Conversion of Edge-to-Loop and Loop-to-Edge Technique Used to Study $[\pi^2 + \pi^2]$ and $[\pi^2 + \pi^4]$ Chemical Reactions

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ABSTRACT: The criterion of the conversion of edge to loop and loop to edge proposed by the Bratislava group is being presented with some chemical insight. The loops are generated inside the reaction or are supplied from outside to facilitate the reaction. These loops are termed nucleophilic, electrophilic, carbene singlet or triplet, or biradical. The supplied loops induce the various centers of the reactants following frontier orbital theory (FOT). In a $[\pi^2 + \pi^2]$ reaction system, when one of the centers of a reactant is induced by a single loop, a linear polyene is obtained. But, when two centers of a reactant are induced, a three- or a four-membered ring is produced. A $[\pi^2 + \pi^4]$ reaction system gives six-, five-, and three-membered ring products. In order to have some chemical insight in these model reactions, more realistic quantum chemical AM1 calculations have been done to characterize one analogous five-membered transition state structure by considering the reaction between SO$_2$ and 1,3-butadiene. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 75: 821–827, 1999

Key words: edge-loop and loop-edge conversion; chemical graph theory; FO theory; AM1 method; transition states

Introduction

Chemical graph theory, an integral part of mathematical chemistry [1–6], plays an important role in many areas of modern chemistry.

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The Bratislava group [7], while giving a graph theoretical treatment of Synthons [8], divided the vertex set into two distinct sets of vertices and termed them virtual and vertex (nonempty) sets. The virtual vertices have been formally treated as functional groups, which do not participate directly in chemical transformation, but they change quite substantially the chemical reactivity. Koca [9, 10] has given a mathematical model of the synthon based on the ideas given by Dugundji and Ugi.
The Bratislava group put forth two very important conditions while studying the chemical reactions. The first condition has been the matching of the cardinality of the vertex sets of the educt and that of the product graphs. Second, when a graph $G_1$ has been converted to $G_2$ through a reaction graph $G_r$ with a mapping $\omega$, the cardinality of $|V(G_r)| \leq |V(G_1)|$. Further, they used the conversion of edge to loop and loop to edge to explain the educt–product synthon graphs. They used transfer of the loop(s) from one center to another center, describing the reaction, chemical distance, and reaction graphs [12] in graph theoretical terms.

An example of a reaction presented as a transformation of a graph from $G_1$ to $G_2$ can be seen in Figure 1.

We can extend their discussion in a chemically meaningful way. In the transformation of Figure 1, if the loops are characterized as nucleophilic, electrophilic, or carbene, then the loop movement, which appears as a graph theoretical consequence only, can be well explained through frontier orbital theory (FOT) [13–16], adopted in the study of organic chemistry. Further, we have tried to generalize the conditions given by them by studying certain chemical reactions involving $[\pi^2 + \pi^2]$ and $[\pi^2 + \pi^4]$ systems.

Here, we have studied two different models (A and B). The central idea behind our method (which will be discussed subsequently) is the study of certain chemical reactions through nucleophilic, electrophilic, or carbene (singlet/triplet), and biradical loops. In model A (Fig. 2) the loops are generated by fragmenting a reactant ($G_i$ or $G_j$), but in model B the loops are being created on $G_2$ through an electrophilic or nucleophilic inductor. The inductor induces the loop at specific centers on $G_2$ following the FOT. Hence, the proposed method is a different one used by the Bratislava group [7, 12] for the transformation of $G_i$ to $G_j$. A computer program [Interstellar Medium–Reagent Matrix (ISM-RM)] is designed to study the chemical reactions through the loop(s).

![FIGURE 1. Edge-loop conversion.](image)

Let $R_1$ and $R_2$ be the two reactants taking part in a particular chemical reaction and $G_1$ and $G_2$ their corresponding vertex adjacency graphs (Fig. 2). In model A, the reagent matrix (RM) contains different fragmentation products of $G_i$ [17], and in model B, the RM contains different inducing agent(s) (supplied from outside). The supplementary reagent matrix, $RM^T$, is the transpose of RM. The reaction scheme shown in Figure 2 can be constructed to study the transformations/reactions of some chemical graphs.

In the reaction scheme $G_i$ is placed at the top left quadrant and $G_2$ is placed at the bottom right quadrant. At the initial stage, when there is no reaction, the top-right and bottom-left quadrants have zero entries. During the course of the reaction the RM is generated by the fragmentation of $G_1$, which contains exclusively different types of loops (nucleophilic, electrophilic, or carbene). This model (A) has been explained in previous work [17]. If the RM contains different loops without the fragmentation of the reactant ($G_i$ or $G_j$), then these loops induce nucleophilic or electrophilic centers at $G_2$, as described in model B. Finally, the reaction proceeds with the RM and $RM^T$ and the reactants from which the desired product is isolated.

Characterization of the RM along with the different loops has been described elsewhere [17]. Seven different loops with their corresponding RMs have been presented using five different rules. To explain model B, an induced loop is characterized by the following rules:

(a) If only a $+1$ or $-1$ entry is present in the RM without fragmentation of $G_i$ or $G_j$, then each entry corresponds to an induced loop. This loop induces the corresponding vertex of $G_2$ to behave either as a two-electron nucleophilic or two-electron-deficit elec-
trophilic center according to the +1 or −1 entry, respectively.

(b) If two +1 entries occur in different rows and different columns of the RM without the fragmentation of G₁ or G₂, then it amounts to two one-electron nucleophilic-induced loops in the RM. Whereas two −1 entries in different rows and columns of the RM without fragmentation of G₁ or G₂ are associated with the two one-electron-deficit electrophilic-induced loops.

**MODEL A**

This model has already been explained by the ISM-RM program by considering some chemical reactions with special attention to organic species which are candidates for the occurrence in the interstellar medium [17].

**MODEL B**

The principle of this model is somewhat different from model A. Here, different loops are induced at G₁ by the nucleophilic or electrophilic inductors. The nucleophilic inductor creates nucleophilic loop(s) at different centers and the electrophilic inductor creates electrophilic centers at different positions following the FOT.

**OUTLINE OF THE EXTENSION OF THE ISM-RM PROGRAM**

In the program ISM-RM, G₁ is fragmented and different loops are generated. But, here, G₁ and G₂ are not broken and G₂ is induced by different inductors. Since the inductions are possible at various centers, we have incorporated the induced loop +1 or −1 at the RM and the program is so designed that the loop goes to each position of the RM automatically. Once a loop occupies a position in the RM, it gives a (transition) product molecule. Hence, the total number of entries in the RM is equal to the total number of products, i.e., \( n \times m \), where \( n \) is the order of G₁ and \( m \) is the order of G₂. But, when two single-electron loops (nucleophilic or electrophilic) are introduced, then we obtained \( (n \times m) \left( \frac{n \times m}{2} \right) \) number of products. This subroutine is incorporated in the ISM-RM program. Another subroutine is incorporated to calculate the total \( E_\pi \) (graph-theoretic \( \pi \)-electronic energy of the chemical graphs [1, 2, 4]) of the molecule and the stable product so obtained is analyzed by the FOT.

After the product is formed its corresponding vertex adjacency matrix, eigenvalues, and \( E_\pi \) are calculated by another program segment. Then the loop introduced in the RM goes to the second position of the RM, and all the above calculations are carried out. Repeating the above process six times (equal to the number of position in the RM) for a 2×3 RM, we obtained 6 product molecules but few molecules are the same molecules (isomorphic). When two loops in the form of (+1, −1) are introduced in the RM, we obtained 30 molecules. A schematic representation of the loop movement is shown in Scheme 1.

**Results and Discussion**

In this work, we have studied the following chemical reactions, making use of our computer program:

(a) \([\pi^2 + \pi^2]\):
  Example: \( L_2 + L_2 \Rightarrow \text{product (transition)} \).

(b) (i) \([\pi^2 + \pi^4]\):
  Example: \( L_2 + L_4 \Rightarrow \text{product (transition)} \).

(ii) \([\pi^4 + \pi^2]\):
  Example: \( L_4 + L_2 \Rightarrow \text{product (transition)} \).

In the above examples \( L_n \) stands for the linear polyene with \( n \) carbon atoms and the product molecules are not the final product but their corresponding transition states.

The reaction \( L_2 + L_2 \Rightarrow \text{product} \) is studied by inducing a single vertex of \( L_2 \) through a loop and inducing both centers of the \( L_2 \) by two loops. The following products are generated by the program:

1. one center induction by a loop (Fig. 3) and
2. two center inductions by two loops (Fig. 4).

Earlier, we mentioned that one of the reactants is to be induced by an electrophilic or nucleophilic inductor. For the formation of \( L_4 \) (i), one of the centers of \( L_2 \) is induced by one electrophilic or nucleophilic inductor and the created loop reacts with the other \( L_2 \), and \( L_4 \) (i) is generated by the mechanism in Figure 5, which obeys the principle of the FOT [13–16].

It may be noted that one of the centers of \( L_1 \) is a reaction forbidden center (zero vector) [17]. When
both the centers of $L_2$ are allowed to react or when both the centers are induced, we have obtained the two possible products (ii) and (iii). Here, the two one-electron nucleophilic loops are created at the induced $L_2$, and these loops react with the other $L_2$ to give (ii) and (iii) (Fig. 6). Both products are explained by the FOT. Here, generation of two one-electron-deficit (electrophilic) loops is not possible at the induced $L_2$. Hence, the products illustrated in Figure 6 are obtained by the one-electron nucleophilic loops. Furthermore, the program gives the $E_\pi$ of (ii) to be $4.96\beta$ and of (iii) to be $4.0\beta$. Hence, (ii) is the more stable product in the studied reaction. Here, it may be mentioned that when

(i)

\[ \text{FIGURE 3. A linear polyene (L$_4$).} \]

(ii)  

\[ \text{FIGURE 4. Three- and four-membered ring adducts.} \]

(iii)  

\[ \text{FIGURE 5. Mechanism of L$_4$ (i) formation.} \]
a two-electron loop (nucleophilic) moves to a center, a full arrow is used; a half arrow is used when a loop with a single electron moves. Similarly, when a full arrow comes from a center to an electrophilic loop, two electrons have come to that loop; a half arrow indicates the coming of a single electron.

(a) Induction by a single loop: In the reaction \( L_2 + L_4 \rightarrow \text{product} \), either \( L_2 \) or \( L_4 \) is to be induced. When the induction is done by a single loop, eight molecules are formed and two molecules are found to be nonisomorphic molecules [(xv) and (xvi)] (Fig. 7).

Here, \( L_4 \) (butadiene) is induced and analyzing its \( \psi_2 \) [highest occupied molecular orbital (HOMO)] and \( \psi_3 \) [lowest unoccupied molecular orbital (LUMO)], one can notice that one and four (two-terminal) centers are capable of forming electrophilic and nucleophilic loops because the coefficient of the atomic orbital \( |c| \) of the two terminal positions is 0.60 (maximum). Now, the product (xv) can be formed both by the electrophilic and nucleophilic loops. In the other product (xvi), the 2- or 3-position is to be induced, but the induction is difficult since \( |c| \) is 0.37 (minimum) in \( \psi_2 \) and \( \psi_3 \).

(b) Induction by two loops: When induction was done by two loops, we obtained 56 molecules, and 8 molecules were found to be nonisomorphic (Fig. 8).

Considering the eight possible (transition) products obtained by double-loop induction, we noticed that the (xvii), (xviii), (xxi), and (xxii) products are obtained without obeying the FOT and hence they are rejected. It may also be noted that (xxiv) is not a chemical graph of conjugated hydrocarbon. The inductions at various positions are not possible by nucleophilic or electrophilic inductors. But, the six-, five-, and three-membered ring transition structures are possible by electrophilic and nucleophilic inductors. The mechanism (based on the program) for the formation of the three-, five-, and six-membered rings are explained in Figure 9.

A QUANTUM CHEMICAL VERIFICATION OF THE TRANSITION STRUCTURES

Considering the possible routes in the program and the qualitative FOT, one can obtain (xix), (xx), and (xxii) transition structures through the model chemical reactions. But, in real practice, it is hard to obtain the three- and five-membered ring transition structures by considering the carbon framework. The six-membered Diels–Alder product is the most obvious product and has been known for a long time to chemists. However, the three-membered ring transition structure is yet to be known by considering this type of cycloaddition reaction. Here, in order to have a chemical insight of the edge-to-loop and loop-to-edge technique, the most probable five-membered ring transition structure has been considered by choosing the reaction between 1,3-butadiene and sulfur dioxide. The two

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\[ \text{FIGURE 6. Formation of three- and four-membered ring adducts.} \]

\[ \text{FIGURE 7. Formation of the acyclic products.} \]

\[ \text{FIGURE 8. Formation of different ring adducts.} \]
FIGURE 9. Mechanism for the formation of three-, five-, and six-membered rings. Note: When $L_2$ is induced, then (xix) and (xxii) are not formed but (xx) is formed.

terminals of the 1,3-butadiene are induced and could react simultaneously with the sulfur center, producing a 5-membered ring structure. In fact, Suarez et al. [18] have done more sophisticated ab initio calculations of this reaction. Here, we have made a less rigorous semiempirical AM1 calculation to catch the transition state (TS) geometry of the above reaction using the MOPAC program [19]. The equilibrium and the saddle point (TS) geometries of the above reaction have been fully optimized using Baker's eigenvector following the eigenvector following (EF) procedure [20]. The TS structure so obtained has also been refined with DMAX = 0.01 and RECALC = 1. The stationary points on the potential energy surface have been characterized using the diagonalized Hessian matrix. The force calculation gives a single imaginary frequency ($\nu = 563.09i$ cm$^{-1}$) and the associated vibrational mode corresponds to the reaction coordinate (Fig. 10). This cheletropic [$\omega^2 + \pi^4$] reaction has been found to be an exothermic and synchronous process. Further, the classical barrier height for the reaction is found to be 3.385 kcal/mol. Both glide angles are 94.9°, and the deformation energies [21] are 0.503 and 26.562 kcal/mol for $SO_2$ and 1,3-butadiene, respectively.

FIGURE 10. Optimized TS geometry of the $SO_2$ and 1,3-butadiene reaction.
The deformation energy clearly indicates that the diene is to be deformed or induced to have a reaction with the SO$_3$ molecule, as proposed in our earlier mechanism (Fig. 9). In fact, this five-membered ring adduct is in good agreement with the experimentally observed results [22].

### Conclusion

Making use of the computer program, reactions of the type $[\pi^2 + \pi^2]$ and $[\pi^2 + \pi^4]$ can be studied. The edge-to-loop and loop-to-edge conversion technique proposed by the Bratislava group can be associated with some chemical ideas. The reactions are studied by fragmenting one of the reactants to different loops (model A) or by inducing a reactant by one inductor (model B). In the second model few new molecules are obtained corroborating the well-studied FOT. The experimental evidence for the formation of a five-membered ring adduct for the reaction of the type $[\pi^2 + \pi^4]$ can also be known from this qualitative graph theoretical study. The mechanism of all the chemical reactions are studied through a computer program. The program along with its extension can be obtained from the authors on request.

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