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TOPOLOGY OF CHEMICAL REACTIONS : THE FRAGMENTATION OF HYDROCARBONS.

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SUMMARY

A topological representation of a bond breaking process, the fragmentation of hydrocarbons, is reported. The results of topological fragmentation are in good agreement with mass spectrometric data. A topological rule has been formulated for the prediction of C-C bond fission.

INTRODUCTION

Previous work by several groups has shown that it is possible to apply the molecular graph theory[1] to various systems of conjugated hydrocarbons[2-5], in the framework of Hückel Molecular Orbital theory, for calculating the resonance energies[4] and in defining aromaticity[5]. Work on topological characterization of cyclic structures has been developed by Trinajstić and others[6,7].

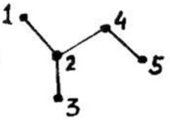
Theoretical studies on hydrocarbon fragments were first started by Wiener[8] and Platt[9]. Their work is based on the studies of thermodynamic properties among a homologous series. Graph theoretical methods, for discussing the problems of chemistry, were developed by Gordon and Kennedy[10]. Randić in 1975 characterized molecular branching in saturated hydrocarbons and correlated his branching index with thermodynamic properties[11]. In this work we propose a topological method for bond breaking processes e.g. the fragmentation of hydrocarbons, and hence, our work may be an approach to characterize a chemical reaction topologically.

It is known[1] that in a molecular graph G, the vertices and edges may be used to construct a number of matrices associated with it[12]. To any graph G, there corresponds a VxV matrix, called the adjacency matrix A of G, where V represents the number of vertices in G. Matrix A is defined by $A = [a_{ij}]$, where a_{ij} is the number of edges joining the vertices v_i and v_j respectively. After arbitrary labelling of the vertices of G, elements of the adjacency matrix are given by the following definition,

$$a_{ij} = \begin{cases} 1 \text{ if i and j are connected} \\ 0 \text{ otherwise} \end{cases}$$

Example: The adjacency matrix of the 2-methylbutane molecular graph is

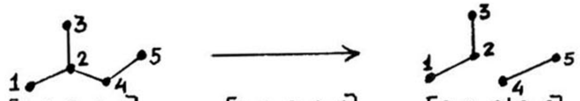
$$A = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$ where G is



The determinants of the adjacency matrices were recently studied by Graovac and Gutman[13], and the characteristic polynomials are used by a number of authors in resonance energy calculations[2-5]. In our work we have partitioned the adjacency matrix into a number of block matrices by near diagonalizing [14], through elementary transformations[15]. Each partitioned block of the parent adjacency matrix represents the adjacency matrix of a molecular fragment of the parent hydrocarbon.

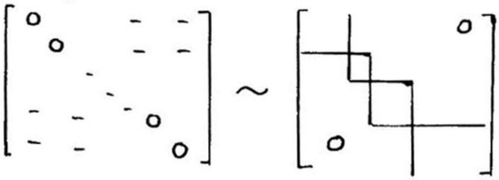
METHOD

An elementary transformation in a given matrix can be done by using some rules which are given in any textbook of matrix algebra[15]. The main operation of the elementary transformation, which we have used, is the subtraction from any row (R_i) or column (C_j) of a non-zero scalar multiple of any other row or column. The operation results in near diagonalization of a given matrix and partitioned blocks along the main diagonal are obtained. Each partition or block of the parent matrix represents the adjacency matrix of a fragment of the parent molecule. The elementary transformation of the adjacency matrix of a labelled graph of 2-methylbutane may be taken as an example.



$$\begin{bmatrix}0&1&0&0&0\\1&0&1&1&0\\0&1&0&0&0\\0&1&0&0&1\\0&0&0&1&0\end{bmatrix}\sim\begin{bmatrix}0&1&0&0&0\\1&0&1&0&0\\0&1&0&0&0\\0&1&0&0&0\\0&0&0&1&0\end{bmatrix}\sim\left[\begin{array}{ccc|cc}0&1&0&0&0\\1&0&1&0&0\\0&1&0&0&0\\\hline0&0&0&0&1\\0&0&0&1&0\end{array}\right]$$

First operation in this transformation is $C_4 - C_1$ which results in the elimination of the element a_{24}. Second operation $R_4 - R_1$ results in the elimination of the element a_{42} from the parent matrix. The blocking in the last matrix represents two adjacency matrices of the fragments  and  respectively, of the parent molecule . The fragments of a molecular graph may also be a complete graph or a vertex only. The graph  represents $C_3H_7^+$ ion or radical and  the $C_2H_5^+$ ion. Further transformation results in breaking of 1-2 bond or 2-3 bond giving a fragment having only one vertex which represents CH_3^+ ion. The fragmentation pattern is thus similar to the electron impact or photo-ionization fragmentation of hydrocarbons in their mass spectrum[16] with peaks corresponding to 15, 29, and 43 etc. m/e values. The whole process of elementary transformation operations can be summarized to,



The fragmentation process is thus easily summarized to the partitioning of an adjacency matrix through elementary transformation.

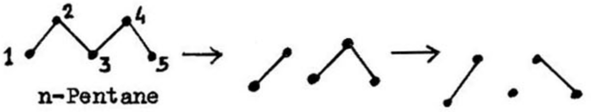
RESULTS AND DISCUSSION

The fragmentations of hydrocarbons induced by electron impact or photo-ionization methods, are reported by Biemann[17] and others[18]. Mass spectrometric data obtained by these authors[16-18] are sufficient to obtain an idea about the bond breaking process in the fragmentation of hydrocarbons. Several methods are now available for bond energy and bond strength calculations of hydrocarbons, e.g. Allinger's force field[19] method and Dewar's MINDO/3 method[20]. The energetics of hydrocarbons show[16] that C-C bonds are much weaker than C-H bonds in alkanes, and that in the molecular ion of the respective alkane, the strengths of C-C bonds are greatly reduced. They can be easily broken, but which bond will break can only be predicted by the fragmentation pattern obtained in mass spectrum. Our work, based on the molecular topology, supports the predictions made by mass spectrometry[17]. In our topological method, the breaking of a C-C bond can be predicted by using a general topological rule,

'If simultaneous operations of elementary transformation eliminate two elements a_{ij} and a_{ji} from an adjacency matrix, the bond $C_i - C_j$ will break up to give molecular fragments.'

Where a_{ij} and a_{ji} are non-zero elements. The verification of this rule will be easily seen in the example given above and in a few examples given below:

a)



n-Pentane

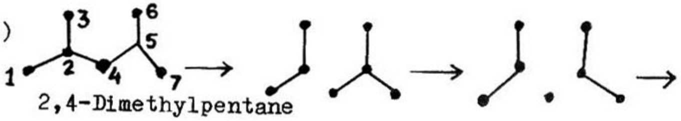
$$\left[\begin{array}{ccccc}0&1&0&0&0\\1&0&1&0&0\\0&1&0&1&0\\0&0&1&0&1\\0&0&0&1&0\end{array}\right]\sim\left[\begin{array}{cc|ccc}0&1&0&0&0\\1&0&0&0&0\\\hline 0&0&0&1&0\\0&0&1&0&1\\0&0&0&1&0\end{array}\right]\sim\left[\begin{array}{cc|c|cc}0&1&0&0&0\\1&0&0&0&0\\\hline 0&0&0&0&0\\\hline 0&0&0&0&1\\0&0&0&1&0\end{array}\right]$$

b)

3-Ethylpentane

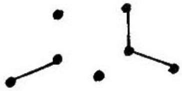
$$\left[\begin{array}{ccccccc}0&1&0&0&0&0&0\\1&0&1&0&0&0&0\\0&1&0&1&0&1&0\\0&0&1&0&1&0&0\\0&0&0&1&0&0&0\\0&0&1&0&0&0&1\\0&0&0&0&0&1&0\end{array}\right]\sim\left[\begin{array}{cc|ccccc}0&1&0&0&0&0&0\\1&0&0&0&0&0&0\\\hline 0&0&0&1&0&1&0\\0&0&1&0&1&0&0\\0&0&0&1&0&0&0\\0&0&1&0&0&0&1\\0&0&0&0&0&1&0\end{array}\right]\sim\left[\begin{array}{cc|ccc|cc}0&1&0&0&0&0&0\\1&0&0&0&0&0&0\\\hline 0&0&0&1&0&0&0\\0&0&1&0&1&0&0\\0&0&0&1&0&0&0\\\hline 0&0&0&0&0&0&1\\0&0&0&0&0&1&0\end{array}\right]$$

c)



2,4-Dimethylpentane

$$\left[\begin{array}{ccccccc}0&1&0&0&0&0&0\\1&0&1&1&0&0&0\\0&1&0&0&0&0&0\\0&1&0&0&1&0&0\\0&0&0&1&0&1&1\\0&0&0&0&1&0&0\\0&0&0&0&1&0&0\end{array}\right]\sim\left[\begin{array}{ccc|cccc}0&1&0&0&0&0&0\\1&0&1&0&0&0&0\\0&1&0&0&0&0&0\\\hline 0&0&0&0&1&0&0\\0&0&0&1&0&1&1\\0&0&0&0&1&0&0\\0&0&0&0&1&0&0\end{array}\right]\sim\left[\begin{array}{ccc|c|ccc}0&1&0&0&0&0&0\\1&0&1&0&0&0&0\\0&1&0&0&0&0&0\\\hline 0&0&0&0&0&0&0\\\hline 0&0&0&0&0&1&1\\0&0&0&0&1&0&0\\0&0&0&0&1&0&0\end{array}\right]\sim$$



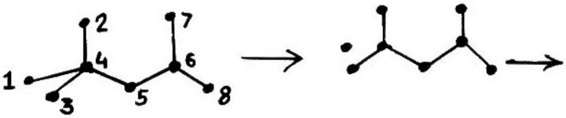
$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

d)

Ethylcyclopropane

$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 \end{bmatrix} \sim \left[\begin{array}{cc|ccc} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 \end{array}\right]$$

e)



2,2,4-Trimethylpentane

$$\begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \sim \left[\begin{array}{c|ccccccc} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array}\right] \sim$$

$$\left[\begin{array}{c|ccc|cccc}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ \cline{2-8}
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0
\end{array}\right]$$

The process can be worked on a series of compounds taking their carbon skeleton molecular graphs to get a pattern of fragmentation. We have applied the method to a number of n-alkanes, branched alkanes, alkenes and to some saturated hydrocarbons having rings with side chains. As the molecular graphs of alkanes and alkenes do not differ, the fragmentation pattern is similar in both classes of compounds. The results obtained by this topological method are in agreement with Biemann's fragmentation rules[17]. We can summarize the results,

a) The fragmentation patterns of n-alkanes consist of graphs corresponding to CH_3^+ , $C_2H_5^+$, $C_3H_7^+$ ions.

b) A branched alkane shows bond fission adjacent to the branching point. This is clear from the examples of 3-ethylpentane and 2,4-dimethylpentane.

c) Saturated rings tend to lose side chains.

d) When branching points of differing degrees are present, as in the case of example (e), a vertex of degree 4 prevails over a vertex of degree 3 in the fragmentation because the former has more possibilities for subtracting rows/columns than the latter.

CONCLUDING REMARKS

In this work we have formulated a topological rule for bond fission. The work may be used in the prediction of other similar reactions. The reverse of the present method is also true and may be used in predicting the bond making in addition reactions[21]. We hope to extend the work[21] in topological explanation of cycloaddition and metathesis[22,23] processes.

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