

TOPOLOGY OF CHEMICAL REACTIONS .II¹. PERICYCLIC REACTIONS

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(Received: July 1981)

ABSTRACT

A topological representation of the electrocyclic ring closure and intramolecular rearrangements, by simple rows/columns transformations of the adjacency matrix, is reported.

INTRODUCTION

Recently graph theory²⁻⁴ has been applied to various problems of chemistry.⁵⁻¹³ The term Molecular Topology is sometimes used in the chemical literature to represent a molecular graph. The chemical graph which has been used is simply a carbon skeleton molecular graph where the edges represent the C-C bonds and the vertices represent the carbon atoms.

Topological representation of chemical reactions appeared in literature when chemical graphs were used as the reaction graphs.¹⁴ It was proposed^{14,15} that a topological representation of a chemical system is a graph where the vertices represent the chemical species and the edges represent the chemical reactions. The chemical reactions which were reported in this way were isomerization reactions and the reacting species were isomers.¹⁶ Later

on Miller's coding system¹⁷ in the allene dimer interconversions and Sinanoğlu's theory of chemical reaction networks,¹⁸ were published. Very recently Balaban¹⁹ used synthon graphs to represent a system of chemical reactions.

In our previous work¹ we have applied the elementary transformation operations²⁰ to the adjacency matrix²⁻⁴ to represent a bond breaking process such as the fragmentation of hydrocarbons. In this work we have shown that the elementary transformation operations can also be used to represent the intramolecular rearrangements like Cope rearrangements and the electrocyclic ring closure processes.²¹ These reactions are classified as pericyclic reactions^{22,23} in organic chemistry.

MATRIX COMPUTATION PROCEDURE

Consider an adjacency matrix A of a molecular graph G . The elementary transformation operations may be applied to the matrix A , e.g. the addition or subtraction of any rows/columns (R_i/C_j) to a non-zero scalar multiple of any other rows/columns (R_m/C_n). The former operations (additions) introduce some elements a_{ij} in the matrix A and the latter (subtractions) eliminate some elements from the matrix A , without loss of its rank.²⁴ If simultaneous rows/columns operations result in the elimination of two elements a_{ij} and a_{ji} , it shows a loss of connectivity between the atoms C_i and C_j which in chemical terms means a bond breaking between the atoms C_i and C_j . Similarly if simultaneous rows/columns operations introduce two elements

a_{mn} and a_{nm} , it shows a bond formation between C_m and C_n atoms. Therefore a bond forming and bond breaking process can easily be represented by the rows/columns operations applied to the adjacency matrix. The reaction topology can thus be written as

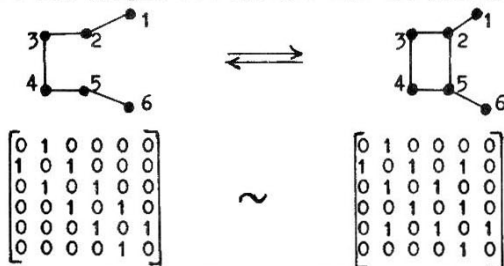
$$A \xrightarrow{R_i/C_j} B$$

where A is the adjacency matrix of the reactant molecule and B is the adjacency matrix of the product. The process represented by the above equation will be a rearrangement of sigma and pi overlaps. The operations can equally be applied to either direction and hence, this represents an equilibrium between reactant and the product. We now take a few examples.

a) Electrocyclic reactions in which a substituted butadiene is converted into a cyclobutene by photochemical or thermal process.²¹

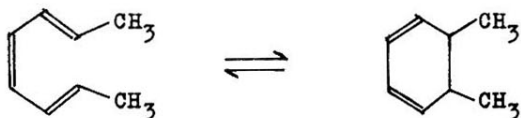


The matrix computation is represented by considering the labelled graphs of reactant and the product,

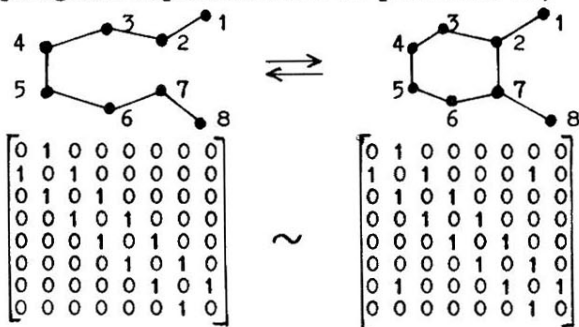


Similarly the electrocyclic ring closure of 2,4,6-octatriene to 5,6-dimethyl-1,3-cyclohexadiene may be

considered,



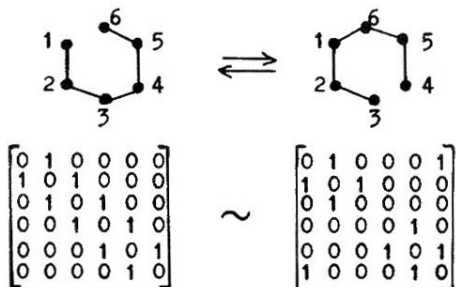
The topological representation is performed as,



b) Cope rearrangements are in general represented by the scheme :



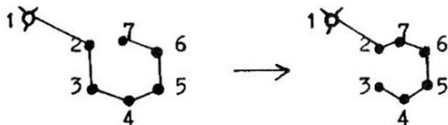
The graphs and the matrix computation are easily represented by the rows/columns transformation



A 1,5 sigmatropic shift is represented as

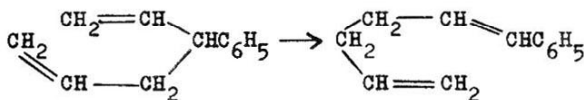


The topology of this process is



$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \sim \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

The group R is symbolized by a vertex (λ) in the graph. Similar treatment is adopted to represent the interconversion of 3-phenyl-1,5-hexadiene and 1-phenyl-1,5-hexadiene



DISCUSSION

The adjacency matrix A of a graph G is a set of elements a_{ij} which represent the atomic connectivity or the chemical bonds between two atoms. We may treat this bond as the overlapping of orbitals. The elementary rows/columns transformations applied to the matrix A results in the readjustment of the elements a_{ij} either by introducing or by eliminating some elements as we have seen above. This shows a readjustment in the electronic system in the molecule or a shift in the overlapping of orbitals. In otherwords the simple elementary rows/columns operations represent an intramolecular rearrangement or a bond making and bond

breaking process.

In the electrocyclic ring closure, the bond formation and bond breaking takes place simultaneously in a concerted ^{23,25,26} manner. The stereospecific nature of these reactions is reported by Woodward and Hoffman²³ and by Dewar.²⁵ Similarly in Cope rearrangement the bond making and bond breaking takes place simultaneously. Recently two-step pathways of these processes are discussed by Doering et.al. and by Dewar et al.²⁷ In the two-step mechanism the formation of the new C-C bond precedes the rupture of the old one, so that the reaction involves a biradical intermediate.²⁷ According to Dewar²⁸ no two bonds may be formed simultaneously. In our method we do not care about the stereospecific nature of the reaction and about the intermediate steps, but a general topology of the reaction is predicted. The target molecules or the products may be formed by the allowed pathways. The intermediate cyclic transition state can be shown by the adjacency matrix of the cyclic state which is formed by the rows/columns transformation,

$$A \text{ --- } A_c \text{ --- } B$$

where A_c is the adjacency matrix of the cyclic transition state, A and B are the matrices of reactant and the products respectively.

If we consider the electrocyclic ring closures of linear polyenes and apply the algebraic method as discussed above, we can easily predict that,

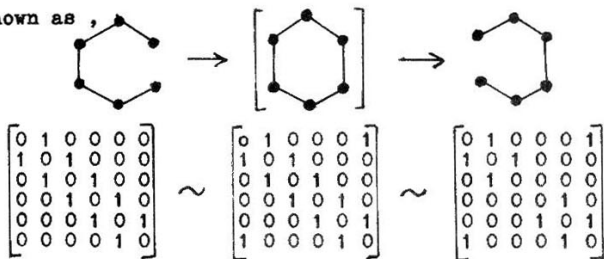
a) The electrocyclic ring closures or openings are

favourable (allowed) when the cyclic states contain an even number of carbon atoms. This is in agreement with the observed facts.^{21,29}

b) The ring closures or openings with the cyclic states containing an odd number of carbon atoms are not favourable as they provide no chance of the appropriate rows/columns transformation of the corresponding adjacency matrices. The ring openings of cyclopropane systems are possible in ionic states under specific conditions.²⁹

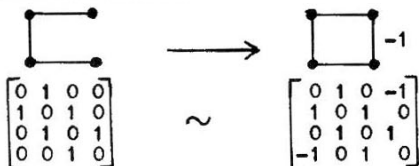
c) Substituted butadienes are easily converted into cyclobutenes on heating²¹. There are more chances of rows/columns transformations in the graphs of substituted butadienes.

In Cope rearrangement the cyclic transition state is shown as ,



similarly the six-membered cyclic transition state can be shown in (3,3) or (1,5) sigmatropic shifts. Balaban³⁰ in 1967 presented the idea of chemical graphs for discussing the reactions with cyclic six-membered transition states. Later on Hendrickson³¹ independently published the similar treatment. Recently Aihara¹³ discussed the theory of pericyclic reactions in the light of aromaticity of the cyclic transition states. In pericyclic reactions the actual

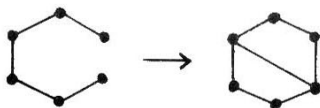
transition state is more aromatic than the reactants and any other transition state of equivalent electronic state which can be imagined. In our algebraic treatment we can easily consider the aromaticity of the cyclic transition state, provided it has the number of electrons appropriate (i.e., $4N + 2$ or $4N$) to the Hückel or Möbius system.²⁶ Whether a cyclic system is Hückel or Möbius depends on the evenness or oddness of the number of sign inversions resulting from the negative overlaps between the adjacent orbitals of different sign.³² In the Möbius graphs the connectivity becomes (-1) showing a positive-negative overlap relationship between two $2p_z$ atomic orbitals.³³ The elementary rows/columns transformation of the adjacency matrix shows the possibility of Möbius structure in the cyclic transition state. The Möbius structures are easily obtained in the four or eight- membered cyclic transition states.



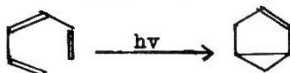
These results are in agreement with the results obtained by Aihara.¹³ In consideration of conrotatory or disrotatory^{23,25} ring closures, the conrotatory species lead to Möbius like closures while disrotatory species give Hückel systems.²⁶

There are also possibilities of other bond formations which can be seen from the possibilities of the rows/columns transformations other than reported above. They may be considered as not allowed processes. The formation of Dewar benzene structure in the six-membered cyclic state is possi-

ble ,



which is clear from the rows/columns transformation operation (not shown). Benzene often forms Dewar benzene with benzvalene and prismane when it is irradiated by ultraviolet light.³⁴ The formation of other bonds are important in some cases e.g. in the following photochemical reaction,



During the reaction two bonds are simultaneously formed.³⁵

CONCLUDING REMARKS

The topological method reported in this paper may be used to represent a class of organic intramolecular rearrangement processes both concerted and two-step reactions. The stereospecific nature of the reactions does not follow by the present method as the isomers (different geometrical isomers) of a product molecule have the same representative graph and hence the same adjacency matrix. The properties of the cyclic transition states can be discussed . In general we can say that the rows/columns transformation operation applied to the adjacency matrix is a mapping on-to the chemical rearrangement.

Acknowledgements

The author is thankful to Dr. R.Chandra of Mathematics Department, St. Andrew's College , Gorakhpur for valuable mathematical discussions and to the college authorities for providing the required facilities.

The author is grateful to Prof. A.T.Balaban for various helpful suggestions and discussion.

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