

TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. CATALYTIC REACTIONS

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Received November 20th, 1985

Recently proposed overlap determinant method is applied to the description of reactions induced by the presence of the transition metal catalysts. The use of this technique is demonstrated on a detailed analysis of a number of examples of thermally forbidden pericyclic reactions in which the interaction with the catalyst removes the symmetry restrictions imposed by Woodward-Hoffmann rules.

Detailed understanding of the role of catalysts in chemical reactions is of crucial importance not only from academic point of view but also from many practical reasons connected with the rational selection of catalysts for a number of industrially important reactions. The formulation of contemporary microscopic theory of catalytic action was stimulated by a number of experimental findings demonstrating that by a proper choice of the catalysts the reactions can be induced that are symmetry forbidden in the sense of the Woodward-Hoffmann rules. From a number of such reactions summarized *e.g.* in the paper by Mango¹ we mention only several examples as the valence isomerization of quadricyclane to norbornadiene catalysed by rhodium complexes² or the rearrangement of hexamethyl(2,2,0) bicyclohexadiene to mellithene³. The similar example of thermally forbidden transformation is represented by $2_s + 2_s$ dimerization of norbornadiene catalysed by complexes of Fe, Co, and Ni⁴⁻⁶. All these examples suggest that the action of the transition metals consists in reducing the symmetry restrictions imposed by Woodward-Hoffmann (W-H) rules⁷. The detailed microscopic mechanisms of catalytic action were formulated in the works by Mango^{1,8-11}, Pettit¹²⁻¹⁴, Van der Lugt¹⁵, and others¹⁶⁻¹⁸. Other possible mechanisms of catalytic effect were discussed also in the study by Zahradník¹⁹. Theoretical analysis in majority of these works is based on the technique of the correlation diagrams modified by the presence of the transition metals. Such analysis reveals that the role of catalysts consists in altering the symmetry properties of frontier orbitals as a result of interaction of the molecular orbitals of the substrate with *d* orbitals of the catalyst.

In view of a number of papers attempting to elucidate the nature of selection rules in chemical reactions from the point of view of topological rather than symmetrical properties of molecular orbitals²⁰⁻²², the attempts recently appear to introduce the topological ideas also into the theory of catalysis²³⁻²⁵. Into the framework of this effort can be included also our recent attempt to formulate on this basis the selection rules in chemical reactivity²⁶.

The aim of this work is to show that the formalism of the overlap determinant method recently extended to free radical and photochemical reactions²⁷ is general enough to be applied also to reactions induced by the presence of catalysts.

THEORETICAL

Despite the principles of the overlap determinant method were sufficiently described in the literature²⁶ there is one specific aspect that makes their short recapitulation nevertheless desirable. This aspect is connected with the construction of the so-called irreducible core, *i.e.* of the set of the bonds actively participating in a given transformation²⁶. In contrast to the majority of normal noncatalysed reactions where such construction is usually trivial, the situation for catalytic reactions is much more complex. In this case the standard technique based on the comparison of structures of the reactants and products of the overall reaction fails since the catalyst, if released from the reaction in the same form in which it enters into reaction, could never modify the value of the overlap determinant. These elementary considerations thus provide a certain theoretical justification for the known experimental fact that the catalytic reactions cannot proceed as a concerted one step process but usually include several elementary reactions. This fact has to be respected by any theoretical treatment of catalytic reactions. Naturally thus appears the requirement of the knowledge of the reaction mechanism. Ideal would be of course if the model of the mechanism is supported experimentally, but even in cases where such support is missing it is possible to propose at least a hypothetical scheme and the overlap determinant criterion can be then regarded as a certain test of its validity or reliability.

After having presented these introductory remarks let us demonstrate the concrete application of the proposed topological formalism on a simple example of catalysed *cis-trans* isomerization of alkenes. This reaction has been shown to be thermally forbidden in the absence of catalyst and the activation barrier amounts to 60 kcal. mol^{-1} (ref.²⁸). The reaction is on the other hand facilitated by the electronic excitation resulting in the depopulation of the bonding π molecular orbital and simultaneous population of antibonding π^* orbital. Catalytic action of transition metals in this reaction is based just on the analogy with photochemical isomerization¹⁹. The metals acting as an effective catalysts of *cis-trans* isomerization are therefore expected to cause similar changes in the distribution of electron density as the above described electronic excitation. Concretely it means, that the active catalyst of *cis-trans* isomerization has to contain one occupied d orbital able to populate the virtual π^* orbital of alkene and/or empty d orbital serving as an acceptor of electron density from the bonding π orbital (Scheme 1). As an example of such catalytically active



SCHEME 1

system one may mention *e.g.* rhodium complex $(C_2H_4)_2Rh$ acac in which the activation barrier is lowered up to 6 kcal mol^{-1} (ref.²⁹).

Since there is no experimental information about the detailed mechanism of the isomerization it is necessary to propose on the basis of above presented general considerations the plausible reaction scheme (Scheme 2). This scheme consists in the first step of the coordination of the alkene to the metal by the classical mechanism of the Dewar-Chat-Duncanson type (DCD)^{30,31}, based on the combination of bonding and back bonding interactions visualized in Scheme 1.



SCHEME 2

After having formed the DCD complex *I*, the next step of the reaction requires its isomerization to the complex *II*. This complex then, in the last step, decomposes with the release of the isomeric alkene and the free catalyst.

In the framework of this scheme let us analyse first the primary step of the reaction, the formation of the DCD type complex *I*. In this case the irreducible core contains from the part of the reactants the π bond of alkene and the electron pair of occupied d_{xz} orbital of catalyst. This set has to be complemented by the bonds entering into the irreducible core from the part of the product. Taking into consideration the elementary MO arguments, these remaining bonds can be described in the form of combinations of bonding π orbital of alkene with originally empty d_{z^2} orbital of the catalyst and the antibonding π^* orbital with originally occupied d_{xz} orbital (Eq. (1))

$$\begin{aligned} \varphi'_1 &= \chi'_1 + \chi'_2 + d'_{z^2} \\ \varphi'_2 &= \chi'_1 - \chi_2 + d'_{xz} \end{aligned} \quad (1)$$

Similarly as in the previous paper²⁶ the primes distinguish the bonds of the product from the bonds of the reactant that are described by Eq. (2)

$$\begin{aligned} \psi_1 &= \chi_1 + \chi_2 \\ \psi_2 &= d_{xz} \end{aligned} \quad (2)$$

The transformation between the basis sets χ and χ' is again described by the assigning tables. Since the formation of the complex *I* does not alter the orientation of any of the participating orbitals it is apparent that the assigning table has the form of simple identity (Eq. (3))

$$\begin{aligned}\chi'_1 &\rightarrow \chi_1 & d'_{z^2} &\rightarrow d_{z^2} \\ \chi'_2 &\rightarrow \chi_2 & d'_{xz} &\rightarrow d_{xz}.\end{aligned}\quad (3)$$

Using this assignment the bonds φ_1 , φ_2 can be converted into the basis χ and their final form is given by Eq. (4)

$$\begin{aligned}\varphi'_1 &\rightarrow \varphi_1 = \chi_1 + \chi_2 + d_{z^2} \\ \varphi'_2 &\rightarrow \varphi_2 = \chi_1 - \chi_2 + d_{xz}.\end{aligned}\quad (4)$$

The overlap determinant (5) constructed from the set of bonds φ_1 , φ_2 , ψ_1 , ψ_2 then suggests that the formation of the DCD complex *I* has to be regarded as allowed

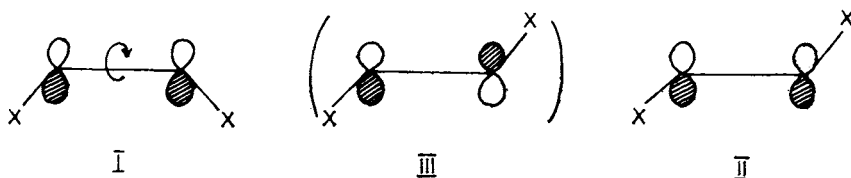
$$D = \begin{vmatrix} 2 & 0^2 \\ 0 & 1 \end{vmatrix} \neq 0. \quad (5)$$

In the next step the complex *I* transforms into the complex *II*. Since both complexes are isomeric it is apparent that the irreducible core contains formally the same bonds from the part of the reactant (complex *I*) as well as from the part of the product (complex *II*) (Eq. (6))

$$\begin{aligned}\varphi'_1 &= \chi'_1 + \chi'_2 + d'_{z^2} & \varphi''_1 &= \chi''_1 + \chi''_2 + d''_{z^2} \\ \varphi'_2 &= \chi'_1 - \chi'_2 + d'_{xz} & \varphi''_2 &= \chi''_1 - \chi''_2 + d''_{xz}.\end{aligned}\quad (6)$$

The transformation of the bonds φ''_1 , φ''_2 from the basis χ'' into the basis χ' requires again to construct the corresponding assigning tables. For this purpose one can use the elementary geometrical considerations based on the model idea that the isomerization proceeds by the rotation of one of the terminal CH_2 groups of the alkene component (Scheme 3). As a result of this rotation around the double π bond one obtains a hypothetical structure *III* the comparison of which with the complex *II* directly suggests the form of the assigning tables (Eq. (7))

$$\begin{aligned}\chi''_1 &\rightarrow \chi'_1 & d''_{z^2} &\rightarrow d'_{z^2} \\ \chi''_2 &\rightarrow -\chi'_2 & d''_{xz} &\rightarrow d'_{xz}.\end{aligned}\quad (7)$$



SCHEME 3

After having performed the transformation described by these tables the overlap determinant can be constructed in a usual way. Its nonzero value confirms the allowed nature of the second key step of the isomerization scheme (Eq. (8))

$$D = \begin{vmatrix} 1 & 2 \\ 2 & 1 \end{vmatrix}^2 \neq 0. \quad (8)$$

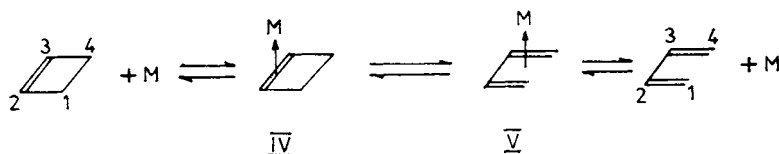
In an entirely analogous way can be analysed also the last step of the scheme, the decomposition of the complex *II*. The corresponding analysis, omitted here for the sake of brevity, confirms that also this last step is to be considered as allowed. Finally one can summarize, that the proposed three-step reaction mechanism does not contradict the expected catalytic effect of the transition metal and can be therefore regarded as plausible.

Similarly can be analysed practically any catalytic reaction and in the following part such an analysis will be demonstrated on a number of examples.

RESULTS AND DISCUSSION

Electrocyclic Reactions

As an elementary example of this type of reactions let us analyse the Cu^+ , resp. Ag^+ , catalyzed disrotatory transformation of cyclobutene to 1,3-butadiene. In the light of the above discussion the whole reaction will be again assumed to proceed by a sequence of elementary steps described by the hypothetical Scheme 4. Similarly



SCHEME 4

as in the previous example this scheme suggests the important role of the coordination between the π system of the hydrocarbons and the metallic ion with the formation of DCD type complexes. The only difference in the mechanism of this coordination against the general Scheme 1 arises from the fact that the role of accepting orbital interacting with the π system cannot play, in Ag^+ or Cu^+ ions with the configuration nd^{10} , the orbitals d but rather orbital s with the principal quantum number $(n + 1)$.

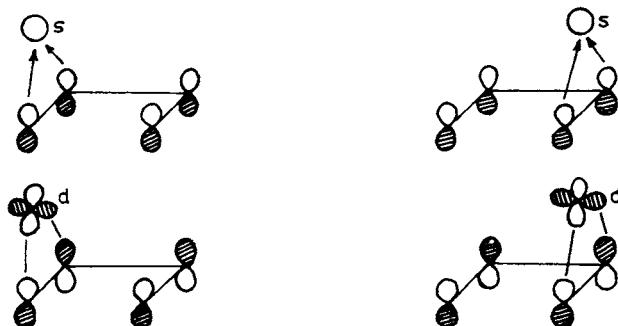
Bonds describing the reactant and the product in the first step of the reaction can be then described by Eq. (9)

$$\begin{aligned}
 \varphi_1 &= \chi_1 + \chi_4 & \varphi'_1 &= \chi'_2 + \chi'_3 + s' \rightarrow \chi_2 + \chi_3 + s \\
 \varphi_2 &= \chi_2 + \chi_3 & \varphi'_2 &= \chi'_2 - \chi'_3 + d'_{xz} \rightarrow \chi_2 - \chi_3 + d_{xz} \\
 \varphi_3 &= d_{xz} & \varphi'_3 &= \chi'_1 + \chi'_4 \rightarrow \chi_1 + \chi_4
 \end{aligned}
 \tag{9}$$

in which we simultaneously used the generally valid result that the coordination does not alter the phase properties of participating atomic orbitals and that, consequently, the assigning tables have the form of simple identity. Overlap determinant constructed from the set of bonds of Eq. (9) suggests that the corresponding reaction step is allowed (Eq. (10))

$$D = \begin{vmatrix} 0 & 0 & 2 \\ 2 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}^2 \neq 0.
 \tag{10}$$

The decisive step in the transformation is represented by the isomerization of the complexes $IV \rightleftharpoons V$. Bonds in the complex IV are described by Eq. (9) and it is therefore necessary to characterize only the structure of the complex V . Immediate use of the elementary MO considerations about the possible interactions between the butadiene and the metallic ion with the configuration d^{10} suggests that the requirements of the DCD model are best satisfied by a simple scheme according to which the lowest totally symmetrical π molecular orbital of butadiene interacts with vacant $(n+1)s$ orbital of the metal. This interaction is accompanied by the back donation from d orbitals of the metal into the lowest unoccupied π^* molecular orbital LUMO (Scheme 5). As can be seen from the scheme this specific choice of the interacting



SCHEME 5

orbitals is in the best way compatible with the experimentally confirmed fact that the ions with d^{10} configuration are coordinated to butadiene by only one π bond³² respecting simultaneously the equivalency of both π bonds.

The above considerations can be mathematically expressed in the form of Eq. (11)

$$\begin{aligned}
 \chi'_1 + \chi'_2 + \chi'_3 + \chi'_4 + s' &\rightarrow \chi_1 + \chi_2 + \chi_3 + \chi_4 + s \\
 \chi'_1 + \chi'_2 - \chi'_3 - \chi'_4 &\rightarrow \chi_1 + \chi_2 - \chi_3 - \chi_4 \\
 \chi'_1 - \chi'_2 - \chi'_3 + \chi'_4 + d'_{xz} &\rightarrow \chi_1 - \chi_2 - \chi_3 + \chi_4 + d_{xz}
 \end{aligned}
 \tag{11}$$

in which we again included the general result of the previous study²⁶ that the assigning tables for the disrotatory opening of the cyclobutene ring have the form of simple identity. The corresponding overlap determinant immediately confirms the expected catalytic effect of the transition metal making the originally forbidden reaction allowed (Eq. (12))

$$D = \begin{vmatrix} 3 & 0 & -2 \\ 0 & 2 & 1 \\ 2 & 0 & 2 \end{vmatrix}^2 \neq 0.
 \tag{12}$$

Finally one can easily verify also the allowance of the third, last, step of the reaction scheme. The bonds participating in the irreducible core of this transformation are described by Eq. (13)

$$\begin{aligned}
 \psi_1 + \chi_2 + \chi_3 + \chi_4 + s &\quad \Omega_1 = \chi_1 + \chi_2 \\
 \psi_2 = \chi_1 + \chi_2 - \chi_3 - \chi_4 &\quad \Omega_2 = \chi_3 + \chi_4 \\
 \psi_3 = \chi_1 - \chi_2 - \chi_3 + \chi_4 + d_{xz} &\quad \Omega_3 = d_{xz}
 \end{aligned}
 \tag{13}$$

in which again the primes discriminating between the reactant and the product were simultaneously omitted. Corresponding overlap determinant is given by Eq. (14)

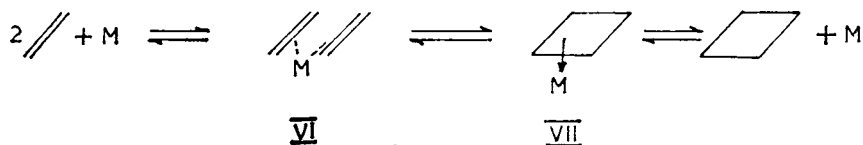
$$D = \begin{vmatrix} 2 & 2 & 0 \\ 2 & -2 & 0 \\ 0 & 0 & 1 \end{vmatrix}^2 \neq 0.
 \tag{14}$$

Cycloaddition Reactions

Typical, and probably the best studied, example of this type of reactions represents the catalysed $2_s + 2_s$ dimerization of ethene and of its derivatives. Besides these transformations were experimentally observed *e.g.* in the isomerization of norbornadiene to quadricyclane² or in the dimerization of cyclopropene derivatives³³ this type of reactions is interesting especially by that it represents the first example on which Mango⁸⁻¹¹ discussed the general conditions of catalytic influence of transition metals. From these Mango's ideas originated also the first proposals considering

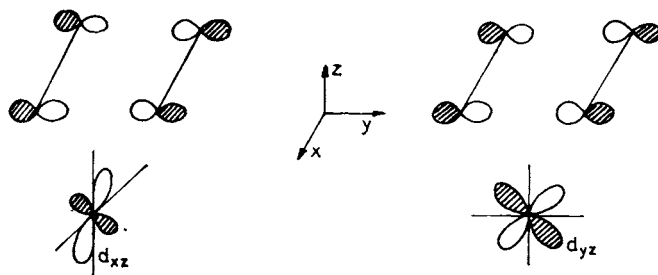
the presence of cyclobutane derivatives as intermediates of important reaction – the olefin metathesis^{12,15,34}. Despite these original ideas about the mechanism of olefin metathesis are now replaced by the alternative scheme involving carbenoid intermediates³⁴⁻³⁶, it is nevertheless useful to use them as a model example for the alternative demonstration of the Mango's analysis in the framework of overlap determinant method. Such a comparison may contribute to the elucidation of certain seeming discrepancies arising for the Mango's metathesis theory from the analysis based on the technique of the correlation diagrams³⁷.

In the light of the above general discussion let us describe the course of the $2_s + 2_s$ cyclization by the formal scheme involving the coordination of two alkenes to the catalyst, the key cycloaddition step and the subsequent decomposition of the complex cyclobutane...metal (Scheme 6). As it follows from the Mango's analysis the



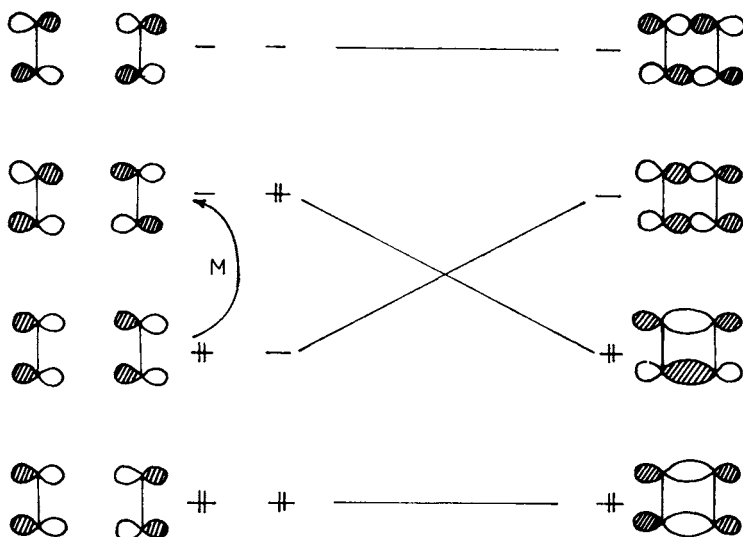
SCHEME 6

allowance of the key step of the reaction, the isomerization of the complex $VI \rightleftharpoons VII$ requires the transition metal to enter into the interaction with one occupied and one virtual d orbital of proper symmetry. In the coordinate system depicted in Scheme 7 the role of these active orbitals play the occupied d_{xz} and vacant d_{yz}



SCHEME 7

orbital. The aim of this specific requirement consists in that it converts the configuration of the ground state of two ethene molecules into the biexcited configuration in which is populated the orbital corresponding to the symmetric combination of antibonding π^* orbitals of ethene fragments that directly correlates with the ground state of the cyclobutane skeleton (Scheme 8).

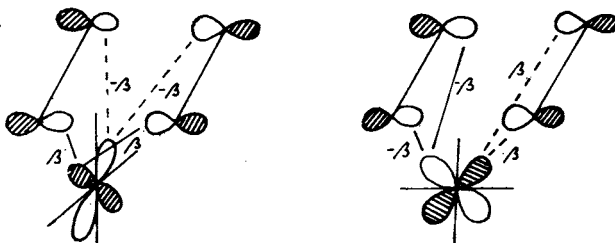


SCHEME 8

In the framework of such model one can analyse the individual steps of the isomerization scheme. Important and in this case already nontrivial task consists in a proper description of the structure of all participating molecules and intermediates. The situation is clear in the case of the first and the last step where the bonds in reactants and products are localised and can be described classically in usual way (Eq. (15))

$$\begin{aligned}
 \varphi_1 &= \chi_1 + \chi_2 & \psi_1 &= \chi_2 + \chi_3 \\
 \varphi_2 &= \chi_3 + \chi_4 & \psi_2 &= \chi_1 + \chi_4 \\
 \varphi_3 &= d_{xz} & \psi_3 &= d_{xz} .
 \end{aligned}
 \tag{15}$$

The more complex problem represents however the description of the bonds in complexes *VI* and *VII* for which the direct construction of corresponding bonds is no



SCHEME 9

more trivial. From that reason we want to present here an universal technique allowing to determine the form of corresponding multicenter linear combinations in a general way.

This method, arising from the analogy with the so-called λ -technique²²⁻²⁵ based on the solution of pseudo-HMO secular determinant. In the case of the complex VI corresponding to the interaction of two ethenes with the transition metal, such a determinant has the general form (16) immediately following from the Scheme 9.

$$\begin{vmatrix} 0 & -1 & 0 & 0 & -\beta & \beta \\ -1 & 0 & 0 & 0 & -\beta & -\beta \\ 0 & 0 & 0 & -1 & \beta & -\beta \\ 0 & 0 & -1 & 0 & \beta & \beta \\ -\beta & -\beta & \beta & \beta & \alpha_{yz} & 0 \\ \beta & -\beta & -\beta & \beta & 0 & \alpha_{xz} \end{vmatrix} = 0 \quad (16)$$

The values α_{xz} , α_{yz} , and β represent in the framework of such model certain adjustable parameters by the change of which it is possible to characterize, to some extent, the influence of the nature of the transition metal. For the purpose of our study such a detailed specification is not, however, necessary and we therefore choose, in the sense of simple nonparametric HMO method $\alpha_{xz} = \alpha_{yz} = 0$ and $\beta = 1$. The set of three molecular orbitals corresponding to the set of three electron pairs in the complex VI is then given by Eq. (17) (numerical values of LCAO expansion coefficients can be omitted since they do not alter the nodal structure of the bonds)

$$\begin{aligned} \varphi_1 &= \chi_1 + \chi_2 - \chi_3 - \chi_4 + d_{yz} \\ \varphi_2 &= \chi_1 - \chi_2 - \chi_3 + \chi_4 - d_{xz} \\ \varphi_3 &= \chi_1 + \chi_2 + \chi_3 + \chi_4 \end{aligned} \quad (17)$$

Similarly the secular determinant for the complex of the type VII has the form (18) and corresponding molecular orbitals

$$\begin{vmatrix} 0 & 0 & 0 & -1 & -\beta & \beta \\ 0 & 0 & -1 & 0 & -\beta & -\beta \\ 0 & -1 & 0 & 0 & \beta & -\beta \\ -1 & 0 & 0 & 0 & \beta & \beta \\ -\beta & -\beta & \beta & \beta & \alpha_{yz} & 0 \\ \beta & -\beta & -\beta & \beta & 0 & \alpha_{xz} \end{vmatrix} = 0 \quad (18)$$

are described by Eq. (19)

$$\begin{aligned}
 \psi_1 &= \chi_1 - \chi_2 - \chi_3 + \chi_4 - d_{xz} \\
 \psi_2 &= -\chi_1 - \chi_2 + \chi_3 + \chi_4 - d_{yz} \\
 \psi_3 &= \chi_1 + \chi_2 + \chi_3 + \chi_4.
 \end{aligned}
 \tag{19}$$

In writing these bonds we have again automatically used the fact, that in the coordinate system depicted in Scheme 9 the assigning tables have the form of simple identity. On the basis of Eqs (15), (17), and (19) it is then possible to construct the overlap determinants for individual steps of the isomerization scheme (Eq. (20))

$$\begin{aligned}
 D(1) &= \begin{vmatrix} 2 & 0 & 2 \\ -2 & 0 & 2 \\ 0 & -1 & 0 \end{vmatrix}^2 \neq 0 \\
 D(2) &= \begin{vmatrix} 0 & -5 & 0 \\ 5 & 0 & 0 \\ 0 & 0 & 4 \end{vmatrix}^2 \neq 0 \\
 D(3) &= \begin{vmatrix} -2 & 0 & 2 \\ 2 & 0 & 2 \\ -1 & 0 & 0 \end{vmatrix}^2 = 0.
 \end{aligned}
 \tag{20}$$

Their values suggest that allowed are only the first two steps, whereas the last one, the decomposition of the complex VII, is forbidden. Consequently one has to consider as forbidden the whole isomerization process. This result seems to be at first sight at variance with the results of Mango's theory. This discrepancy is, however, only seeming since it is necessary to realize that this theory, in its original form¹, has discussed the condition of conservation of coordinate bonds only from the point of view of the isomerization of the complexes VI \rightleftharpoons VII without considering the first and the last steps. The more recent attempts to extend this simple scheme by taking into account these steps reveal, in agreement with the results of this analysis, the forbidden nature of the overall process^{11,37}. This is due to the fact that the metallic catalyst is not regenerated in the same form in which it enters into the reaction, but in "excited" form with "inverted" population of *d* orbitals ($d_{xz}^2 d_{yz}^0 \rightarrow d_{xz}^0 d_{yz}^2$). The possibility of participating of such excited configurations in the reactions catalyzed by the transition metals was discussed for the first time by Van der Lugt¹⁵ and later also by Mango¹¹. Both these authors proved that the symmetry restrictions of Woodward-Hoffmann rules can be overcome if the energetic difference between the virtual and occupied *d* orbitals of the metal is small enough to ensure the sufficiently low energy of the inversely populated excited configuration of *d* orbitals. The regeneration of the catalyst in the original form in which it entered into reaction, or, in another words the closure of the catalytic cycle can be achieved

in such cases, *e.g.* by the nonradiative dissipation of the excess excitation energy by the mechanism of the vibronic coupling.

All the above examples, together with the results of the previous studies, dealing with the analysis of thermal and photochemical reactions clearly demonstrate that the formalism of the overlap determinant method represents very simple and universal tool for the analysis of chemical reactions. The specific feature of the proposed generalization to the catalytic reactions is the close relation of the overlap determinant method to the molecular aspects of the transformations; this predestines also the main field of application of the proposed approach to the homogeneous catalysis.

Nevertheless it will be probably also applicable to those heterogeneously catalyzed reactions in which the molecular aspects³⁸ of the transformation prevail over the specific effects of the solid phase.

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Translated by the author.