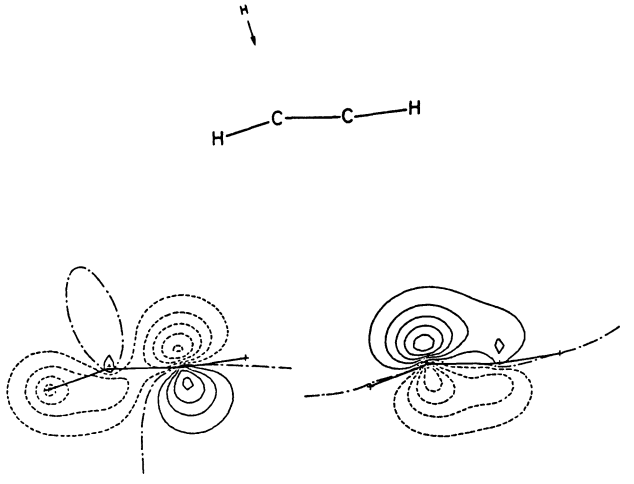
On account of a mathematical property of such localized orbitals, the mode of interaction is described by a few pairs of localized orbitals each belonging to one of the two reacting molecules. If one of the reactants possesses only one orbital, like proton or hydride anion, the mode of interaction is represented by a single localized orbital of the other reactant. One can trace the change of the pattern of such a single "frontier orbital" to visualize a given chemical reaction. An animated film for chemical reactions could be made in this way for the purpose of instruction.

Two examples of IHMO are indicated below:



The IHMO of ethyl radical for the abstraction of a hydrogen atom by methyl radical.

Full lines indicate the lobes with + sign, and dotted lines with - sign. The line —·—·— indicates the nodal plane.



The IHMO of acetylene for the addition of hydrogen atom.

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