

Computational Techniques: Taking Organic Photochemistry to Cyberspace

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ABSTRACT

Photochemistry deals with chemical reactions taking place in the presence of light. Immense amount of solar energy received from sun can be utilized for these reactions. The computational investigation of realistic models of organic compounds is becoming a standard practice nowadays. Computer programs can mimic the process of photochemical reactions and predict the outcome of such reactions and thereby, eliminate the need of some lab testing. Current review describes the photochemical reaction *from absorption of energy to formation of photoproduct*, using computational techniques such as Gaussian 94, MOLCAS, CAS-SCF/MP2 etc. available in standard quantum chemistry packages. This makes computer an important and inseparable tool for chemists and many industrial processes.

Keywords

Photochemistry, organic compounds, absorption, photoproduct, computational techniques

1. INTRODUCTION

It has been from the last decade that the considerable increase in speed of computers has led to computational investigation of realistic model of organic compounds. Present applications range from the investigation of the mechanism of synthetically useful reactions to the study of short lived organic intermediates detected in the interstellar medium. Reaction path computations, until recently, were limited to the research of thermal reactions and thereby to the reactions on a single potential energy surface. In photochemical process, the reaction path has two streams; one with reactants on the excited state and the other with the products accumulated on the ground state. In computations, practical problem lies in defining the funnel region which connects the excited state stream to the ground state energy surface. Computational tools have been developed in the last decade to explore electronically excited state reaction path [1-4]. The aim and objective of such approach in the photochemical mechanisms is to completely describe the molecular level from *energy* absorption to product formation. This review focuses on the theoretical tools, with case study to show their application.

2. EXCITED STATE PROCESS

Fig.1 provides a schematic view of the course of photochemical reaction.

With the absorption of light, the system is promoted to the excited state $R \xrightarrow{+h\nu} R^*$

In adiabatic reaction pathway:

Photoproduct Formation in excited state:

$R^* \rightarrow P'^*$ (Photochemical Process)

Photoproduct formation in ground state:

$P'^* \xrightarrow{-h\nu} P'$ (Photophysical Process)

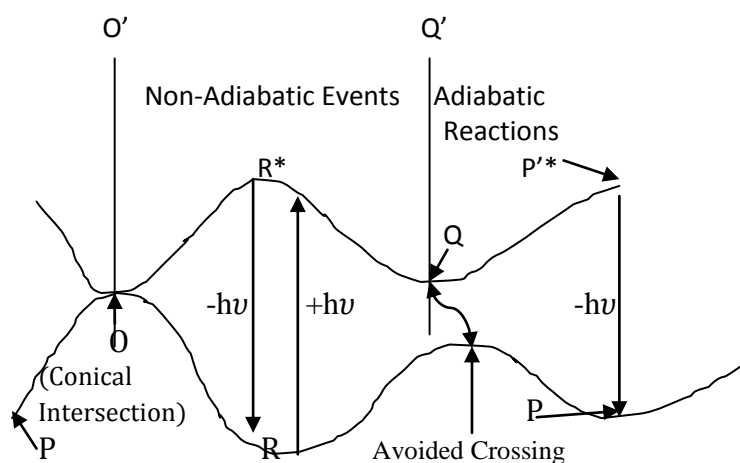


Fig. 1 Excited State Process

In Non-adiabatic reaction pathway:

$R^* \xrightarrow{-h\nu} R$ (Photophysical Process)

$R^* \rightarrow P$ or P' (Photochemical Process)

Occurrence of photochemical reaction depends upon the relative rates of photochemical processes that generate new molecular structures versus the competing photo physical processes that convert between electronic states at the same nuclear geometry.

2.1 Photochemical Versus Photophysical Process

There are two different mechanisms:

2.1.1 Non Adiabatic Radiationless Decay

Conical intersection represents real surface crossing and is accessible, the Landau-Zener Model [5] provides a semi classical model for fast radiationless decay. Accessible is a reaction coordinate with sufficiently low energy barrier that leads from initial excited state to crossing zone. Here, internal conversion takes place within a single vibrational oscillation near by the surface crossing. Time taken for this decay is in picoseconds (ps) or femtoseconds (fs).

2.1.2 Adiabatic Radiationless Decay

If the crossing at the surface are not present or are if present and inaccessible, the process is governed by the density of vibrational states and Franck-London factors with result due to overlapping of ground and excited state vibrational wave functions according to Fermi golden rule. This is a slow process and the conversion rates for aromatic hydrocarbons are approximately $10^5 - 10^6$ sec

3. PHOTOCHEMICAL PATHS: PRACTICAL COMPUTATION

The study of photochemical mechanisms presents a considerable challenge for computational chemistry. To follow the reaction path from Franck London region to the ground state product is the main aim. There are two different approaches to the computation of excited state:

- (i) Wavefunction method
- (ii) Response method

Response theories are undergoing a revival and seem to be capable of reproducing the energy difference between the excited states and ground states

Standard wave function methods are widely used in computation. The ab-initio method is the main wave function method used for geometry optimization and is implemented in programs such as Gaussian 94 [6], MOLCAS [7], COLUMBUS [8] and GAMESS[9]. For accurate energetic CAS- SCF/MP2 [10,11] is implemented. This gives reliable results at low cost.

4. PHOTOCHEMICAL ISOMERISATION OF BENZENE TO BENZVALENE: A CASE STUDY

This study is done using CAS-SCF method [12]. : Photochemical isomerisation of benzene to benzvalene is represented in Fig 2

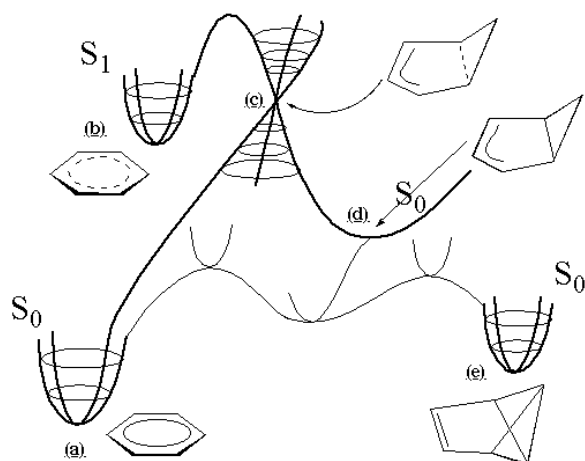


Fig 2: Photochemical isomerisation of benzene to benzvalene

Using CAS-SCF method:

- Select input file (.com extension)
- Output of the calculations viewed (.log extension)
- Initial active orbitals are needed for computation (chosen by Hartree-Fock calculation)

Hartree-Fock calculation: It is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state.

```
{benz_rhf.com}
RHF/STO-3G
Pop=Full
Nosymm
{benz_rhf.log}
```

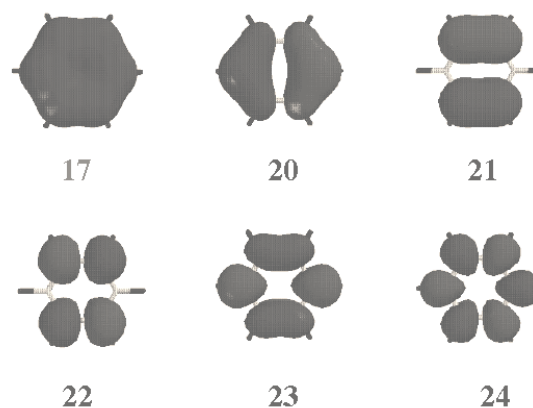
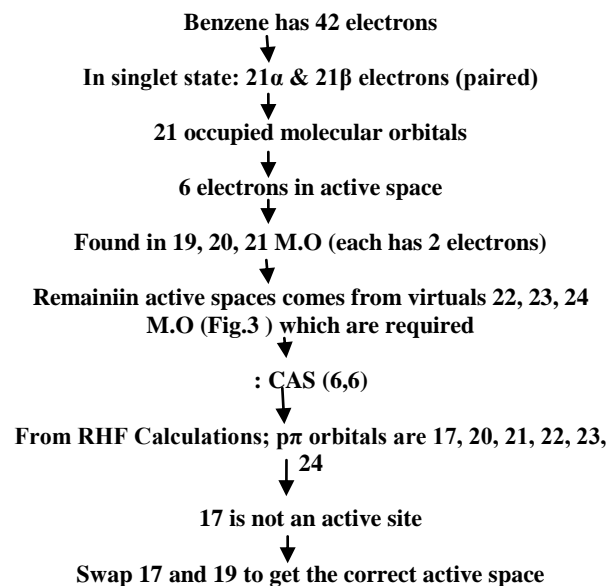


Fig 3: Active Molecular Sites

```
{benz_cas_sto3g.com}
CAS (6,6)/STO-3G
Guess=(read,alter)
Nosymm Pop=Full
{benz_cas_sto3g.log}
```

Note that for the above calculation it is better to copy the checkpoint file and run a separate job, if something goes wrong the active space can be reselected again from the original RHF job.

In order to check if the CASSCF calculation has been successful there are a number of tests that can be made.

1. The energy converges.
2. Orbital occupation numbers (diagonal elements of the density matrix) are not very close to zero or two (within three decimal places roughly). For the above calculation the occupancies are 1.95, 1.87, 1.87, 0.13, 0.13, 0.05.
3. Localise the orbitals. The orbitals should localise onto atomic sites and can be checked with an orbital plotter(e.g. Gauss view) to verify that they are the correct orbitals to include in the active space.

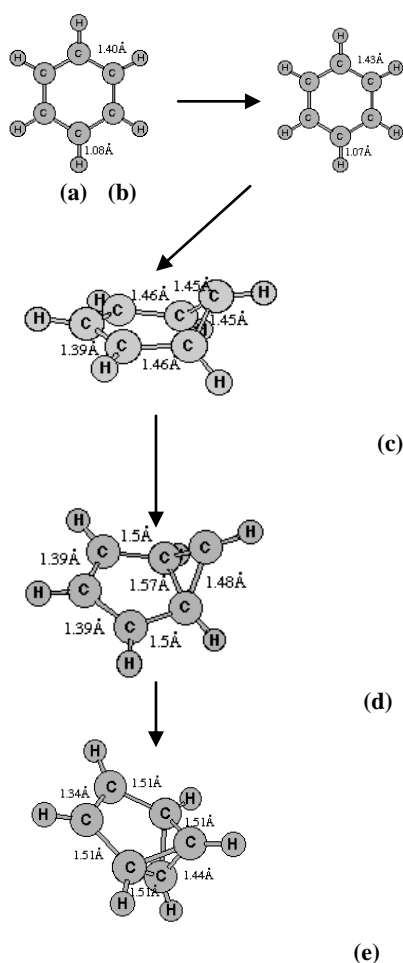


Fig 4: Geometrical Optimization

There are many critical points on the S_0 , S_1 , S_2 surfaces associated with the photochemical isomerisation of benzene. Here are some points on the reaction path of benzene (a) to benzvalene (e). Structures of the same are represented in Fig. 4.

5. CONCLUSION

Photochemical reactions occur at lightning speed where electrons jump from ground state to excited state and vice-versa, hidden from the prying eyes of the scientists. However, it is possible to map the mysterious reactions in photochemistry by using standard packages in computers. These software give various plausible pathways of chemical reactions which are referred as Simulation or Modelling. Theoretical results have been confirmed by real experiments so the theory and practice cross-fertilize each other.

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