TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. REORGANISATION OF ELECTRON DENSITY IN ALLOWED AND FORBIDDEN REACTIONS

Robert PONEC

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6, Suchdol 2

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The selection rules in chemical reactivity are discussed from the point of view of the differences in the character of the electron density reorganisation in allowed and forbidden reactions. It was shown that the allowed reactions are characterised by the maximum conservation of electron pairing along the whole reaction path. On the other hand for the forbidden reactions a critical point lies on the corresponding concerted reaction coordinate in which one electron pair is completely splitted.

In our previous study[1] a simple formalism was proposed allowing to classify the nature of chemical reactions on the basis of the analysis of topological properties of molecular structures of the reactant and the product. The wide applicability of such approach was demonstrated on a number of examples including various types of not only thermal but also photochemical reactions[2]. In accordance with a number of recent related studies[3-9] the proposed analysis demonstrates that the validity of Woodward–Hoffmann rules[10] is not conditioned by the conservation of the orbital symmetry but that it probably has much deeper topological reasons. In this study we want to demonstrate the close relation of selection rules in chemical reactivity with the fundamental differences in the character of the electron reorganisation in allowed and forbidden reactions.

THEORETICAL

Besides the earlier attempts to justify the Woodward–Hoffmann rules from the point of view of the orbital symmetry[11,12] a number of recent papers attempts to demonstrate that the validity of these rules is probably due to even more fundamental topological factors[4-9]. In the previous study[1] we have introduced a simple formalism allowing to analyse these important topological propertiees of chemical structures. This analysis requires, similarly as the technique of the so-called correlation diagrams, only the knowledge of the structure of the reactants and the products. Such a description is however only very crude and does permit nothing more than a simple clas-

sification of the reactions in terms of allowedness and forbiddeness. If, however, one is interested in a more detailed study of the reaction mechanism *e.g.* from the point of view of the structure of the transition states and possible intermediates it is evident that the original simple formalism has to be properly modified. The aim of this modification is to extend the applicability of the topological approach to the description of not only reactants and products but also of all transient species corresponding to the arbitrary position on the reaction coordinate. In formulating this generalisation we shall use the intuitive principle according to which, for reaction to be allowed, the reactant has to transform itself into the product without the change of their topological structures.*

Similarly as in the previous study the structure of the reactant and the product will be characterised by the so-called bonding functions constructed in the form of Slater determinant from the bonds forming in a given reaction the irreducible core.[1] (Eq. (*1*))

$$\begin{aligned} \Phi_R &= |r_1\bar{r}_1 r_2\bar{r}_2 \ldots r_n\bar{r}_n| \\ \Phi'_P &= |p'_1\bar{p}'_1 p'_2\bar{p}'_2 \ldots p'_n\bar{p}'_n| \end{aligned} \tag{1}$$

The corresponding bonds are described in terms of familiar linear combinations in the orthonormal basis of atomic orbitals χ and χ', where the primes again distinguish between the orbitals of the reactant and the product. In the next step the product bonds $p'_1, p'_2 \ldots p'_n$ are converted, using the assignment tables, from the original basis of orbitals χ' into the basis of orbitals χ serving simultaneously to describe the bonds of the reactant. The form of these tables depends on the actual reaction mechanism and in the original paper[1] a simple method of their construction was proposed. On the basis of the transformation described by these tables the original bonding function Φ'_P is converted into the modified function Φ_P used in the whole following analysis. (Eq. (*2*))

$$\begin{gathered} p'_1 \to p_1 \quad p'_2 \to p_2 \ldots p'_n \to p_n \\ \Phi'_P \to \Phi_P \end{gathered} \tag{2}$$

The concerted mechanism of the chemical reaction is now formally described by a mapping $F(q)$ transforming, in dependence on the variation of the argument q (generalised reaction coordinate) the reactant bonding function Φ_R into the corresponding modified product bonding function Φ_P. The concrete form of this mapping is not very important if only it satisfies the requirement of continuity and mutual unambiguity. In this paper we use, without the loss of generality, a simple trigono-

* (This principle can be mathematically formulated in the form of requirement of homeomorphism of the reactant and the product topological spaces[8].)

metric formula (3) describing the bonding function of the general transient species in the form of the combination of the functions Φ_R and Φ_P.*

$$\Phi(\varphi) = \frac{\cos\varphi}{N(\varphi)}\Phi_R + \frac{\sin\varphi}{N(\varphi)}\Phi_P \tag{3}$$

The variable φ changing in the interval $0 - \pi/2$ plays the role of the generalised reaction coordinate. The numerical factor $N(\varphi)$ appears in Eq. (3) only as the normalising factor ensuring the function $\Phi(\varphi)$ to satisfy the equation (4). (The integration proceeds over all space (r_i) and spin (ξ_i) coordinates).

$$\int \Phi^2(\varphi)\,\mathrm{d}x_1\,\mathrm{d}x_2 \ldots \mathrm{d}x_N = 1 \quad \mathrm{d}x_i = \mathrm{d}r_i\,\mathrm{d}\xi_i \tag{4}$$

From this equation the relation (5) follows for the magnitude of $N(\varphi)$.

$$N^2(\varphi) = 1 + \sin 2\varphi S_{RP} \tag{5}$$

The symbol S_{RP} denotes the overlap integral of the functions Φ_R and Φ_P defined by Eq. (6)

$$S_{RP} = \int \Phi_R\Phi_P\,\mathrm{d}x_1\,\mathrm{d}x_2 \ldots \mathrm{d}x_N\,. \tag{6}$$

The general method of calculating this integral in terms of the so-called overlap determinant was introduced in our previous study[1] and need not be repeated. We remember only that the reactions for which the corresponding determinant is different from zero can be characterized in the framework of Woodward–Hoffmann rules as allowed. On the other hand for the forbidden reactions the overlap determinant is zero. As will be demonstrated this difference has the fundamental consequences for the character of the reorganisation of the electron density in allowed and forbidden reactions. To characterise this reorganisation we shall not use, however, the function $\Phi(\varphi)$ but the closely related matrix $\Omega(\varphi)$ the definition equation of which suggests the analogy with the density matrix. (Eq. (7))

$$\int \Phi^2(\varphi)\,\mathrm{d}\xi_1\,\mathrm{d}x_2\,\mathrm{d}x_3 \ldots \mathrm{d}x_N = \sum_\mu \sum_\nu [\Omega(\varphi)]_{\mu\nu}\,\chi_\mu\chi_\nu\,. \tag{7}$$

In the light of this analogy the matrix $\Omega(\varphi)$ can be regarded as the "topological density matrix" of the transient species $X(\varphi)$ in a general point of the concerted

* This form of the mapping was chosen in analogy with Pancíř trigonometrical formula[7].

reaction coordinate. The knowledge of the matrix $\Omega(\varphi)$ for different values of the angle φ allows then to characterise the structure of the intermediate species and the character of the electron redistribution in the course of the reaction. The detailed form of the matrix $\Omega(\varphi)$ given by Eq. (*8*) results from the combination of the original definition equation (*7*) and Eq. (*4*)

$$\Omega(\varphi) = \frac{1}{N^2(\varphi)} \{\cos^2 \varphi \Omega_{RR} + \sin^2 \varphi \Omega_{PP} + \sin \varphi \cos \varphi (\Omega_{RP} + \Omega_{PR}) . \qquad (8)$$

This equation suggests that the actual form of the matrix $\Omega(\varphi)$ depends not only on the individual density matrices Ω_{RR} and Ω_{PP} of the reactant and the product but that in the general case also some "interference" overlap densities Ω_{RP} and Ω_{PR} appears. Whereas the matrices Ω_{RR} and Ω_{PP} can be simply expressed by familiar formulae in terms of AO expansion coefficients $\varrho_{\mu i}$, $\pi_{\nu j}$ of the reactant and product bonds (bonding orbitals) r_i, p_j, (Eq. (*9*)),*

$$r_i = \sum_\mu \varrho_{\mu i} \chi_\mu \qquad (9a)$$

$$p_j = \sum_\nu \pi_{\nu j} \chi_\nu \qquad (9b)$$

$$(\Omega_{RR})_{\mu\nu} = 2 \sum_i^{occ} \varrho_{\mu i} \varrho_{\nu i} \qquad (9c)$$

$$(\Omega_{PP})_{\mu\nu} = 2 \sum_j^{ocl} \pi_{\mu j} \pi_{\nu j} \qquad (9d)$$

the calculation of the interference terms is much more complicated and requires to take into the consideration the nonorthogonality of the functions Φ_R and Φ_P. The corresponding general expressions for the matrix elements of the matrix $(\Omega_{RP} + \Omega_{PR})$ in the orthonormal basis of atomic orbitals χ are given by Eq. (*10*) in which the symbol D_{RP} denotes the overlap determinant

$$(\Omega_{RP} + \Omega_{PR})_{\mu\nu} = 2 D_{RP} \sum_i^{ocl} \sum_j^{occ} (-1)^{i+j} A_{ij} (\varrho_{\mu i} \pi_{\nu j} + \varrho_{\nu i} \pi_{\mu j}) \qquad (10)$$

constructed from the functions $r_1, r_2 \ldots r_n$, $p_1, p_2 \ldots p_n$ and A_{ij} its corresponding minor. As it follows from the Eq.(*10*) the overlap densities Ω_{RP} and Ω_{PR} are proportional to the overlap determinant D_{RP}. This implies that these interference terms

* In the framework of the topological approach these coefficients are zero except the centers connected by the classical bond.

participate in the general expression (*10*) only in the case of allowed reactions for which the overlap determinant is nonzero. On the other hand in the case of forbidden reactions the matrix $\Omega(\varphi)$ is given by a simple weighted sum of the matrices Ω_{RR} and Ω_{PP} of isolated reactant and the product (Eq. (*11*))

$$\Omega(\varphi) = \cos^2 \varphi \Omega_{RR} + \sin^2 \varphi \Omega_{PP} \,. \tag{11}$$

As it will be shown later the differences in the form of Eqs (*8*) and (*11*) describing the topological density matrices in allowed and forbidden reactions leads to the specific differences in the character of the reorganisation of the electron density that will be demonstrated, in the following part, on a detailed analysis of several examples including different types of thermal pericyclic reactions.

RESULTS AND DISCUSSION

Electrocyclic Reactions

The elementary example of this type of reactions represents the transformation of 1,3 butadiene to cyclobutene. In the framework of the general approach described in the previous theoretical part the structure of the reacting molecules is described in terms of bonding functions Φ_R and Φ'_P (Eq. (*12*)) where the individual bonds are expressed in the form of strictly localised bonding orbitals.

$$\begin{aligned} \Phi_R &= |r_1\bar{r}_1 r_2\bar{r}_2| & \Phi'_P &= |p'_1\bar{p}'_1 p'_2\bar{p}'_2| \\ r_1 &= 1/\sqrt{2}\,\chi_1 + 1/\sqrt{2}\,\chi_2 & p'_1 &= 1/\sqrt{2}\,\chi'_2 + 1/\sqrt{2}\,\chi'_3 \\ r_2 &= 1/\sqrt{2}\,\chi_3 + 1/\sqrt{2}\,\chi_4 & p'_2 &= 1/\sqrt{2}\,\chi'_1 + 1/\sqrt{2}\,\chi'_4 \end{aligned} \tag{12}$$

The structure of the butadiene could be of course described also using the set of π molecular orbitals (at arbitrary level of approximation) but in the framework of the topological approach the classical description in terms of localised bonds is to be preferred. The reason for this preferency consists in that such construction of the bonding function requires, in characterising the molecular structure only the very elementary information about the topology of the molecule.*

After having specified the bonds forming the irreducible core the original product bonding function Φ'_P is converted, with the aid of assignment tables, into the modified functions Φ_P^{dis} and Φ_P^{con} used in the construction of the overlap determinants.

* By the term molecular topology we express (similarly as *e.g.* Prof. Prelog) the bonding relations in the molecule consisting in which atom is bonded to which and by what type of the bond.

Their actual form is given by Eq. (*13*)

$$S_{RP}^{dis} = (D_{RP}^{dis})^2 = \begin{vmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{vmatrix} = 0 \tag{13a}$$

$$S_{RP}^{con} = (D_{RP}^{con})^2 = \begin{vmatrix} 1/2 & 1/2 \\ 1/2 & -1/2 \end{vmatrix}^2 = 1/4\,. \tag{13b}$$

Using these values and combining Eqs (*3*), (*5*), (*8*) and (*11*) the corresponding topological density matrices $\Omega^{dis}(\varphi)$ and $\Omega^{con}(\varphi)$ can be derived for any value of the argument φ. The knowledge of these matrices opens the possibility to characterise the structure of the transient species at the arbitrary point of the concerted reaction coordinate (Eq. (*14*)).

$$\Omega^{dis}(\varphi) = \cos^2\varphi \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} + \sin^2\varphi \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix} \tag{14a}$$

$$\Omega^{con}(\varphi) = \frac{1}{1 + 0{\cdot}25 \sin 2\varphi} \left\{ \cos^2\varphi \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} + \sin^2\varphi \begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix} + \right.$$

$$\left. + \sin\varphi \cos\varphi \begin{pmatrix} 1/2 & 1/2 & 0 & -1/2 \\ 1/2 & 1/2 & 1/2 & 0 \\ 0 & 1/2 & 1/2 & 1/2 \\ -1/2 & 0 & 1/2 & 1/2 \end{pmatrix} \right\} \tag{14b}$$

Such characterisation consists in determining the values of the occupation numbers of "natural orbitals" resulting from the diagonalisation of the topological density matrices for different values of the argument φ. In order to obtain a rough qualitative insight into the detailed process of the electron reorganisation let us discuss, in general features, the results of such analysis. First of all it is evident that for $\varphi = 0$ and $\pi/2$ the matrices $\Omega(\varphi)$ reduce themselves, irrespective of the reaction mechanism, to the corresponding reactant and product matrices Ω_{RR} and Ω_{PP}. The diagonalisation of these matrices leads to the integer values of the occupation numbers 2 and 0 confirming thus the strict discrimination between the occupied and virtual orbitals resulting from the specific one-determinantal form of the bonding functions Φ_R and Φ_P. In the course of the chemical reaction described by the mixing of the reactant and product functions (Eq. (*3*)) the above strict picture of the electron distribution considerably changes and the diagonalisation of the corresponding matrices $\Omega(\varphi)$

already leads, irrespective of the reaction mechanism, to noninteger values of the occupation numbers. At first sight there is thus no significant difference between the conrotatory and disrotatory reaction. The more detailed examination of the calculated values nevertheless indicates that the process of the electron reorganisation proceeds in allowed and forbidden reactions in completely different way. The differences can be the most simply demonstrated graphically in the form of dependence of calculated occupation numbers on the value of the argument φ. In our case such dependence is depicted in Fig. 1. It demonstrates that in the case of allowed conrotatory cyclisation the electron redistribution proceeds in such a way that the occupation numbers conserve the values close to the ideal values 0 and 2 confirming thus the tendency of the system to retain the closed shell character along the whole reaction path. On the other hand in the case of forbidden disrotatory reaction the specificity of the electron reorganisation manifest itself in the tendency to reduce the gap between the values of occupation number of originally occupied and virtual orbitals. This tendency finally leads for the symmetrical structure corresponding to $\varphi = \pi/4$ to the appearance of the pair of degenerated orbitals with occupation numbers equal to unity. Such a picture suggests a complete splitting of one of the electron pairs indicating thus the biradical nature of the corresponding structure.

Summarising the above results one may conclude that the proposed topological analysis has confirmed the fundamental difference between the allowed and forbidden mechanism of the butadiene cyclisation. This difference manifests itself not only in the overall nature of the process of electron reorganisation but above all in the structure of critical „intermediate" characterised by the density matrix $\Omega(\pi/4)$. This structure is thus in some respect specific and intuitively one may expect that

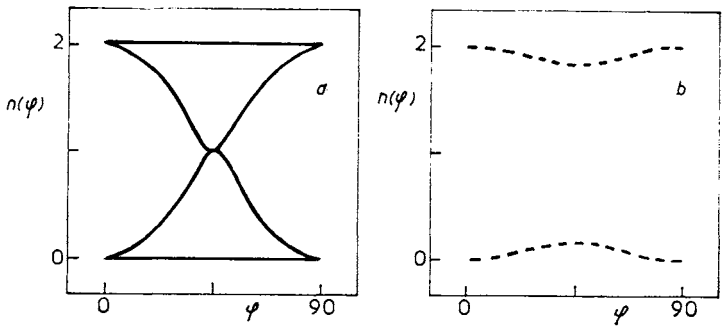


FIG. 1

Dependence of calculated eigenvalues of topological density $\Omega(\varphi)$ matrix on the magnitude of the argument φ for the case of forbidden *a* and allowed *b* cyclisation of 1,3-butadiene to cyclobutene. Broken line corresponds to degenerated pair of eigenvalues

in the above introduced topological analysis it plays a similar role as the transition state for the description in terms of potential energy hypersurfaces.

As will be shown below the above picture of the electron reorganisation is not characteristic only for the studied case of butadiene cyclisation but it is more general. As a next example demonstrating the validity of the above conclusions let us analyse in details the cyclisation of 1,3,5 hexatriene to 1,3 cyclohexadiene. This reaction can be characterised as the transformation of the type $3\pi \rightarrow 2\pi + \sum$. The individual bonds are again described in terms of familiar localised orbitals (Eq. (*15*))

$$\begin{aligned} r_1 &= 1/\sqrt{2}\,\chi_1 + 1/\sqrt{2}\,\chi_2 & p'_1 &= 1/\sqrt{2}\,\chi'_2 + 1/\sqrt{2}\,\chi'_3 \\ r_2 &= 1/\sqrt{2}\,\chi_3 + 1/\sqrt{2}\,\chi_4 & p'_2 &= 1/\sqrt{2}\,\chi'_4 + 1/\sqrt{2}\,\chi'_5 \\ r_3 &= 1/\sqrt{2}\,\chi_5 + 1/\sqrt{2}\,\chi_6 & p'_3 &= 1/\sqrt{2}\,\chi'_6 + 1/\sqrt{2}\,\chi'_1 . \end{aligned} \tag{15}$$

In the next step the bonds p_1, p_2. p_3 are transformed, with the aid of assigning tables, into the basis of unprimed orbitals χ and corresponding overlap determinants are constructed. Using their values and combining Eqs (*8*) and (*11*) the general expressions for the topological density matrices $D^{\text{dis}}(\varphi)$ and $D^{\text{con}}(\varphi)$ can be obtained. For the sake of brevity these expressions will not be given in details but we restrict ourselves only to the presentation of the final picture of the electron reorganisation schematically visualised in the form of dependence of the occupation numbers on the magnitude of the argument φ. (Fig. 2). As demonstrates the figure the form of this dependence is just the same as for the previous case of butadiene cyclisation confirming thus not only the biradical nature of the critical intermediate but also the overall similarity in the character of the electron reorganisation.

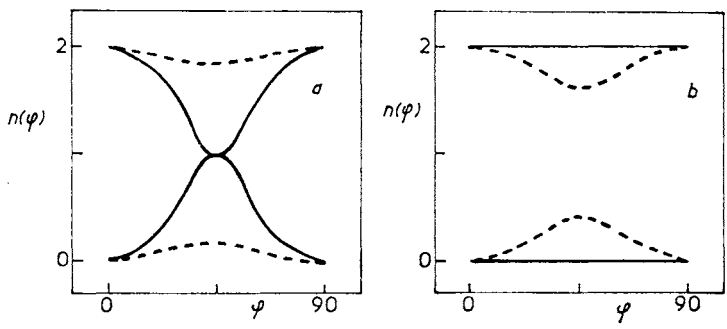


FIG. 2

Dependence of calculated eigenvalues of topological density matrix $\Omega(\varphi)$ on the magnitude of the argument φ for the case of forbidden *a* and allowed *b* cyclisation of 1,3,5 hexatriene to 1,3-cyclohexadiene. Broken line corresponds to degenerated pair of eigenvalues

Cycloaddition Reactions

The most simple representative of this type of pericyclic reactions represents the dimerisation of alkenes leading to cyclobutane derivatives. The reaction can in principle proceed as supra-supra or supra-antara process, the first of them being forbidden on the basis of Woodward–Hoffmann rules. In the framework of the topological approach the reaction can be characterised as the transformation of the type $2\pi \rightarrow \rightarrow 2\sum$. The corresponding bonds are described by Eq. (*16*)

$$r_1 = 1/\sqrt{2}\,\chi_1 + 1/\sqrt{2}\,\chi_2 \qquad p'_1 = 1/\sqrt{2}\,\chi'_1 + 1/\sqrt{2}\,\chi'_4 \tag{16}$$
$$r_2 = 1/\sqrt{2}\,\chi_3 + 1/\sqrt{2}\,\chi_4 \qquad p'_2 = 1/\sqrt{2}\,\chi'_2 + 1/\sqrt{2}\,\chi'_3$$

and the assigning tables are then given by Eq. (*17*)

$$2s + 2s \quad \chi'_1 \rightarrow \chi_1 \quad \chi'_3 \rightarrow -\chi_3 \tag{17a}$$
$$\chi'_2 \rightarrow \chi_2 \quad \chi'_4 \rightarrow -\chi_4$$

$$2s + 2a \quad \chi'_1 \rightarrow \chi_1 \quad \chi'_3 \rightarrow \chi_3 \tag{17b}$$
$$\chi'_2 \rightarrow \chi_2 \quad \chi'_4 \rightarrow -\chi_4\,.$$

The overlap determinants constructed in the usual way confirms the prediction of Woodward–Hoffmann rules preferring for the thermal reaction the $2s + 2a$ mechanism. Using the values of the overlap determinants the bonding functions of the general intermediate can be constructed which in the case of the critical point corresponding to $\varphi = \pi/4$ has the following form (Eq. (*18*))

$$\Phi_{s,s}(\pi/4) = 1/\sqrt{2}\,\Phi_R + 1/\sqrt{2}\,\Phi_P^{s,s} \tag{18}$$
$$\Phi_{s,a}(\pi/4) = 0{\cdot}632\Phi_R + 0{\cdot}632\Phi_P^{s,a}$$

The diagonalisation of the corresponding topological density matrices leads to the values of occupation numbers confirming again the validity of the general picture of reorganisation of electron density in allowed and forbidden reactions. (Eq. (*19*))

$$2s + 2s \quad n_1 = 2{\cdot}00 \quad n_2 = 1{\cdot}00 \quad n_3 = 1{\cdot}00 \quad n_4 = 0{\cdot}00 \tag{19}$$
$$2s + 2a \quad n_1 = 1{\cdot}85 \quad n_2 = 1{\cdot}85 \quad n_3 = 0{\cdot}15 \quad n_4 = 0{\cdot}15$$

To the same conclusions leads also the analysis of Diels–Alder reaction represented by the model addition of ethene to butadiene. For the sake of brevity we shall not repeat the whole procedure but we restrict ourselves only to the presentation of the final form of bonding functions of the critical structure $X(\pi/4)$ together with the values

of the occupation numbers resulting from the corresponding density matrices $D(\pi/4)$ (Eqs (*20, 21*))

$$\Phi_{s,s}(\pi/4) = 0{\cdot}686\Phi_R + 0{\cdot}686\Phi_P^{s,s} \tag{20a}$$

$$\Phi_{s,a}(\pi/4) = 1/\sqrt{2}\,\Phi_R + 1/\sqrt{2}\,\Phi_P^{s,a} \tag{20b}$$

$$4a + 2s \quad n_1 = 2{\cdot}00 \quad n_2 = 1{\cdot}59 \quad n_3 = 1{\cdot}59 \quad n_4 = 0{\cdot}00 \quad n_5 = 0{\cdot}41 \quad n_6 = 0{\cdot}41 \tag{21a}$$

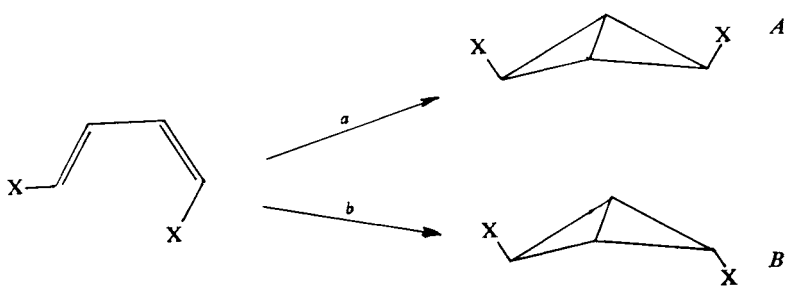
$$4s + 2a \quad n_1 = 1{\cdot}88 \quad n_2 = 1{\cdot}88 \quad n_3 = 1{\cdot}00 \quad n_4 = 0{\cdot}12 \quad n_5 = 0{\cdot}12 \quad n_6 = 1{\cdot}00\,. \tag{21b}$$

Valence Isomerisations

As an example of this specific type of reactions let us analyse in details the cyclisation of 1,3 butadiene to [1,1,0]bicyclobutane. The reaction can be characterised as the transformation of the type $2\pi \rightarrow 2\sum$. The bonds forming the irreducible core are described in the form of linear combinations of orbitals χ and χ' (Eq. (*22*)

$$r_1 = 1/\sqrt{2}\,\chi_1 + 1/\sqrt{2}\,\chi_2 \qquad p_1' = 1/\sqrt{2}\,\chi_1' + 1/\sqrt{2}\,\chi_3' \tag{22}$$
$$r_2 = 1/\sqrt{2}\,\chi_3 + 1/\sqrt{2}\,\chi_4 \qquad p_2' = 1/\sqrt{2}\,\chi_2' + 1/\sqrt{2}\,\chi_4'\,.$$

The reaction can in principle proceed by two different mechanisms leading to the formation of two isomeric products A and B (Scheme 1). For thermally initiated



SCHEME 1

reaction the mechanism leading to product *A* is preferred. As it was shown in our previous study[1] this mechanism is characterised by the assignment table (*23*) allowing to transform the bonds

$$\chi_1' \rightarrow \chi_1 \qquad \chi_3' \rightarrow \chi_3 \tag{23}$$
$$\chi_2' \rightarrow \chi_2 \qquad \chi_4' \rightarrow -\chi_4$$

p_1, p_2 into the basis of unprimed orbitals χ and the form of these transformed bonds is given by Eq. (*24*)

$$p'_1 \to p_1 \quad \chi'_1 + \chi'_3 \to \chi_1 + \chi_3 \qquad (24)$$
$$p'_2 \to p_2 \quad \chi'_2 + \chi'_4 \to \chi_2 - \chi_4 \,.$$

On the other hand the trivial form of assignment tables for the forbidden reaction leading to product B ensures the the transformation to be a simple identity. The overlap determinants corresponding to both types of reactions are then given by Eq. (*25*)

$$S_a = \begin{vmatrix} 1/2 & 1/2 \\ -1/2 & 1/2 \end{vmatrix}^2 = 1/4 \qquad (25)$$

$$S_b = \begin{vmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{vmatrix}^2 = 0 \,.$$

On the basis of these values the bonding functions of the critical structure $X(\pi/4)$ are described by Eq. (*26*)

$$\Phi_a(\pi/4) = 0{\cdot}632\Phi_R + 0{\cdot}632\Phi_P^a \qquad (26)$$
$$\Phi_b(\pi/4) = 1/\sqrt{2}\,\Phi_R + 1/\sqrt{2}\,\Phi_P^b \,.$$

The diagonalisation of the corresponding topological density matrices leading to the values of the occupation numbers presented in Eq. (*27*) again confirms the general validity of the above presented picture of the electron reorganisation.

$$a)\quad n_1 = 1{\cdot}85 \quad n_2 = 1{\cdot}85 \quad n_3 = 0{\cdot}15 \quad n_4 = 0{\cdot}15 \qquad (27)$$
$$b)\quad n_1 = 2{\cdot}00 \quad n_2 = 1{\cdot}00 \quad n_3 = 1{\cdot}00 \quad n_4 = 0{\cdot}00 \,.$$

CONCLUSIONS

A number of above examples clearly demonstrates that the existence of the selection rules in chemical reactivity is closely connected with the fundamental differences in the character of the reorganisation of the electron density. In the so-called allowed reactions this reorganisation proceed in such a way that all transient species conserve as closely as possible the closed shell character. On the other hand the forbidden reactions are characterised by the complete splitting of one of the electron pairs and by the formation of the biradical intermediates. The structure of these biradical species closely resembles the typical Jahn–Teller systems. On the basis of this analogy, if it is justified, one may expect these intermediates to display the typical features of Jahn–Teller systems including *e.g.* the structural instability. Here it is encouraging to remark that these expectations are confirmed by the recent results of sophisticated

ab initio study by Schaeffer[13] indicating the instability of the symmetrical structure corresponding to expected "transition state" for the disrotatory butadiene cyclisation.

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