TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY

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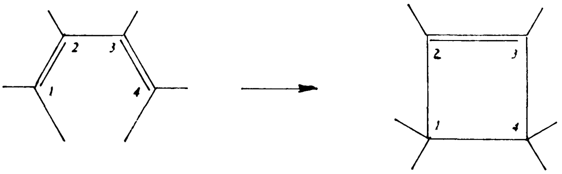
A simple formalism is proposed allowing to characterise the nature of chemical reactions. In comparison with existing techniques the presented method does not require to perform either quantum chemical calculations or to use the group theory. This makes the method convenient not only for pedagogical purposes but also as a routine tool for organic chemists.

Problem of the qualitative characterisation of chemical reactivity has two fundamental aspects. At first it is necessary to characterise the structure of the reacting molecules. In the second step one has to decide, whether the transformation of one structure to another is possible. The first of these two aspects was resolved already by the classical structural theory. Usual description of the chemical reaction in terms of classical structural formulae says however nothing about whether the reaction can really proceed. This aspect of the problem was succesfully treated by the quantum chemistry in terms of the Woodward–Hoffmann (W–H) rules[1]. In this approach the structure of the reacting molecules is characterised by two sets of molecular orbitals; one for the reactant and one for the product. Reactions are then classified as allowed or forbidden on the basis of the correlation diagrams visualising the assignment of orbitals from the individual sets. For such classification could be performed, some symmetry element must be conserved during the whole reaction. This condition is not, however, fulfilled in a majority of experimentally interesting reactions simply because the required high symmetry of the reactant or the product is lowered, *e.g.* by the substitution. In such cases the reactions should be, strictly speaking, classified as allowed and the disjunct character of the classification would be lost. Fortunately such is not the case and the W–H rules still remain formally valid. The question thus naturaly arises to what extent the deviations from the perfect symmetry can be tolerated without disturbing the validity of these rules. In recent years a number of papers dealing with this problem was published[2-7]. They demonstrate that not symmetrical but topological (nodal) properties of the wave functions are decisive for the validity of the W–H rules.

The aim of this paper is to introduce a simple method of analysis of nodal properties of the wave functions. The method does not require to perform either quantum chemical calculations or to use the group theory. This makes the analysis, in comparison with existing techniques, perhaps more simple and more familiar to the thinking of the organic chemist.

THEORETICAL

In our approach the reaction is regarded as a specific transformation of the bonds leading from the reactans to the products. In order to make this idea more concrete it is necessary to introduce a proper mathematical language allowing to describe the bonds and their transformations. The molecule is regarded as a certain set, the elements of which are the individual bonds. The structure of the reactant and the product will be then described by two sets M_R and M_P. In classifying the character of the reaction it is necessary to characterize the mutual relation of these sets similarly, as in correlation diagrams we search for the mutual assignment of molecular orbitals. In a subsequent part a simple empirical algorithm allowing to analyse this relation is proposed.



SCHEME 1

As an example let us discuss a simple isomerisation reaction R → P represented, *e.g.* by the cyclisation of the 1,3-butadiene to cyclobutene. The set M_R of the butadiene bonds is written down in Eq. (*1*), (Scheme 1).

$$M_R \equiv \{\pi_{12}, \pi_{34}, \sigma_{12}, \sigma_{23}, \sigma_{34}, 2\sigma_{C_1H}, 2\sigma_{C_4H}, \sigma_{C_3H}, \sigma_{C_2H}\} . \tag{1}$$

Similarly the set M_P contains the bonds (Eq. (*2*)), (Scheme 1).

$$M_P \equiv \{\pi_{23}, \sigma_{14}, \sigma_{12}, \sigma_{23}, \sigma_{34}, 2\sigma_{C_1H}, 2\sigma_{C_4H}, \sigma_{C_2H}, \sigma_{C_3H}\} . \tag{2}$$

From the comparison of these two sets it follows that the majority of the bonds remains untouched by the transformation (*e.g.* all CH bonds and the σ bonds of the butadiene skeleton). These bonds will be omitted from the considerations. Such a reduction was originally proposed by Hoffmann[1] with the aim to simplify the construction of the correlation diagrams. After this reduction the reaction is represented by the transformation of two butadiene π bonds (π_{12}, π_{34}) into two bonds of cyclobutene (π_{23}, σ_{14}). Schematically we can therefore describe the reaction as the transformation of the type $2\pi \to \pi + \Sigma$. The set of bonds participating in the transformation will be called irreducible core. Its finding in our case was trivial. Some complications may, however, appear in cases where the structure of the reacting molecules is described by more then one classical formula (*e.g.* benzene and its two Kékulé structures). These cases will be discussed in more details later.

Chemical reaction is regarded as a specific reorganisation of the reduced set μ_R (π_{12}, π_{34}) of the reactant bonds into the set μ_P of the product bonds. Since during the reaction certain bond of the reactant does not transform itself into a certain bond of the product, the relation of the sets μ_R and μ_P cannot be analysed on the basis of simple assignment of the bonds. In formulating a convenient formalism we shall use the analogy with the mapping analysis[3,8]. The sets μ_R and μ_P will be characterized by the approximate wave functions Φ_R and Φ_P. These functions are constructed in the form of the Slater determinant from individual chemical bonds represented by strictly localised orbitals. The function Φ_R for the butadiene has therefore the form (Eq. (*3*)).

$$\Phi_R = |\pi_{12}\bar{\pi}_{12}\pi_{34}\bar{\pi}_{34}| \,. \tag{3}$$

Similarly is defined the function Φ_P for cyclobutene (Eq. (*4*)).

$$\Phi_P = |\pi_{23}\bar{\pi}_{23}\sigma_{14}\bar{\sigma}_{14}| \,. \tag{4}$$

For one could work with these functions it is necessary to specify the meaning of the symbols π_{ij} and σ_{ij}. Qualitatively they say that the atoms *i* and *j* are connected by either π or σ bond. For quantitative characterization these bonds will be described by the usual linear combination of atomic orbitals. In our approach we do not need to know the detailed analytical form of these orbitals.

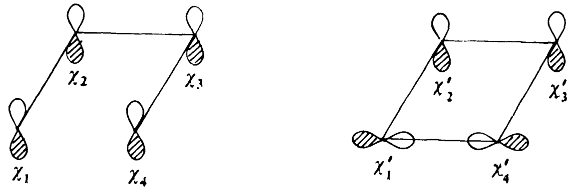
The nature of the reaction is characterized on the basis of nodal properties of the functions Φ_R and Φ_P. The similarity of these functions can be quantitatively measured by the value of the overlap integral. If the nodal structure of the functions Φ_R and Φ_P dramatically differs the overlap will be zero. This is the case of forbidden reactions. In allowed reactions, on the other hand, the nodal structure of the functions is similar. This statement represents an alternative formulation of the Goddard's "orbital phase continuity principle"[5].

The bonds in the butadiene are described by Eq. (*5*), (Scheme 2).

$$\pi_{12} = \chi_1 + \chi_2 \,; \quad \pi_{34} = \chi_3 + \chi_4 \,. \tag{5}$$

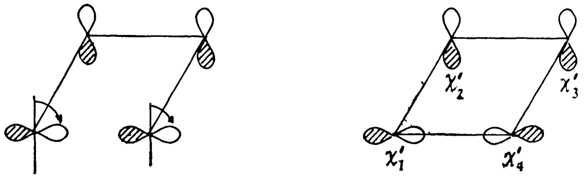
Similarly, the bonds in the cyclobutane are described by Eq. (*6*), (Scheme 2).

$$\pi_{23} = \chi'_2 + \chi'_3 \,; \quad \sigma_{14} = \chi'_1 + \chi'_4 \,. \tag{6}$$



SCHEME 2

The dashes in Eq. (*6*) aim to emphasize that the orbitals in the product are generally different from the orbitals in the reactant (*e.g.* due to different orientation in space). Since the orbitals χ and χ' differ, the functions Φ_R and Φ_P cannot be used for the calculation of the overlap directly. First it is necessary to find the relation transforming the orbitals χ and χ'. The form of this relation is determined by the reaction mechanism. Let us analyse the conrotatory reaction first. This mechanism is characterized by the rotation at the centers C_1 and C_4 in the same direction. During this rotation the original orbitals χ_1 and χ_4 change their orientation in space. Let us analyse now the mutual relation of these reoriented orbitals with the orbitals χ'_1 and χ'_4 in the product (Scheme 3). It is seen that the orientation of the rotated orbital at the centre C_1 is the same as the orientation of χ'_1. Formally one can say that orbital χ'_1 is equivalent to orbital χ_1. On the other hand the orientation of the rotated orbital at the center C_4 is opposite to the orientation of χ'_4. These results can be expressed in the form of the assignment table (Eq. (7)).



SCHEME 3

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 \\ \chi'_4 &\rightarrow -\chi_4 \,. \end{aligned} \tag{7}$$

The assignment of the remaining orbitals in trivial since their orientation does not change during the reaction (Eq. (*8*)).

$$\begin{aligned} \chi'_2 &\rightarrow \chi_2 \\ \chi'_3 &\rightarrow \chi_3 \,. \end{aligned} \tag{8}$$

This assignment allows us to express the bonds of both the reactant and the product in terms of single basis set (Eq. (*9*)).

$$\begin{aligned} \pi_{12} &= \chi_1 + \chi_2 \quad \pi_{23} = \chi'_2 + \chi'_3 \xrightarrow{f_{\text{con}}} \chi_2 + \chi_3 \\ \pi_{34} &= \chi_3 + \chi_4 \quad \sigma_{14} = \chi'_1 + \chi'_4 \xrightarrow{f_{\text{con}}} \chi_1 - \chi_4 \,. \end{aligned} \tag{9}$$

The mapping f_{con} represented by the Eqs (7, 8) thus transforms the original function Φ_P into the mapped function Φ_P^* (Eq. (*10*)).

$$\Phi_P \xrightarrow{f_{\text{con}}} \Phi_P^* \,. \tag{10}$$

This mapped function is then used to calculate the overlap with the function Φ_R Their overlap can be expressed in terms of certain "overlap determinant" (Eq. (*11*))

$$D = \int \Phi_R \Phi_P^* \, d\tau = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}^2 \,. \tag{11}$$

Matrix elements of this determinant are defined in terms of overlap integrals of individual bonds. Since our bonds are described in terms of nonspecified orbitals the overlaps cannot be calculated in usual way. We shall therefore use the method analogous to ZDO approximation. The element a_{11} in D is then given by the overlap integral of the π_{12} bond in butadiene with the π_{23} bond in cyclobutene (Eq. (*12*))

$$a_{11} = \int (\chi_1 + \chi_2)(\chi_2 + \chi_3) \, d\tau = 1 \,. \tag{12}$$

The remaining elements can be expressed analogously. The final form of the determinant is given in Eq. (*13*)

$$D_{\text{con}} = \begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix}^2 \neq 0 \,. \tag{13}$$

The nonzero value of D_{con} shows, that the conrotatory mechanism preserves the nodal structure of the functions Φ_R and Φ_P. The reaction is allowed.

We shall show now that the disrotatory mechanism leads to forbidden reaction. Disrotatory reaction is characterized by the rotation at the centers C_1 and C_4 in the opposite direction. From the Scheme 4 one can see that the rotated orbital at the centre C_1 is oriented similarly as χ'_1. The same is true of the rotated orbital at the center C_4 and χ'_4. The assignment equation has therefore the following form

$$\begin{aligned} \chi'_1 &\to \chi_1 \quad \chi'_3 \to \chi_3 \\ \chi'_2 &\to \chi_2 \quad \chi'_4 \to \chi_4 \,. \end{aligned} \tag{14}$$

SCHEME 4

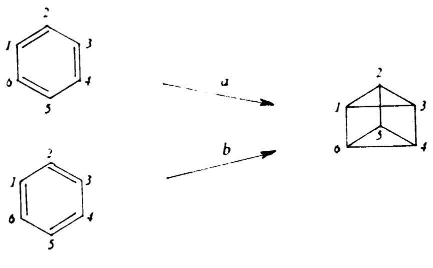
Using this table one can again transform the bonds of the product from the base χ' to the base χ, (Eq. (*15*))

$$\pi_{12} = \chi_1 + \chi_2 \quad \pi_{23} = \chi'_2 + \chi'_3 \xrightarrow{f_{\mathrm{dis}}} \chi_2 + \chi_3 \tag{15}$$

$$\pi_{34} = \chi_3 + \chi_4 \quad \sigma_{14} = \chi'_1 + \chi'_4 \xrightarrow{f_{\mathrm{dis}}} \chi_1 + \chi_4 \,. \tag{16}$$

The zero value of the corresponding overlap determinant shows, that the reaction is forbidden.

The application of the proposed method may not be in all cases as simple as in our model reaction of butadiene to cyclobutene. A slight modification of the formalism is necessary for reactions where the structure of at least one of the reacting molecules is not sufficiently described by only one classical formula. As an example of such reaction let us analyse now the cyclization of benzene to prismane, (Scheme 5). The



SCHEME 5

bonds in the benzene molecule can be formally localised in two different ways. The reduction according to Eq. (a) leads to the set $\mu_A(\pi_{12}, \pi_{34}, \pi_{56}, \sigma_{25}, \sigma_{13}, \sigma_{64})$. On the other hand the reduction according to reaction (b) leads to different set $\mu_B(\pi_{16}, \pi_{23}, \pi_{45}, \sigma_{25}, \sigma_{13}, \sigma_{46})$. These sets are equivalent since they both characterise the reaction as the transformation of the type $3\pi \rightarrow 3\Sigma$. This equivalency suggests that the reaction has to be regarded as the transformation of the whole π electron sextet of benzene. Because of impossibility to describe this sextet properly by only one set of localized bonds (corresponding to one Kékulé structure) we use in the construction of the overlap determinant directly π molecular orbitals. These orbitals have not, however, to be known precisely *i.e.* including AO expansion coefficients but only their nodal properties are important. It is sufficient therefore to describe them by schematical Eq. (*17*).

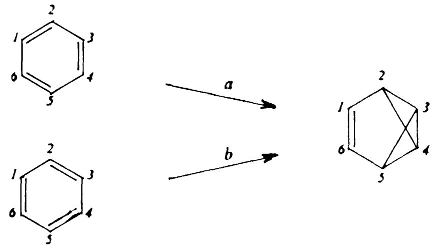
$$\begin{aligned}\varphi_1 &= \chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6 \\ \varphi_2 &= \chi_2 + \chi_3 - \chi_5 - \chi_6 \\ \varphi_3 &= \chi_1 + \chi_2 + \chi_6 - \chi_3 - \chi_4 - \chi_5 \,.\end{aligned} \tag{17}$$

Bonds in the product can be of course still described classically in terms of localized orbitals (Eq. (*18*)).

$$\begin{aligned}\sigma_{13} &= \chi_1' + \chi_3' \rightarrow \chi_1 + \chi_3 \\ \sigma_{25} &= \chi_2' + \chi_5' \rightarrow \chi_2 + \chi_5 \\ \sigma_{46} &= \chi_4' + \chi_6' \rightarrow \chi_4 + \chi_6 \,.\end{aligned} \tag{18}$$

Overlap determinant constructed from these orbitals directly leads to the correct result that the reaction is forbidden. It is apparent that the construction of the overlap determinant is much more simple than the standard technique of the correlation diagrams.

As a next example illustrating the concept of irreducible core let us analyse the transformation of benzene to benzvalene. This reaction can be described in terms of classical formulae by two formally equivalent schematic equations (a) and (b) in Scheme 6. Despite this equivalency the process of reduction according to Eq. (a) leads to the set $\mu_A(\pi_{12}, \pi_{34}, \pi_{56}, \sigma_{16}, \sigma_{24}, \sigma_{35})$ whereas the reduction according to Eq. (b) leads to different set $\mu_B(\pi_{23}, \pi_{45}, \sigma_{24}, \sigma_{35})$. We have thus two possibilities to characterise this reaction. Either to consider it as a six electron transformation ($3\pi \rightarrow \pi +$



SCHEME 6

$+ 2\Sigma$) according to Eq. (*a*) or the four electron transformation ($2\pi \rightarrow 2\Sigma$) according to Eq. (*b*). This ambiguity is removed by using the concept of irreducible core. From the comparison of the sets μ_A and μ_B it follows that only the second represents the irreducible core for our reaction. The transformation of benzene to benzvalene represents therefore the four electron problem and it is thus entirely equivalent to the rearrangement of 1,3-butadiene to bicyclo[1,1,0]butane. The concept of irreducible core thus provides the missing information required by Halevi[9,10] to complement the correlation diagrams for making them able to answer unambiguously the question about the nature of this reaction.

The proposed formalism can be similarly applied to the analysis of any reaction. In the following part such application is demonstrated on a number of examples. First of all the well known Woodward–Hoffmann rules are alternatively derived.

RESULTS AND DISCUSSION

Cycloaddition Reactions

2 + 2 *Cycloadditions*: The typical example of 2 + 2 cycloadditions is represented by the dimerization of ethene. This reaction is required to proceed by $2_s + 2_a$ mechanism on the basis of Woodward–Hoffmann rules. We shall demonstrate that the same conclusions follow also from our analysis. The reactants in this reaction are two molecules of ethene, the product is cyclobutene. After eliminating the bonds not directly contributing to the transformation the reaction can be characterized as a rearrangement of two ethene π bonds into two cyclobutene σ bonds (Scheme 7), $2\pi \rightarrow 2\Sigma$. Bonds in the reactant and in the product are described by Eq. (*19*).

SCHEME 7

$$\begin{aligned} \pi_1 &= \chi_1 + \chi_2 \quad & \sigma_1 &= \chi'_1 + \chi'_4 \\ \pi_2 &= \chi_3 + \chi_4 \quad & \sigma_2 &= \chi'_2 + \chi'_3 \end{aligned} \qquad (19)$$

Let us consider the *supra-supra* mechanism first. This mechanism is described on the basis of Scheme 7 by the assignment equation (*20*).

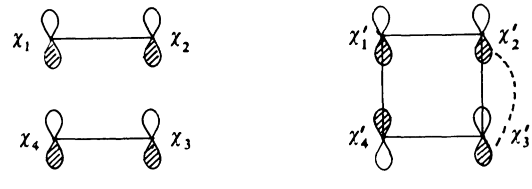
$$\begin{array}{ll} \chi_1' \rightarrow \chi_1 & \chi_3' \rightarrow -\chi_3 \\ \chi_2' \rightarrow \chi_2 & \chi_4' \rightarrow -\chi_4 \end{array} \tag{20}$$

Using this equation one can easily write down the bonds participating in the reaction (Eq. (*21*)).

$$\begin{array}{l} \pi_1 = \chi_1 + \chi_2 \quad \sigma_1 \xrightarrow{\text{s+s}} \chi_1 - \chi_4 \\ \pi_2 = \chi_3 + \chi_4 \quad \sigma_2 \xrightarrow{\text{s+s}} \chi_2 - \chi_3 \end{array} \tag{21}$$

Overlap determinant (*22*) constructed on the basis of these equations equals zero indicating thus the forbiddeness of the reaction.

$$D_{s,s} = \begin{vmatrix} 1 & 1 \\ -1 & -1 \end{vmatrix}^2 \tag{22}$$



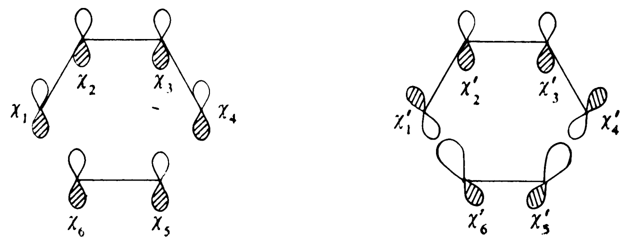
SCHEME 8

The difference between $2_s + 2_a$ and $2_s + 2_s$ mechanism consists only in mutual assignment of orbitals. From the Scheme 8 it is apparent that $2_s + 2_a$ mechanism is characterized by the assignment table (*23*).

$$\begin{array}{ll} \chi_1' \rightarrow \chi_1 & \chi_3' \rightarrow -\chi_3 \\ \chi_2' \rightarrow \chi_2 & \chi_4' \rightarrow \chi_4 \end{array} \tag{23}$$

Corresponding overlap determinant shows that the $2_s + 2_a$ mechanism leads to allowed reaction.

4 + 2 *Cycloadditions*: The whole class of these transformations represented by the Diels–Alder reactions can be reduced to the study of the general example characterized on the basis of irreducible core by the transformation $3\pi \rightarrow \pi + 2\Sigma$. The typical example of such reaction is the addition of ethene to butadiene. We shall analyse



SCHEME 9

the $4_s + 2_s$ mechanism first (Scheme 9). Bonds in the reactant and in the product can be described by Eq. (*24*).

$$\begin{array}{ll} \pi_{12} = \chi_1 + \chi_2 & \pi_{23} = \chi'_2 + \chi'_3 \\ \pi_{34} = \chi_3 + \chi_4 & \sigma_{16} = \chi'_1 + \chi'_6 \\ \pi_{56} = \chi_5 + \chi_6 & \sigma_{45} = \chi'_4 + \chi'_5 \end{array} \qquad (24)$$

Supra-supra mechanism is characterized by the assignment equation (*25*).

$$\begin{array}{ll} \chi'_1 \rightarrow -\chi_1 & \chi'_4 \rightarrow -\chi_4 \\ \chi'_2 \rightarrow \chi_2 & \chi'_5 \rightarrow \chi_5 \\ \chi'_3 \rightarrow \chi_3 & \chi'_6 \rightarrow \chi_6 \end{array} \qquad (25)$$

This assignment leads to nonzero value of the overlap determinant (*26*) in harmony with the allowed nature of the reaction.

$$D_{s,s} = \begin{vmatrix} 1 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 1 \end{vmatrix} \neq 0 \qquad (26)$$

On the other hand the $4_s + 2_a$ mechanism characterized by the assignment (*27*) is forbidden.

$$\begin{array}{ll} \chi'_1 \rightarrow \chi_1 & \chi'_4 \rightarrow \chi_4 \\ \chi'_2 \rightarrow \chi_2 & \chi'_5 \rightarrow \chi_5 \\ \chi'_3 \rightarrow \chi_3 & \chi'_6 \rightarrow -\chi_6 \end{array} \qquad (27)$$

Analogously can be analysed also other 4 + 2 cycloadditions. As an example let us discuss in details the addition of allyl anion to ethene (Scheme 10). This reaction has not been observed experimentally but it serve us as a model example of the whole

SCHEME 10

series of 1,3 dipolar additions. Because of impossibility to characterise the structure of the allyl anion by only one set of localized bonds one has to use for the construction of the overlap determinant directly π molecular orbitals φ_1, φ_2. Since numerical values of the A0 expansion coefficients are unimportant for the topological analysis, the corresponding molecular orbitals can be specific only schematically by Eq. (*28*)

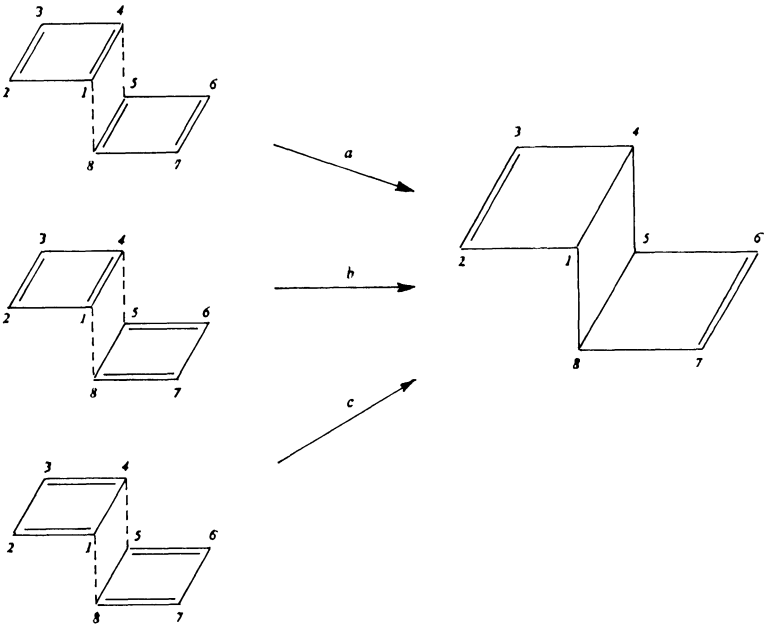
$$\begin{aligned} \varphi_1 &= \chi_1 + \chi_2 + \chi_3 \\ \varphi_2 &= \chi_1 - \chi_3 \,. \end{aligned} \tag{28}$$

Bonds in the product are already well described by the localized model and can be therefore described by the usual way (Eq. (*29*))

$$\begin{aligned} \sigma_{15} &= \chi_1' + \chi_5' \xrightarrow{\mathrm{s+s}} \chi_1 + \chi_5 \\ \sigma_{34} &= \chi_3' + \chi_4' \xrightarrow{\mathrm{s+s}} \chi_3 + \chi_4 \\ n &= \chi_2' \xrightarrow{\mathrm{s+s}} \chi_2 \,. \end{aligned} \tag{29}$$

Overlap determinant constructed from these bonds shows that the reaction is allowed Similarly it can be shown that $4_s + 2_a$ mechanism is forbidden.

Other cycloaddition reactions: As a next example demonstrating the applicability of the proposed method let us analyse in details the *supra-supra* dimerization of cyclobutadiene. Its ground state is represented by rectangular structure with alternating single and double bonds. The dimerization can be then described by three reaction schemes (Scheme 11, reactions *a*–*c*). In contrast to the rearrangement of benzene to benzvalene all these alternatives have to be considered as nonequivalent since they describe three distinguishable modes of interaction. From this it follows that in analysing the feasibility of the dimerization we have to consider all three reactions as entirely independent. The first reaction (*a*), characterised as a transformation of the type $2\pi \rightarrow 2\Sigma$ is then entirely analogous to the dimerization of ethene and as a such is forbidden. The same is true of 4 + 4 cycloaddition according to Eq. (*c*), ($4\pi \rightarrow 2\pi + 2\Sigma$). Since the reaction is known to proceed it is clear that the only possibility to make it allowed is to consider it as 4 + 2 addition according to Eq. (*b*).



SCHEME 11

The concept of irreducible core thus helped us in this case to discriminate between possible reaction mechanisms.

The proposed formalism can be also applied to the analysis of more complicated types of cycloadditions as for example 2 + 2 + 2 trimerization of ethene to cyclohexane and 2 + 2 + 2 + 2 intramolecular cyclization of cyclooctatetraene to cubane. This latter reaction was discussed in details by Hoffmann as an example in which the straightforward application of the correlation diagrams leads to errorneous conclusion[1]. It is encouraging that the proposed formalism is free of similar limitations.

Sigmatropic Reactions

1,3 *Rearrangements*: On the basis of irreducible core the whole class of these reactions can be characterized as a transformation $\pi + \Sigma \rightarrow \Sigma + \pi$. The most simple example is represented by the 1,3 migrations in allyl derivatives (allyl rearrangement) (Scheme 12). The important bonds are described by Eq. (*30*).

$$\begin{aligned} \pi &= \chi_1 + \chi_2 \quad & \sigma &= \chi_1' + h' \\ \sigma &= \chi_3 + h \quad & \pi &= \chi_2' + \chi_3' \end{aligned} \qquad (30)$$

SCHEME 12

As can be seen from the Scheme 12 the suprafacial mechanism is characterized by the assignment equation (*31*).

$$\begin{array}{ll} \chi'_1 \rightarrow \chi_1 & \chi'_3 \rightarrow \chi_3 \\ \chi'_2 \rightarrow \chi_2 & h' \rightarrow h \end{array} \tag{31}$$

From this equation it follows that the overlap determinant is equal to zero (Eq. (*32*).)

$$D_s^{1,3} = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0 \tag{32}$$

On the other hand the antarafacial rearrangement characterized on the basis of Scheme 13 by the assignment equation (*33*) is allowed.

$$\begin{array}{ll} \chi'_1 \rightarrow \chi_1 & \chi'_3 \rightarrow \chi_3 \\ \chi'_2 \rightarrow \chi_2 & h' \rightarrow -h \end{array} \tag{33}$$

SCHEME 13

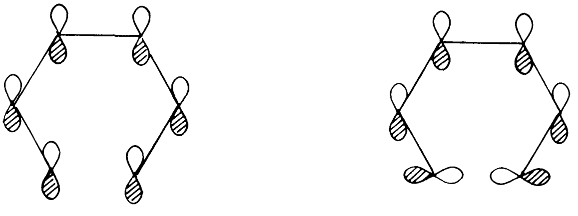
1,5 *Rearrangements*: Analogously can be analysed also the 1,5 migrations. For the sake of brevity only the resulting overlap determinants are presented in Eqs ((*34a*), (*34b*)). In harmony with the Woodward–Hoffmann rules they demonstrate that the reaction is allowed by the suprafacial mechanism and forbidden by the antarafacial one.

$$D_s^{1,5} = \begin{vmatrix} 0 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{vmatrix}^2 \neq 0 \tag{34a}$$

$$D_a^{1,5} = \begin{vmatrix} 0 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & -1 \end{vmatrix}^2 = 0 \tag{34b}$$

Electrocyclic Reactions

Mutual transformation of the butadiene to cyclobutene as an example of $2\pi \rightarrow \pi + \Sigma$ reactions was discussed above and will not be repeated here. Let us start therefore by the analysis of the cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene as a representative of the general transformation $3\pi \rightarrow 2\pi + \Sigma$ (Scheme 14). Conrotatory reaction mechanism is characterized by the assignment equation (*35*) (for the sake of brevity only orbitals χ'_1 and χ'_6 the reorientation of which is crucial for the closure of the ring are included)



SCHEME 14

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 \\ \chi'_6 &\rightarrow -\chi_6 \, . \end{aligned} \tag{35}$$

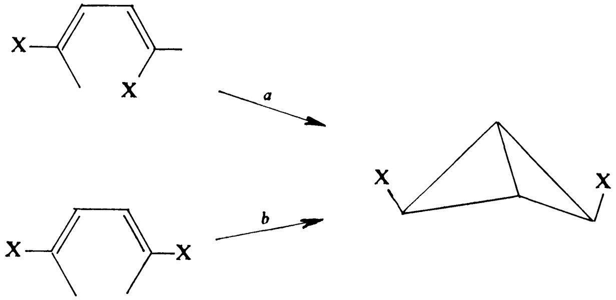
Overlap determinant (*36*) constructed in the basis of this assignment shows that the reaction is forbidden.

$$D_{\text{con}} = \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \end{vmatrix}^2 = 0 \tag{36}$$

On the other hand the disrotatory mechanism characterized by the assignment (*37*) leads to allowed reaction.

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 \\ \chi'_6 &\rightarrow \chi_6 \end{aligned} \tag{37}$$

As a next example let us consider the mutual transformation of the butadiene to bicyclo[1,1,0]butane (Scheme 15). This reaction is interesting not only by its stereospecificity but also by that the construction of correlation diagrams is not here without problems[10]. We shall demonstrate that the proposed formalism removes these difficulties.



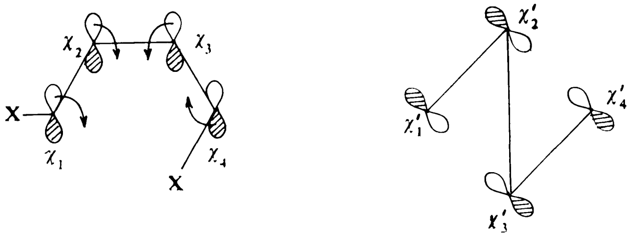
SCHEME 15

Let us analyse the reaction (*a*) in Scheme 15 first. Orbitals of the bonds forming the irreducible core are described by Eq. (*38*).

$$\pi_{12} = \chi_1 + \chi_2 \quad \sigma_{13} = \chi_1' + \chi_3'$$
$$\pi_{34} = \chi_3 + \chi_4 \quad \sigma_{24} = \chi_2' + \chi_4' \tag{38}$$

Reaction mechanism (*a*) is characterized by the assignment equation (*39*) (Scheme 16).

$$\chi_1' \rightarrow \chi_1 \quad \chi_3' \rightarrow \chi_3$$
$$\chi_2' \rightarrow \chi_2 \quad \chi_4' \rightarrow -\chi_4 \tag{39}$$



SCHEME 16

The overlap determinant constructed by the usual way shows that the reaction is allowed (*40*).

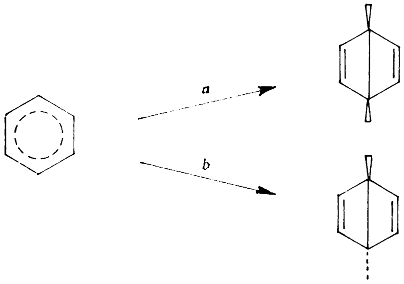
$$D = \begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix}^2 \neq 0 \tag{40}$$

On the other hand reaction proceding according to Eq. (*b*), characterized by the assignment (*41*) is forbidden.

$$\chi_1' \rightarrow \chi_1 \quad \chi_3' \rightarrow \chi_3$$
$$\chi_2' \rightarrow \chi_2 \quad \chi_4' \rightarrow \chi_4 \qquad (41)$$

Valence Isomerisations

As a typical example of these reactions let us analyse the transformation of the benzene to bicyclo[2,2,0]hexadiene (Dewar benzene). The reaction can in principle proceed



SCHEME 17

by two different mechanisms (Scheme 17). Irreducible core characterizes this reaction as a transformation of the type $2\pi \rightarrow \pi + \Sigma$. Corresponding bonds can be described by Eq. (*42*).

$$\pi_{12} = \chi_1 + \chi_2 \quad \pi_{23} = \chi_2' + \chi_3'$$
$$\pi_{34} = \chi_3 + \chi_4 \quad \sigma_{14} = \chi_1' + \chi_4' \qquad (42)$$

The reaction proceding according to Eq. (*a*) is characterized by the disrotation at centers C_1 and C_4. Assignment table has therefore the form (*43*).

$$\chi_1' \rightarrow \chi_1 \quad \chi_3' \rightarrow \chi_3$$
$$\chi_2' \rightarrow \chi_2 \quad \chi_4' \rightarrow \chi_4 \qquad (43)$$

Overlap determinant constructed on the basis of this assignment characterizes the reaction as forbidden, Eq. (*44*).

$$D = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0 \qquad (44)$$

On the other hand conrotation at centers C_1 and C_4 described by the assignment (*45*) is allowed. Consequently, if this isomer of the Dewar benzene were formed during some reaction it would always rearrange to more stable benzene.

$$\begin{aligned} &\chi_1' \rightarrow \chi_1 \quad \chi_3' \rightarrow \chi_3 \\ &\chi_2' \rightarrow \chi_2 \quad \chi_4' \rightarrow -\chi_4 \end{aligned} \tag{45}$$

This example demonstrates that the transformation of the benzene to Dewar benzene is entirely analogous to the cyclization of the butadiene to cyclobutene. This is the consequence of the fact that both reactions have the same irreducible core (reaction is of the type $2\pi \rightarrow \pi + \Sigma$). All these examples demonstrate that the proposed formalism is able to reproduce the whole class of W–H rules in a very simple and unambiguous way. It is just this simplicity which makes the method especially convenient not only from the pedagogical point of view but also for the routine use by organic chemists.

The applicability of the method is not, however, restricted only to reactions governed by W–H rules but it seems to be even more general. As an example of the reaction violating the conditions for the applicability of the W–H rules let us analyse in details the 1,2 elimination (Eq. (*46*)).

$$\text{H—CH}_2\text{—CH}_2\text{—X} \rightarrow \text{CH}_2\text{=CH}_2 + \text{HX} \tag{46}$$

Irrespective of whether the reaction proceeds as *syn* or *anti* elimination the only symmetry element conserved during the whole process is represented by the plane containing the bonds CH, CC and CX. This element of symmetry does not bisects any of the bonds broken or formed in the reaction and it is thus of no value for the construction of the correlation diagram. Our method, on the other hand, is able to discriminate between possible reaction mechanisms and rationalize thus the experimental data.

Let us consider the synchronous *syn* mechanism of elimination first.The irreducible core characterises the reaction as the transformation of the type $2\Sigma \rightarrow \pi + \Sigma$. Corresponding bonds are described by Eq. (*47*), Scheme 18.

$$\begin{aligned} \sigma_1 &= \chi_1 + h_\beta \qquad & \pi &= \chi_1' + \chi_2' \\ \sigma_2 &= \chi_2 + x \qquad & \sigma &= h_\beta' + x' \end{aligned} \tag{47}$$

SCHEME 18

The mutual assigment of the orbitals required by the *syn* mechanism is trival, Eq. (*48*).

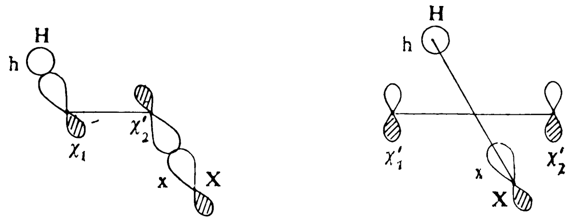
$$\begin{array}{ll} \chi_1' \rightarrow \chi_1 & h_\beta' \rightarrow h_\beta \\ \chi_2' \rightarrow \chi_2 & x' \rightarrow x \end{array} \qquad (48)$$

From this assignment it follows that the reaction is forbidden*) (see overlap determinant (*49*))

$$D = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0\,. \qquad (49)$$

Let us analyse now the *anti* mechanism of elimination (Scheme 19). Orbitals of the reagent and the product bonds are again described by Eq. (*47*). Different is however the assignment table (Eq. (*50*))

$$\begin{array}{ll} \chi_1' \rightarrow \ \ \chi_1 & h_\beta' \rightarrow h_\beta \\ \chi_2' \rightarrow -\chi_2 & x' \rightarrow x\,. \end{array} \qquad (50)$$



SCHEME 19

Overlap determinant constructed on its basis shows that the reaction is allowed. In order the reaction could procede as a synchronous process it is necessary that simultaneously with the formation of the C=C bond the H—X bond is formed. This is however quite difficult from the sterical point of view since the atoms H and X lie in the remoted antiperiplanar position. This of course negatively influences the possibility ot the formation of the H—X bond especially in the initial stages of reaction. Thus, despite the reaction is formally allowed one may expect the presence of certain energy barier arising from the sterical factors. These conclusions are, however, valid only for reaction proceeding in the gas phase under the monomolecular conditions.

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* As suggested by Goddard[5] there exists also an alternative mechanism of *syn* elimination consisting in direct participation of free electron pair at the heteroatom X in the formation of the HX bond. Reaction proceeding by this mechanism is allowed.

In solution or on the surface of polar metal oxides the reaction may be considerably facilitated by the acidobasic catalysis.

CONCLUSIONS

All presented examples suggest that the proposed topological analysis represents very simple and effective means of characterization of the feasibility of chemical reactions. The easy algorithmisation and numerical simplicity makes this method, in comparison with existing techniques, attractive for classification of reactivity in computer designed synthesis. We are of course aware of the fact that the method may have also some limitations but so far we were unable to find any reaction violating the proposed formalism. The method is not restricted to only ground state reactions but can be easily extended to photochemical reactions as well. Such extension is being prepared in our laboratory and will be published elsewhere[11].

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