

## TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY

### Concertedness in pericyclic reactions

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#### Abstract

The technique of the so-called More O'Ferrall diagrams was modified by incorporating the framework of recently introduced topological theory of chemical reactivity. On the basis of this modification, a new simple criterion was introduced, allowing the unequivocal classification of the mechanisms of pericyclic reactions from the point of view of concertedness and/or nonconcertedness.

#### 1. Introduction

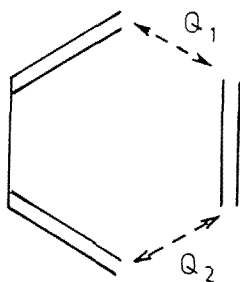
The concept of concerted reaction was introduced into the chemical reactivity theory [1] to denote the process in which the scission of old and the formation of new bonds is mutually coupled in such a way that it proceeds synchronously or – in other words – "in concert". Even if such a definition is apparently entirely clear, its practical use as a criterion is considerably complicated by the fact that the formation or the rupture of the bond is a microscopic process inaccessible to direct experimental observation. This of course suggests the necessity of a search for other, more easily exploitable criteria of concert. As one such criterion is usually regarded the considerable stereospecificity accompanying the formation of the products in allowed pericyclic reactions. The fact that the origin of the synchronization in the process of formation and scission of the bonds was also always intuitively related to certain energetic favorization led to another widespread opinion that all allowed reactions are automatically concerted. On the other hand, nonconcertedness, advocated by frequently observed stereorandomization [2], was practically always expected in forbidden reactions.

The continuing accumulation of experimental material, however, made it still more apparent that all the above criteria, both kinetic and stereochemical [3–6], cannot be regarded as absolute [7] since there are probably both concerted reactions which are forbidden [4, 8] as well as nonconcerted ones which are allowed [9, 10]. This of course stimulated a number of subsequent studies with the aim of specifying the very concept of concertedness. In this connection it is necessary to mention the study by Lowe [11], who clearly demonstrated a certain incompatibility arising

from the frequent confusion of concertedness in the sense of the synchronization between the formation and scission of the bonds and concertedness as a kinetic characteristic denoting that the reaction proceeds as an elementary process without intermediates. To overcome this incompatibility, Lowe proposed to distinguish strictly between the above two cases and to reserve the concept of concertedness, in harmony with the original intuitive ideas, to express only the synchronization in the bonding reorganization. The same interpretation also lies as the basis of another important approach, known as the technique of More O'Ferrall diagrams [12, 13]. In spite of the unquestionable role this approach played in the elucidation of various problems concerning mechanisms of pericyclic reactions, in the question of concertedness its use is restricted, since besides a number of clear cases there is also a number of situations the classification of which remains fuzzy. Our aim in this study is to demonstrate that this important restriction can be very simply circumvented and the criterion discriminating between concerted and nonconcerted reactions defined unequivocally. This generalization arises from a recently proposed topological approach based on the exploitation of the so-called similarity index [14, 15].

## 2. Theoretical

Before starting the presentation of the proposed criterion, let us first recapitulate the basic ideas underlying the technique of More O'Ferrall diagrams. This technique can be best demonstrated on a reaction the course of which is governed by the variation of two nuclear coordinates  $Q_1$ ,  $Q_2$  representing the lengths of two newly formed bonds. As an example of such a process may serve, for example, the Diels–Alder reaction (scheme 1). If we now regard the reaction mechanism classically as



Scheme 1.

a sequence of consecutive scissions and formations of bonds, the course of the reaction can be described in a pictorial way as a line (corresponding to the reaction coordinate) connecting the reactant and the product in a schematic diagram (fig. 1) in which the degree of formation of individual bonds is evaluated on individual axes

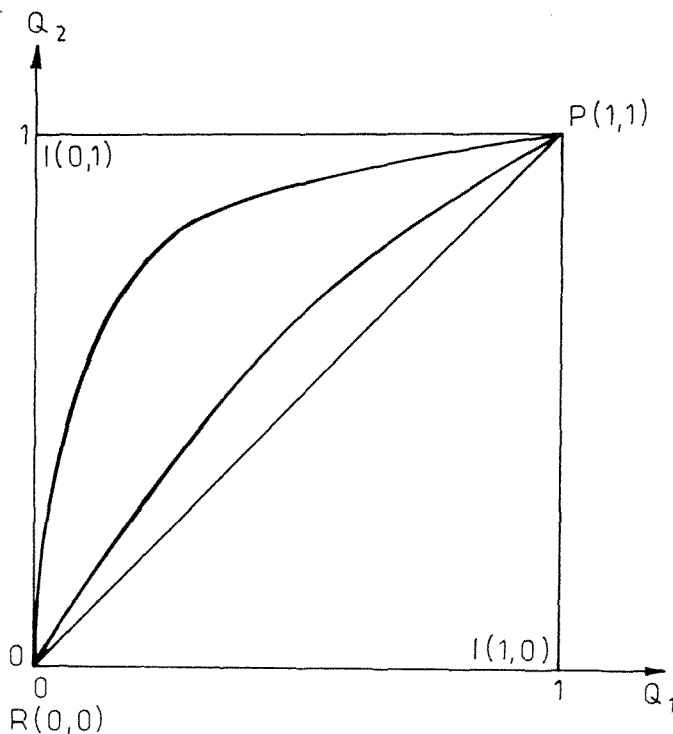


Fig. 1. Schematic representation of reaction paths in More O'Ferrall diagrams.

by the conventional scale ranging from 0 to 1. It is apparent that the concerted process, characterized by the ideal synchronization in the formation of both bonds is, within the framework of this approach, characterized by the diagonal line connecting two opposite corners  $R, P$ . The second limiting case of the ideal asynchronization then corresponds, in the same diagram, to the two-step line going along the periphery and including the corners with the coordinates  $[1, 0]$  and  $[0, 1]$  corresponding to intermediates. Between these two idealized extremes there then exists a practically continuous scale of cases corresponding to most different real situations where the asynchronization in the formation of the bonds is only partial. Since the degree of this synchronization is given by the detailed form of the corresponding line, it is apparent that the extent of deviations from the ideally synchronous diagonal line or the closeness of approach to the ideally nonconcerted two-step line provides a simple means of characterizing the concertedness and/or nonconcertedness of the reaction. In spite of being conceptually simple, the above criterion is, however, difficult to apply practically since the inevitable arbitrariness in evaluating the degree of corresponding deviations makes it difficult to determine where precisely, in a practically continuous scale of processes differing in the degree of bonding

synchronization, lies the borderline separating the asynchronous but still concerted reactions from the nonconcerted ones.

In the following, the modification allowing us to remedy this important limitation of the original technique will be introduced. The basic idea of such a modification arises from the results of our previous studies dealing with topological theory of chemical reactivity in terms of the so-called similarity index [14, 15]. Applying this approach to purely concerted processes described in the sense of the generalized overlap determinant method by

$$\Psi(\varphi) = \frac{1}{N(\varphi)} (\Psi_R \cos \varphi + \Psi_P \sin \varphi) \quad \varphi \in \langle 0, \pi/2 \rangle, \quad (1)$$

we have noticed that the transient species  $X(\varphi)$  by which the system passes during its movement along the reaction path can be dissected into two disjunct classes in such a way that the elements of one class are characterized by their predominant similarity to the reactant, whereas the elements of the other class are more similar to the product [16]. The possibility of dissecting the set of transient structures which in this case seems to have no practical impact starts, however, to play a crucial role in the case of processes described by a more complex model taking into account the participation of intermediates. In order to demonstrate how this role is related to the formation of the criterion of concertedness, it is necessary to first say a few words about the extension of the original description of the chemical reaction so as to allow the required inclusion of an intermediate. For the sake of parallelism with the above discussion of O'Ferrall diagrams, we restrict ourselves to the simplest case of processes which include one intermediate only.

In formulating the mathematical formalism describing such a process, we again employ the philosophy of the generalized overlap determinant method [17], in the framework of which the inclusion of a single intermediate can be naturally achieved by extending the original eq. (1) to the form:

$$\Psi(\vartheta, \varphi) = \frac{1}{N(\vartheta, \varphi)} (\Psi_R \cos \vartheta \cos \varphi + \Psi_P \cos \vartheta \sin \varphi + \Psi_I \sin \vartheta). \quad (2)$$

The parameters  $\vartheta, \varphi$  play the role of two generalized reaction coordinates, the systematic variation of which allows us, as demonstrated by the simple transformation relations

$$Q_1 = \frac{1}{\pi} [2\varphi + |\vartheta|(1 - 4\varphi/\pi) - \vartheta], \quad (3a)$$

$$Q_2 = \frac{1}{\pi} [2\varphi + |\vartheta|(1 - 4\varphi/\pi) + \vartheta], \quad (3b)$$

to characterize the structure of all the transient species  $X(\vartheta, \varphi)$  similarly to the original coordinates  $Q_1, Q_2$ . The principal advantage of this approach in comparison to the

original technique consists of a detailed characterization of the structure of the transient species  $X(\vartheta, \varphi)$  "inside" the region delimited by the definition interval of the variables  $\vartheta, \varphi$  ( $\vartheta \in \langle -\pi/2, \pi/2 \rangle$ ,  $\varphi \in \langle 0, \pi/2 \rangle$ ). This opens the possibility of quantification of More O'Ferrall diagrams, necessary for the formulation of the required criterion of concertedness. Before starting the discussion of the ideas on which such a criterion is based it is, however, necessary to mention some other problems accompanying the exploitation of eq. (2).

The first concerns the way of inclusion of the intermediate. In contrast to the simple case of eq. (1), requiring only the knowledge of functions  $\Psi_R, \Psi_P$  of the reactant and the product (which usually creates no problems), eq. (2) explicitly contains also the function  $\Psi_I$  of the intermediate. The condition for the exploitation of the formalism thus is the preliminary knowledge of the structure of the corresponding intermediate. This, however, usually represents no problem since the structure of the appropriate intermediate can be frequently estimated on the basis of chemical intuition. Thus, in the case of pericyclic reactions, for example, it is possible to suppose that the intermediates will correspond to biradicaloids, the structure of which will be dominated, in dependence on the degree of eventual substituent-induced polarity, by the biradical or zwitterionic contributions.

In connection with the practical use of eq. (2), it is necessary to also mention yet another specific feature related to the formalism of the overlap determinant method. This feature concerns the necessity of transforming all the wave functions  $\Psi_R, \Psi_P, \Psi_I$  into the common basis of AO with the aid of so-called assigning tables. Since the construction of these tables is sufficiently described in the literature [18, 19], it is possible to avoid repeating the unnecessary details and to continue directly to the primary aim of this study – the formation of the required criterion of concertedness. As already stressed above, the philosophy of this criterion is closely related to the possibility of dissecting the set of transient species lying "inside" More O'Ferrall diagrams into regions characterized by their dominant similarity to crucial basis structures. The corresponding dissection, where, in addition to the region of the reactant and the product, enters into play also the region of the intermediate, is defined by the set of inequalities:

$$r_{IX(\vartheta, \varphi)} < r_{RX(\vartheta, \varphi)} > r_{PX(\vartheta, \varphi)}, \quad (4a)$$

$$r_{IX(\vartheta, \varphi)} < r_{PX(\vartheta, \varphi)} > r_{RX(\vartheta, \varphi)}, \quad (4b)$$

$$r_{RX(\vartheta, \varphi)} < r_{IX(\vartheta, \varphi)} > r_{PX(\vartheta, \varphi)}. \quad (4c)$$

The individual similarity indices  $r_{RX(\vartheta, \varphi)}, r_{PX(\vartheta, \varphi)}, r_{IX(\vartheta, \varphi)}$  are defined in direct analogy to the original study [15] in terms of topological density matrices by:

$$r_{RX(\vartheta, \varphi)} = \frac{1}{N_R(\vartheta, \varphi)} \text{Tr } \Omega_{RR} \Omega(\vartheta, \varphi), \quad (5a)$$

$$r_{PX}(\vartheta, \varphi) = \frac{1}{N_P(\vartheta, \varphi)} \text{Tr } \Omega_{PP} \Omega(\vartheta, \varphi), \quad (5b)$$

$$r_{IX}(\vartheta, \varphi) = \frac{1}{N_I(\vartheta, \varphi)} \text{Tr } \Omega_{II} \Omega(\vartheta, \varphi). \quad (5c)$$

The crucial importance of the above dissection for the formulation of the criterion of concertedness now consists in that it provides a basis for the unequivocal classification of reaction mechanisms according to which regions of the diagrams are actually crossed by the line characterizing the reaction coordinate. The situation can be very clearly demonstrated graphically in a schematic diagram (fig. 2), which suggests the

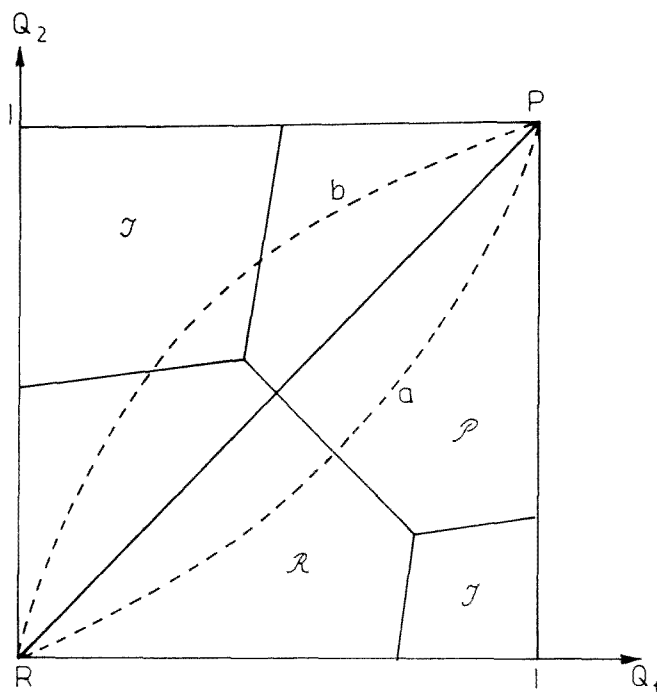


Fig. 2. Schematic classification of the reaction mechanisms in terms of partitioning of modified More O'Ferrall diagrams. Line *a* represents an asynchronous but concerted process, line *b* a nonconcerted process.

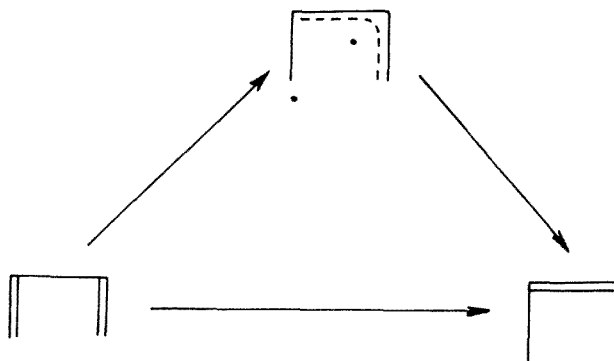
possibility of classifying as concerted the processes for which the corresponding reaction coordinate goes, similarly as in the limiting case of a strictly synchronous process, from the region of the reactant directly to the region of the product. On the other hand, where the reaction coordinate enters into the region of the intermediate, the corresponding processes can be characterized as nonconcerted.

In connection with this conceptually very simple criterion, it is also useful to notice that its credibility is supported not only intuitively but can also be justified theoretically in a way which enlightens the origins of the frequently expected and also criticized parallelism between the synchronization of the process of the bonding reorganization and the shape of the energy profile of the reaction. Such theoretical support originates from Bader's quantum topological studies concerning the mutual relation of structural and energetic stability of the system [20]. In this connection, a theorem is important which says that energetic stability also implies structural stability. From this then follows – in a reverse implication – that systems unstable structurally will also be unstable energetically. Since the important points (or regions) of structural instability are just the borderlines separating in our approach the individual regions  $R$ ,  $P$ ,  $I$ , it is apparent that to points where the reaction coordinate crosses the border separating two structurally stable points in the space of structures must correspond, on the basis of the above theorem, to the energetically unstable point on the reaction coordinate in the configuration space (i.e. on the PE hypersurface). This, together with the results of the study by Mezey [21], implies that any nonconcerted reaction – i.e. a reaction going from the point of view of our criterion via two borderlines of structural instability – necessarily proceeds by a two-step reaction mechanism via at least one energetically stable intermediate. This straightforward mutual parallelism, with the generally accepted interpretation regarding as synonyms the concept of the nonconcerted reaction and the reaction going via the intermediate, unfortunately cannot similarly be transferred to concerted reactions, since the fact that in a concerted process the reaction coordinate passes only via one borderline of structural instability does not imply that the energetic profile of the reaction necessarily needs to go (even if it can) via only one energetic maximum. Here is probably hidden the origin of the problems arising from the widespread identification of the concertedness as a synonym for reactions going without intermediates.

### 3. Results and discussion

Having presented the basic idea of the proposed new criterion, let us demonstrate in the following its practical use on a concrete example of several selected pericyclic reactions. As the simplest case of such a process, let us choose first the thermally forbidden disrotatory cyclization of butadiene to cyclobutene, for which the structure of the corresponding intermediate can be estimated both from the elementary valence considerations and from semi-empirical MINDO calculations by Dewar [22].

After having proposed the structure of the intermediate, the next step consists of the transcription of the classical structure of the participating molecular species (scheme 2) into the form of approximate wave functions, which in our case are given by



Scheme 2.

$$\Psi_R = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2|, \quad (6a)$$

$$\Psi_P = |\pi_{23} \bar{\pi}_{23} \sigma_{14} \bar{\sigma}_{14}|, \quad (6b)$$

$$\Psi_1 = \frac{1}{\sqrt{2}} (|\phi_1 \bar{\phi}_1 \phi_2 \bar{\chi}| + |\phi_1 \bar{\phi}_1 \chi \bar{\phi}_2|). \quad (6c)$$

In these functions,  $\psi_i$  denotes the occupied HMO orbitals of butadiene,  $\pi$  and  $\sigma$  the localized molecular orbitals describing the bonds in the product, and  $\phi_i$  and  $\chi$  correspond to occupied orbitals of the allyl radical and the localized atomic orbital at the terminal carbon of the intermediate, respectively.

In harmony with the philosophy of the overlap determinant method, the above wave functions are in the second step transformed into the common basis of atomic orbitals. The details of this transformation can be found elsewhere [18, 19]. After this transformation and subsequent mathematical manipulations (eqs. (2)–(5)), the resulting More O'Ferrall diagram is given in fig. 3. This form of the figure is very interesting, since it demonstrates that in this special case the question of the reaction mechanism can be answered even without the knowledge of the actual reaction path only on the basis of the topology of the dissection. It can be seen, namely, that no reaction path connecting the reactant and the product can avoid the region of the intermediate, so that the reaction must be nonconcerted irrespective of whether it is synchronous or not. This result thus once again underlines the importance of the strict discrimination of concertedness and synchronicity suggested by Lowe [11] and recently stressed also by Dewar [9].



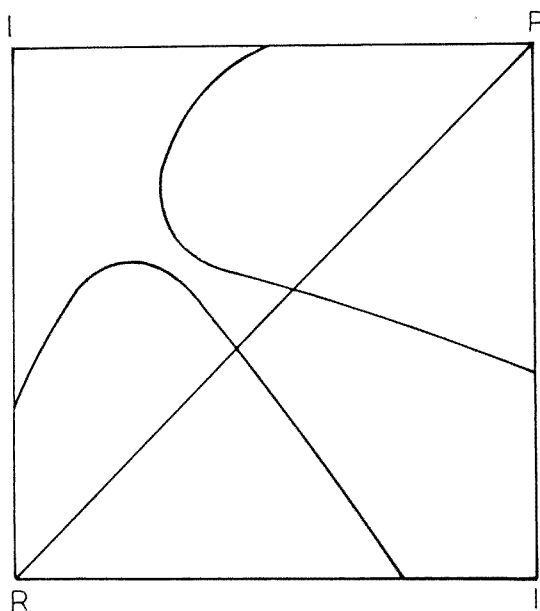


Fig. 3. The partitioning of the More O'Ferrall diagram for thermally forbidden disrotatory cyclization of butadiene to cyclobutene.

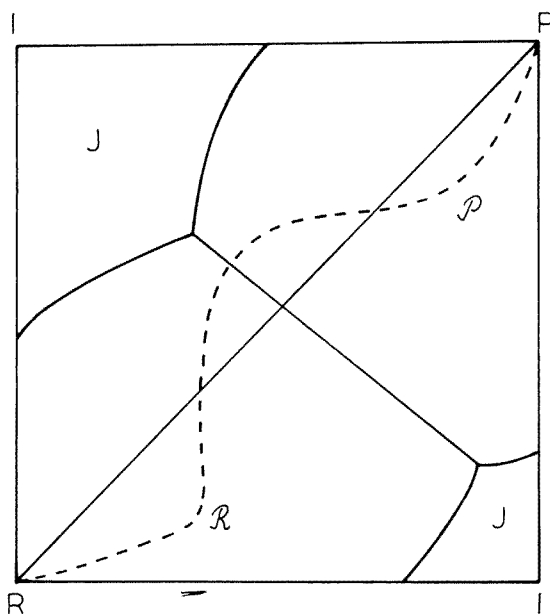


Fig. 4. The More O'Ferrall diagram with the corresponding reaction path for the thermally allowed butadiene to cyclobutene cyclization.

Such a simple picture is, however, rather exceptional, and in the majority of cases including, for example, the alternative conrotatory butadiene cyclization, the topology of the partition has the form of fig. 2, for which the knowledge of the actual reaction path is necessary. The determination of these reaction paths represents, however, another independent problem, for the solution of which we proposed a new variational procedure based on the exploitation of the so-called least motion principle [23,24]. However, since the corresponding formalism exceeds the scope of the present introductory study, we postpone this for some independent publication. Nevertheless, without anticipating, the resulting reaction path calculated by the approximate procedure [24] together with the corresponding partition for the allowed butadiene cyclization is given in fig. 4, which demonstrates that the allowed reaction is in harmony with the expectation of the Woodward–Hoffmann rules concerted.

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