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Reaction Co-ordinates of *Ene* Reactions in Configuration Space

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Abstract

The *ene* reaction proceeds through a concerted mechanism in which *H* of the alkene is transferred to the enophile while another **σ** bond is formed and the **π** bond migrates within the ene fragment. Concerted electron shift results in the cyclic transition state, which are stabilized by favourable orbital interactions. The molecular instances of *ene* reaction in selected systems were studied with a focus on the relationship among their properties, geometries and associated electronic delocalization. Relation between the HOMO-LUMO energy gap and electronegativity of hetero atom with activation energy were computed. *Ab initio* studies on *ene* reactions between propene and (i) ethene (ii) iminomethane and (iii) methanal were performed using GAMMES suite of programmes by geometry optimization method. Transition state geometries were located and confirmed by frequency calculations at B3LYP/aug-cc-pVDZ level of theory. The bond lengths, bond angles, dihedral angles and energetics of the optimized structures are reported. It is found that the hydrogen bond shrinks with the increase in electronegativity of the reaction centre of the enophile.

Key words: Pericyclic reactions, ene reaction, substituent effect.

Introduction

We understand the structure of matter by considering the atoms and molecules as potential wells of electrons. The escape of electrons from one potential well to another is termed as a chemical reaction. Since they are quantum mechanical entities, their passage from one potential well to another cannot be described in space and time using our present mathematical technique. We therefore constructed a configuration space whose co-ordinates are determined by the number of potential wells participating in the reaction. The most probable trajectory on this space is called reaction co-ordinate by which we can follow atomic and molecular events preceding the actual formation of the products. This paper is about computing the reaction co-ordinates of three selected *ene* reactions. The energy necessary to attain the transition state is usually provided by thermal or photochemical excitation of the reactants and no other reagents are involved. The transition states are stabilized by favourable orbital interactions.

The π-bonded molecule that contains at least one active H-atom is an *ene*. A chemical reaction between the ene and another compound with a multiple bond called the enophile in order to form a new *σ* bond with migration of the ene-double bond and 1,5 hydrogen shift is the *ene reaction*. This reaction resembles both cycloaddition and a [1, 5] sigmatropic shift of Hydrogen. A sigmatropic reaction is a pericyclic reaction where the net result is one sigma bond being changed to another sigma bond. The product is a substituted alkene with the double bond shifted to the allylic position.

The reaction between ene and enophile is an interesting topic due to its complicated nature of the reaction mechanism and its importance in industrial applications. The ene reaction, which is also known as Alderene reaction constitutes one of the simplest ways to form C-C bonds. This process was systematically studied by Alder[1] and developed "activation strain model" from the "distortion/ interaction model", which was developed by Ess and Houk[2]. This allowed us to gain more insight into the physical factors which control how the activation barriers arise on different fundamental processes. The activation strain model is a fragment approach for understanding chemical reactions, on which the height of reaction barriers is described and understood in terms of the original reactants[3]. This model is a systematic extension of the fragment approach from equilibrium structures to transition states as well as "non stationary" points.

Although the mechanism of *ene* reaction is similar to other pericyclic reactions, the number of theoretical studies about *ene* reaction is much less[4]. Houk & co-workers have computed the transition state structure of the reactions of propene and methanal[5] and found that the regioselectivity is determined by a stabilizing electrostatic interaction. *Ene* reactions involving alkenes (*Alder-ene* reaction)[6], singlet oxygen[7], azo compounds[8], carbonyl functionalities[9] and nitroso groups[10] have been employed in carbon-carbon or carbon-hetero atom transformations with olefins. It is reported that most of these reactions proceeds through a concerted step involving cyclic transition state. Xin Lu showed theoretically at B3LYP/6-31G* level that the *ene* reaction between *o*-isotoluene and nitro compounds[11] adopts a concerted pericyclic path. The pericyclic reaction between propene and ethene is the parent *ene* reaction studied here theoretically.

Our present work has three fold objectives (i) to optimize the geometry of reactants, products and transition states, (ii) to evaluate the energetics of the *ene* reaction and (iii) to provide some useful insight into the mechanism of *ene* reaction

Computational Methods

In computational chemistry, quantum chemical calculations are typically performed within a finite set of basis functions. For the atoms of elements belonging to I and II periods are cc-pVNZ where N = D, T, Q, 5, 6…. (D = double, T = Triple…..), cc-pV stands for correlation consistent polarised valence basis sets. An augmented version of the preceding double zeta basis sets with added diffuse functions is represented by aug-cc-pVDZ. One of the most commonly used density functional versions is B3LYP, which stands for Becke, 3-Parameter, Lee-Yang-Parr. The 6-31G* basis set is a valence double-zeta polarised basis set.

Computations were performed using GAMMES suite of programmes and visualizations are performed using chemcraft visualization software. All reactants, transition states, and products were optimized using B3LYP/aug-cc-pVDZ level of theory. The frequency calculations were performed at the same level of theory. Single point energies were calculated at second order Moller-Plesset Perturbation (MP2) method with the 6-31G* basis set using optimized structures.

Results and Discussion

The computational studies of *ene* reaction of propene with the enophiles like (i) ethene, (ii) iminomethane and (iii) methanal explores the effect of substituent on the enophile. The geometry of reacting species, their transition states, products and energy of these three ene reactions were determined with the aid of GAMESS software. The transition state of the reaction between propene and ethene is labeled as CTS while NTS and OTS represent the transition states with that of iminomethane and methenal respectively.

Geometry of Optimized Molecules :

We have optimized all the geometries of the reactants $CH_3CH=CH_2$, $CH_2=CH_2$, $CH_2=NH$ and $CH_2=O$; their transition states (CTS, NTS and OTS) and the products C_5H_{10}, C_4H_9N and C_4H_8O at B3LYP/aug-cc-pVDZ level of theory. The values shown in Table-1 illustrate the change in bond lengths and bond angles when the reactants are transformed to products through transition states. The computation of dihedral angles shows that all reactants except propene are planar, while the atoms of all the transition states and products are not in the same plane.

Pericyclic reactions are due to the interactions of Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO). The HOMO of the transition state shows maximum delocalization in OTS, minimum in CTS and the molecular orbitals are found to be delocalized in a mobius strip manner.

Table 1 Values of bond lengths and bond angles in the optimized geometries

Molecule	Bond Length, ^{o}A		Bond angle, ^{o}	
$CH_3CH=CH_2$	C-C	1.337	C-C-C	125.01
$CH_2=CH_2$	C-C	1.335	H-C-C	121.64
$CH_2=NH$	N-C	1.272	H-N-C	110.84
$CH_2=O$	O-C	1.207	O-C-H	121.82
CTS	C-C	2.730	C-C-C	110.22
	C-H	1.461	C-C-H	103.35
NTS	C-N	2.630	N-C-C	108.87
	N-H	1.294	H-N-C	108.38
OTS	C-C	1.962	C-C-C	97.15
	O-H	1.377	C-O-H	106.49
C_5H_{10}	C-C	1.504	C-C-C	125.80
C_4H_9N	C-C	1.534	C-C-N	111.30
C_4H_8O	C-C	1.534	C-C-O	113.84

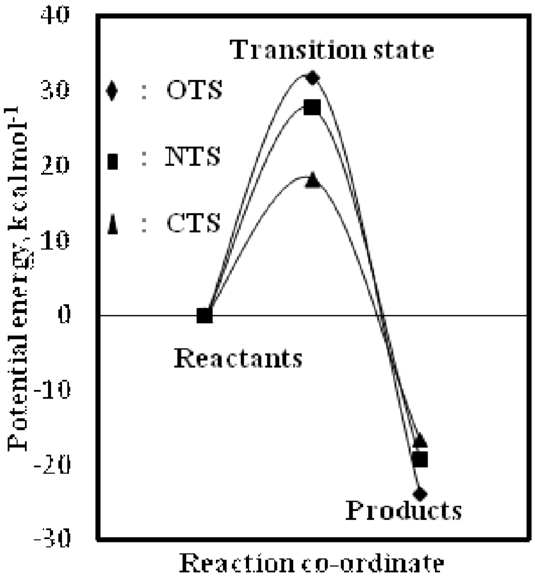

Fig. 1. The potential energy diagram from the energy values in kcal mol^{-1}.

Energy Parameters :

From the energy values of the reactants, products and transition states, it is found that the transition states are of highest energy and the products are of lowest energy. The sum of energies of propene and ethane (E_R) was found to be -196.5161807 Hartree and the energy of the transition state (E_{TS}) was -196.4659976 Hartree while that of products (E_P) was -196.5546019 Hartree. The activation energy (E_{TS} - E_R) was calculated to be 0.0501831 Hartree or 31.4903971 kcal mol^{-1}. In the reaction between propene and iminomethane the value of activation energy was 27.7068883 kcal mol^{-1} and that in the reaction between propene and methanal was 18.2201294 kcal mol^{-1}. From the potential energy diagram (Fig. 1) it is clear that the activation energy decreases when the reaction centre of the enophile is substituted by a more electronegative atom.

When comparing the molecular orbitals of the transition states of three reactants; it is observed that the HOMO of the transition state with maximum delocalization is for OTS, minimum is for CTS and NTS is in between. The dominant orbital interaction is in between HOMO of propene (C-C π-bond) its C-H antibond and LUMO of enophile. LUMO energy increases in the same order as the activation energy. The distance between the two heavy atoms belonging to the ene and enophile in CTS, NTS and OTS are 2.73, 2.63 and 2.58°A respectively. This shows that the distance between two heavy atoms decreases in the order C-C > C-N > C-O. This indicates that a short strong Hydrogen bond (SSHB) exists in OTS, NTS and CTS. This SSHB is responsible for reducing the activation energy of the reaction on both CH_2=O and CH_2=NH. While comparing the energies of the reactions it is found that the activation energy decreases with the decrease in electronegativity of the heavy atom of the reactant molecule.

Conclusion

Reactions of propene with ethene, iminomethane and methanal are studied here computationally. *Ene* reaction is recognized as a powerful C-C bond forming method in synthetic organic chemistry. The propene-iminomethane and propene-methanal reactions have the potential for the preparation of nitrogen and oxygen heterocycles respectively. These reactions proceed through a concerted mechanism. The geometries of the reactants, products and transition states of the reactions were optimized and their energies were evaluated. The potential energy diagram shows that the activation energy decreases with increase in electronegativity of the reaction centre of the enophile. The gradual decrease in the bond length C-C > C-N > C-O reveals the existence of short strong hydrogen bonds (SSHB). Our present work gives a new technique for the theoretical prediction of feasibility of different complex reactions.

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